FREEPORT-McMoRan

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November 7, 2014

Ms. Danielle Taber
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Arizona Department of Environmental Quality
1110 W. Washington St.
Phoenix, AZ 85007

Re: **Data Gaps Work Plan for Sierrita VRP; AZ VRP Site Code: 100073-03**

Dear Ms. Taber:

The enclosed document is the Data Gaps Work Plan being submitted in response to the letter that Freeport-McMoRan Sierrita Inc.(Sierrita) received from the Arizona Department of Environmental Quality (ADEQ) regarding the Groundwater Investigation Report dated September 12, 2014. This report was preceded by the response letter from Sierrita dated November 3, 2014.

Sincerely,

Diana Kelts
Chief Environmental Engineer
Freeport-McMoRan Sierrita Inc.

20141107_001

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VOLUNTARY REMEDIATION PROGRAM

DATA GAPS WORK PLAN

Sierrita Mine
Green Valley, Arizona

November 2014

ARCADIS

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Data Gaps Work Plan

Sierrita Mine
Green Valley, Arizona

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ARCADIS

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Acronyms and Abbreviations

ADEQ	Arizona Department of Environmental Quality
APP	Aquifer Protection Permit
AWQS	Arizona Aquifer Water Quality Standards
bgs	below ground surface
CLEAR	Copper Leach Electrowinning and Regeneration
COIs	constituents of interest
CSM	conceptual site model
DQO	Data Quality Objective
ETI	Esperanza Tailings Impoundment
ft	feet
GPL	Groundwater Protection Level
mg/L	milligrams per liter
MOC	Mitigation Order on Consent
pCi/L	picocuries per liter
POC	Point of Compliance
QAPP	Quality Assurance Project Plan
SAP	Sampling and Analysis Plan
Sierrita	Freeport-McMoRan Sierrita Inc.
Site	The Sierrita VRP study area
SOP	Standard Operating Procedure
SPLP	Synthetic Precipitation Leaching Procedure
STI	Sierrita Tailings Impoundment
SX/EW	solution extraction/electrowinning
S.U.	standard units.
µmhos/cm	micromhos per centimeter
URS	URS Corporation
USC	Upper Santa Cruz
USEPA	United States Environmental Protection Agency
VRP	Voluntary Remediation Program

1. Introduction

This document presents a work plan to collect groundwater and soil data for the Sierrita Mine located near Green Valley, Arizona (Figure 1). The data collection is to be performed under the Arizona Department of Environmental Quality's (ADEQ) Arizona Voluntary Remediation Program (VRP). Freeport-McMoRan Sierrita Inc. (Sierrita) submitted an application to enter into the VRP on June 19, 2007 to evaluate certain operations and constituents that are not considered by other regulatory programs, such as the Mitigation Order on Consent (MOC), Docket No. P-50-06, and the Sierrita area-wide Aquifer Protection Permit (APP) No. P 101679. The VRP program is not applicable to actions taken under the MOC, A.R.S. § 49-172(B)(3)(c). Most facilities at Sierrita are governed by the area-wide APP. Discharge controls, compliance with Aquifer Water Quality Standards (AWQS), future closure, and other actions for the APP facilities are governed by the APP and are not intended to be addressed under the VRP. On August 15, 2007, ADEQ accepted Sierrita into the VRP as site code 100073-03.

The Site to be addressed in the VRP includes a portion of the total property boundary of Sierrita (Figure 1). Site characterization activities for the VRP were conducted between July 2008 and July 2009 following the 2008 ADEQ-approved VRP Work Plan (URS Corporation [URS] 2008a). The results of those characterization activities were reported to ADEQ (URS 2012; ARCADIS 2013a, 2013b). Following these submittals, additional data collection was identified to complete the VRP investigation at Sierrita. The primary objective of this work plan is to collect the remaining data identified by ADEQ and Sierrita to complete Site characterization for the VRP.

An overview of the VRP conceptual site model (CSM) is provided in Section 2 to address an ADEQ information request in a letter to Sierrita dated April 11, 2014. Section 3 includes a summary of the data gaps identified to date for the VRP and a description of the additional site characterization activities. The proposed groundwater sampling program is presented in Section 4.

All work activities described in this work plan will be performed in accordance with the Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP) /QAPP addendum (URS 2008b) prepared for groundwater investigation activities at Sierrita and data collection/data management for the VRP program, respectively. ARCADIS has prepared a SAP and QAPP Addendum to address updates to laboratory analysis methods and standard operating procedures (SOPs) for data collection described in

this work plan. The SAP Addendum is included in Appendix A, and the QAPP addendum is included in Appendix B.

2. CSM Overview

A comprehensive description of the VRP CSM was provided in the groundwater investigation report (ARCADIS 2013a). The CSM provides the foundation for identifying further data collection needs for the VRP. An overview of the CSM is presented in this section to provide context for the data gaps that will be filled through the investigation activities described in this work plan. This section also includes the following information requested by ADEQ (ADEQ 2014):

ADEQ Comment	**Section number where information is provided:**
ADEQ Comment No. 3: VRP suggests that Sierrita include soil and sediment data into the site's conceptual site model and subsequent groundwater investigation.	Data are provided in Section 2.5. Review of these data indicates no potential for connection between soil/sediment and groundwater.
ADEQ Comment No. 4: VRP requests that Sierrita provide an all-inclusive data set for any and all groundwater wells installed before, during, and after the Work Plan period.	The data set and description of the existing well network are included in Section 2.4.
ADEQ Comment No. 15: Figures 5 and 6: VRP would like to remind Sierrita of the commitment made in their February 22, 2012 letter titled Voluntary Remediation Program - Soil and Sediment Characterization Report in regards to developing "updated geologic cross-sections" based upon new information obtained during any soil and groundwater work. As such, VRP recommends including at least two updated cross-sections (north-south and east-west, or best-fit based on well locations) for each of the investigation areas (background, west, central, and east). Please include applicable wells and respective information such as: total depth, screening interval, groundwater elevation, known faults, and a legend that matches the formations discussed in the report.	Cross sections are provided in Section 2.2.

2.1 Site Location and Description

Sierrita operates an open pit mine and mineral concentration facility located in Pima County, approximately 6 miles northwest of Green Valley, Arizona (Figure 1). Green

Valley lies approximately 25 miles south of the City of Tucson, Arizona. Sierrita operations include conventional crushing and flotation, followed by differential flotation, leaching and roasting of molybdenum disulfide, rhenium recovery, molybdenum disulfide production and packaging, molybdenum trioxide production and packaging, leach stockpiles, and solution extraction/electrowinning (SX/EW).

Currently, there are both active operations and former operations at the Site. For purposes of data presentation and discussion, the Site is divided into four spatial areas, referred to as "investigation areas". These investigation areas reflect different operational areas of the Site. The investigation areas are shown on Figure 2, and are identified as follows:

- Background Areas (North and West)
- West Investigation Area
- Central Investigation Area
- East Investigation Area

Figure 3 provides an overview of the groundwater wells monitored during the 2008-2009 VRP investigation monitoring period ("2008-2009 VRP program"), and Figures 4 through 7 show the facilities and features of each investigation area in closer detail.

2.2 Hydrogeology

Sierrita is located in the Upper Santa Cruz (USC) Basin and Range Lowlands Hydrogeologic Province. The USC Basin is a north-trending alluvial valley drained by the Santa Cruz River (ELMA and Dames and Moore 1994). The principal hydrogeologic units at the Site include the alluvial aquifer, the basin fill aquifer, and the bedrock hydrostratigraphic unit. Alluvial deposits occur as thin, discontinuous deposits throughout the Site, typically within natural drainage channels. The basin fill aquifer primarily occurs east of Demetrie Wash and is not present in the Sierrita pit or plant areas. The bedrock hydrostratigraphic unit underlays the entire Site and exhibits a wide range of permeabilities, indicative of micro- and macro-scale fracturing. Cross sections that illustrate the hydrogeological features of the Site are presented on Figures 8 through 16.

The surface water regime of the Site is divided into four major surface water drainage basins, each associated with one of the four major washes that cross the Site. The washes include Demetrie, Amargosa, Esperanza, and Tinaja Washes. An unnamed drainage (Unnamed Wash) connects with the Tinaja Wash south of the Esperanza Wash. The locations of the washes are shown on Figure 2.

2.3 Geology and Geochemistry

The principal geologic formations at Sierrita include:

1. Alluvial Deposits
2. Basin Fill Deposits
3. Bedrock Complex, consisting of:
    a. Tinaja Peak Formation
    b. Pantano Formation
    c. Tertiary Intrusives
    d. Ruby Star Granodiorite
    e. Demetrie Volcanics
    f. Harris Ranch Quartz Monzonite
    g. Ox Frame Volcanics

Groundwater geochemistry at Sierrita is in part controlled by the type of underlying geologic formations. As described in the groundwater investigation report CSM (ARCADIS 2013a), the geochemistry of the basin fill aquifer and bedrock hydrostratigraphic unit is conducive to dissolution of major cation, anion, and trace metals that may occur naturally in the mineralized system. The different mineralized bedrock formations and the basin fill deposits contribute directly to the variability in groundwater constituent of interest (COI) concentrations. As stated in the VRP Work Plan, the objective of the VRP is to assess potential impacts to soil, groundwater, and sediment from past releases and historical Sierrita operations for COIs. COIs include

uranium, radionuclides, and other mining-related metals (aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, potassium, selenium, sodium, thallium, and zinc). The COI list for the VRP investigation was selected based on a review of the list of groundwater constituents currently monitored or regulated at Sierrita under its APP permit, historical groundwater quality data for the Sierrita Mine, and current and historical mining processes and operations. These constituents also naturally occur in soils, rock, and groundwater common to mineralized mining areas. Uranium concentrations and isotopic composition in the bedrock hydrostratigraphic unit reflect naturally occurring mineralization processes. Subsequently, radionuclides present in the bedrock hydrostratigraphic unit within the other investigation areas are detectable but consistent, with few exceptions, with levels of radionuclides measured in the background areas. Soil data collected for the VRP will reflect the variety of natural geologies exposed at the surface of the Site.

2.4 Current Well Network and Monitoring Programs

Sierrita maintains a network of monitoring wells within and adjacent to Site boundaries. These wells are monitored for the MOC, Docket No. P-50-06, and/or the Sierrita area-wide APP, No. P 101679. Some of these wells were also monitored for the VRP program. Maps provided in Appendix C show which wells are monitored for which program.

The network of groundwater wells sampled at the Site for the 2008-2009 VRP program is shown on Figure 3. Many of these wells are also part of ongoing groundwater monitoring programs under the MOC and/or APP. These groundwater monitoring programs sample select wells quarterly for radionuclides, general chemistry, and/or dissolved metals. Table 1 summarizes the constituents currently measured under these programs, compared for reference to the constituent list for the 2008-2009 VRP monitoring program. Because wells at the Site are sampled under the MOC or APP, additional data are available for some wells, which are reported to ADEQ regularly per MOC and APP requirements. Appendix D provides an all-inclusive data set, with all of the groundwater quality results reported for wells sampled since the 2008-2009 VRP program.

The wells sampled for the 2008-2009 VRP program represent a subset of all the wells currently on and around the Site. A map provided in Appendix C shows all the wells on and immediately surrounding the property.

2.5 Sources of Constituents

This section summarizes the primary and secondary sources of COIs at the Site and at each of the investigation areas. Further description and details about the sources of COIs are provided in the groundwater investigation report (ARCADIS 2013a).

2.5.1 Primary Sources of Constituents

Primary sources of COIs to groundwater at the Site may include natural background or contributions from operations. Groundwater issues with respect to current operations are addressed primarily under the APP.

Collectively, geochemical data have indicated that impacts from operations are limited in areal extent. The general chemistry of the basin fill aquifer and background bedrock hydrostratigraphic unit is conducive to the dissolution of trace metals that may occur naturally in the mineralized system. Radionuclide COIs in the bedrock hydrostratigraphic unit are consistent with those in the Background Areas.

In the West Investigation Area, Headwall No. 3, and the SX-3 Stormwater Pond have contributed to the presence of limited metal and general chemistry COIs in groundwater, as observed in the bedrock hydrostratigraphic unit at BW-02. Higher chloride levels compared to background were also observed in samples from PZ-16 (a bedrock well downgradient from Headwall No. 5) and MH-27 (a bedrock well downgradient from Headwall No. 2). However, the extent of contribution to groundwater at these locations is limited, as shown by MH-20 (downgradient of the SX-3 Stormwater Pond and BW-02) and MH-19 (downgradient from Headwall No. 5 and PZ-16), which show concentrations of COIs consistent with background and/or below numeric AWQS.

In the East Investigation Area, groundwater concentrations of COIs, except sulfate (which is being addressed under the MOC), are representative of the natural background concentrations of the basin fill aquifer. Seepage from the Sierrita Tailings Impoundment (STI) and Esperanza Tailings Impoundment (ETI) has not resulted in increases in metal or radionuclide COI concentrations above background and/or numeric AWQS.

In the Central Investigation Area, the concentration of COIs in the alluvial aquifer is affected in the vicinity of active operations extending from Bailey Lake to downgradient of Amargosa Pond. Engineering controls in this area limit the potential for COI migration in groundwater. Samples from wells installed downgradient from the

engineering controls in this area (MH-22 and MH-23, respectively) show low concentrations of metal and radionuclide COIs. Groundwater concentrations in these wells also show high alkalinity concentrations, indicating that acidic leaching solutions have not migrated downgradient in groundwater.

Groundwater in the vicinity of Former CLEAR Plant operations and downgradient of the Former Raffinate Pond show concentrations of certain COIs that are higher than background and/or numeric AWQS, although sampling locations are within the facility boundary. Concentrations of chloride and other general major anions/cations in groundwater near the Former CLEAR Plant reflect former processes, which used sodium and potassium chloride brines and sodium hydroxide and ferric chloride reagents to produce metallic copper. Groundwater near the Former Raffinate Pond reflects a combination of natural background (the downgradient monitoring well is screened in Ruby Star Granodiorite) or contribution of former operations.

2.5.2 Secondary Sources of COIs

COIs released to sediment and soil would represent a potential secondary source of COI to groundwater. However, the soil investigation reports for the Site have shown, with the exception of a data gap for one constituent, that surface soil and sediment are not sources of COIs to groundwater.

The soil data collected to date included 261 soil samples (plus 12 duplicates), which were analyzed for 18 metal COIs and five radiological COIs. These samples were collected from in and around each of nine facility operations in the Central Investigation Area, as well as the former Rhenium Pond subarea in the East Investigation Area. These areas were identified as locations where potential releases of COIs could occur to surface soil and/or sediment.

ADEQ has established soil groundwater protection levels (GPLs) for metals, which are a screening method to determine if residual contaminant concentrations could cause or threaten to cause contamination of groundwater. Soil GPLs were compared to all soil and sediment data collected from the Site as reported by URS (2012) and ARCADIS (2013b).

These data indicate that, with one exception, none of the metals in soil have the potential to be a source of COIs to groundwater that would cause groundwater COIs to be elevated compared to numerical AWQS. Comparison of antimony concentrations to standard GPLs indicated exceedances in the Former CLEAR Plant and in the Central Investigation Area. However, a site-specific GPL can be calculated, which will more

accurately reflect potential for migration of COIs from soil to groundwater. The GPL calculation requires that soil samples are analyzed for synthetic precipitation leaching procedure (SPLP), which was not completed for antimony in soil. Therefore, a site-specific GPL for antimony is identified as a data gap for the VRP.

The VRP investigation did not include the collection and analysis of water samples to determine if surface water is a potential source to groundwater. However, 36 sediment samples were collected from 18 locations during the 2008-2009 VRP program to assess whether COI releases have occurred to sediment in these drainage channels. These samples were collected from alluvial channels that flow from the historical site areas into Demetrie Wash.

The analytical results for all of the sediment samples were lower than GPLs.

Therefore, the results of the investigation show that soil and sediment at the Site (with the exception of antimony, to be addressed) does not represent a secondary source of COIs to groundwater.

2.6 Groundwater Transport

This section summarizes the primary transport mechanisms controlling COI transport for the Site and at each of the investigation areas. Further description and details are provided in the groundwater investigation report (ARCADIS 2013a).

Groundwater transport of COIs at the Site are principally controlled by the geological formation and nature of the formations. The geological formations include relatively high permeability alluvial and basin fill sediments and low permeability bedrock complexes of volcanic and intrusive origin, with variable fracturing.

The alluvial deposits at the mine site are limited to natural drainage channels, including Demetrie Wash, Amargosa Wash, Esperanza Wash, and Tinaja Wash. During significant rainfall events, which occur mostly during the wet season (mid-June through September), these channels exhibit underflow, with hydraulic conductivities measured up to 150 feet/day (ft/day; ELMA 2001). During other parts of the year (the dry season), these sediments are typically dry, with the groundwater level occurring in the underlying bedrock. COI transport within these sediments is therefore limited to the wet season and/or significant precipitation events, when flushing occurs.

The basin fill deposits occur generally east of Demetrie Wash, trending from the northwest and extending east below the tailings impoundments, and are not present in the Sierrita pit or plant areas. The thickness of the basin fill deposits increases to the east up to more than 1,000 ft near the southeast corner of the STI. These sediments have hydraulic conductivities in the order of 100 ft/day (ELMA 2001) and are hydraulically connected to the Demetrie Wash to the east of the STI. However, COI migration along the Demetrie Channel does not continue to the south, as indicated by analytical samples collected from well MH-22, located in the channel directly south of the Central Investigation Area.

Various bedrock formations are present throughout the Site, but are considered one hydrostratigraphic unit. The overall permeability of the bedrock hydrostratigraphic unit is considered low. The units are variably fractured and jointed. These zones of higher permeability can act as preferential flow conduits for the migration of constituents in groundwater. Migration of COIs along fracture zones is limited due to chemical reactions along flow paths such as pH neutralization, mineral precipitation, and sorption reactions. The limited COI migration has been seen (for example) in wells MH-19 and MH-20 (downgradient from impacted wells in the West Investigation Area) or at MH-22 and MH-23 (downgradient from impacted wells in the Central Investigation Area).

The driving mechanism of vertical transport of COIs is precipitation, which occurs during the wet season, when rapid pulses of water move into the alluvium. However, responses may be complex at the Site, given that engineering controls, including sumps and interceptor systems downgradient of former and active facilities, function to collect alluvial groundwater. Storm water management systems also control infiltration of precipitation to the alluvial aquifer. Surface water-groundwater system interaction, particularly with respect to response to precipitation events, was identified as a data gap to interpret the source-distribution dynamics of groundwater COIs and connectivity (or lack thereof) among facility operations, alluvial groundwater quality, and bedrock groundwater quality.

General COI migration for each of the individual areas is summarized as follows:

- East Investigation Area - transport of COIs is primarily controlled by flow in basin fill aquifer. The Demetrie Wash extends through southwestern portion of the area, which is in hydraulic connection with the basin fill deposits. The STI deposits overlie the basin fill deposits (Figure 9), with downgradient COI

migration to the east from these deposits monitored using a well field to the east of the STI.

- CLEAR Plant, Central Investigation, and Western Investigation Areas – Former facilities in these areas were constructed atop bedrock and/or alluvial sediments. COI migration in the alluvium (wash channels) will transport laterally along the alluvium and vertically from the alluvium into bedrock. Lateral migration will likely occur in the alluvial channels during wet periods, with slow and limited lateral migration in the bedrock, as has been indicated from hydraulic testing to date and confirmed by groundwater monitoring.

3. Program Objectives, Data Quality Objectives and Criteria for Measurement Data

Site characterization activities for the VRP were performed in 2008 and 2009. Table 2 summarizes these activities and the objectives as described in the 2008 VRP Work Plan. Following these activities, the data were assessed, and data gaps were identified in the groundwater investigation report (ARCADIS 2013a). Table 2 has been updated to show a summary of results, preliminary conclusions, and recommendations for each groundwater sampling location. ADEQ provided comments on the groundwater investigation report and identified additional data gaps (ADEQ 2014). A summary of these data gaps, and the responses or action items identified, is presented in Table 3. These data gaps identify supplemental site characterization activities for focused areas in each investigation area.

The Data Quality Objective (DQO) process is a series of planning steps designed to ensure that the type, quantity, and quality of environmental data used in decision-making are appropriate for the intended purpose. The U.S. Environmental Protection Agency (USEPA) has issued guidelines to help data users develop project-specific DQOs (USEPA 2006). These guidelines were followed for the development of the DQOs for the data gaps identified in Tables 2 and 3.

Step 1: State the Problem

The purpose of this step is to describe the problem to be studied so that the focus of the investigation will be unambiguous.

The problem to be addressed in this phase is that groundwater and soil concentrations of COIs must meet the ADEQ criteria specified in the QAPP in order to fulfill the

requirements of the VRP program. However, some data gaps exist with respect to characterization of the nature and extent of groundwater COIs at the Site, including potential migration pathways of COIs. For soil, data gaps exist as to the potential for antimony to leach from soil to groundwater at concentrations that could exceed the AWQS. Therefore, the purpose of this work plan is to collect additional groundwater and soil data that can be used to complete the characterization of the nature and extent of COIs in groundwater and soil in focused areas of the Site.

Step 2: Identify the Goals of the Study

This step identifies what questions the investigation will attempt to address and what actions may result.

The goal of the study is to fulfill remaining data gaps related to COI nature and extent at focused areas at the Site. The data gap assessment activities will provide the data to assess if any further actions are needed at the Site to fulfill the requirements of the VRP program.

Step 3: Identify Information Inputs

The purpose of this step is to identify the environmental data that need to be obtained and measurements that need to be taken to resolve the decision statement.

The data needed to achieve the objective of this effort are outlined in Table 3.

Step 4: Define the Boundaries of the Study

This section specifies the spatial and temporal boundaries of this investigation.

The investigation effort will be performed within the VRP-defined spatial Site boundaries as shown on Figures 1 and 2.

Groundwater COI levels, as well as groundwater levels, are expected to vary seasonally due to rainfall patterns. Therefore, groundwater COIs will be collected at a minimum of January and July to characterize COI concentrations during the wet seasons. Soil metal COIs are not expected to significantly vary on a short-term temporal basis; therefore, no temporal data needs were identified for the soil data collection program.

Step 5: Develop the Analytic Approach

The purpose of this step is to develop an approach to analyze the study results and draw conclusions from the data.

The approach to analyze groundwater and soil COI concentrations, obtained by sample collection and chemical analysis, will be to update the CSM for groundwater and soil at the Site.

Step 6: Specify Performance or Acceptance Criteria

The purpose of the step is to derive the performance or acceptance criteria that the collected data will need to achieve in order to minimize the possibility of either making erroneous conclusions or failing to keep uncertainty estimates within acceptable levels.

Data validation and verification procedures described in the QAPP addendum (Appendix B) are designed so that the data meet acceptance criteria.

Step 7: Optimize the Design for Obtaining Data

The final step of the DQO process is to develop a resource-effective design for collecting and measuring environmental data.

Section 4 of this work plan, along with the SAP Addendum (Appendix A), describes the design and process for obtaining environmental data, respectively.

4. Supplemental Site Characterization Activities

The sections below describe the supplemental site characterization activities for the overall Site and for each investigation area. Table 2 provides a review of the 2008-2009 VRP program objectives, findings, and recommendations for further monitoring or sampling on a well-by-well basis. Additional data gaps were identified in the groundwater investigation report and by ADEQ, and these data gaps are summarized in Table 3. Subsequently, the sections below describe the means to collect data for each well and/or area identified in Tables 2 and 3.

4.1 Site-Wide Monitoring

The data gap assessment identified the need for additional groundwater collection to provide a more complete data set of current groundwater conditions. This proposed groundwater monitoring program (the "2015 VRP program") is presented in Table 4 and on Figure 17. The 2015 VRP program includes both existing and new wells planned to be installed for the VRP program. The location and installation of new wells are described in further detail in Sections 4.2 through 4.6. Many wells within the proposed monitoring network are already sampled for the APP and/or MOC programs for Sierrita. Table 4 distinguishes those wells and the current monitoring program for each. Wells previously sampled as part of the 2008-2009 VRP program, which are not planned to be monitored for the 2015 VRP program, are listed in Table 5.

Groundwater sampling for the VRP is proposed for January and July 2015, coinciding with the Site's wet seasons, to characterize current groundwater COI concentrations. Sample collection, preparation, and laboratory analyses will be in accordance with the QAPP addendum (Appendix B). The QAPP addendum details the parameters to analyzed and corresponding USEPA Method.

4.2 East Investigation Area

Supplemental characterization activities in the East Investigation Area include assessing background concentrations of basin fill deposits and continuing to monitor groundwater wells in this area. These activities will meet the following objectives:

- Provide an update of groundwater conditions north, east, and south of the STI.
- Determine background conditions for the basin fill deposit.

To assess background analyte concentrations in the basin fill deposits, a new well will be installed (MW-2014-04), as shown on Figure 7. This location will represent background conditions because it is hydrologically upgradient of the STI, and is approximately 8,000 ft (1.5 miles) downgradient from the Central Investigation Area. A review of the available geological maps (Spencer et al. 2003) indicates that sufficient basin fill materials exist at this location to enable a well installation.

The anticipated well construction details are presented in Table 6. The well will be drilled to the base of the basin fill deposits, or approximately 50 ft into saturated sediments, with the well screened across the saturated interface. It is anticipated that the well will be approximately 400 to 450 ft deep, based on the static water depth observed at MH-8 through MH-10, which was between 300 and 370 ft below ground surface (bgs). The well will be developed and, if sufficiently saturated, sampled as part of the proposed 2015 groundwater sampling plan.

The planned groundwater well monitoring program for the East Investigation Area, with stated rationale for sampling at each well, is summarized in Table 4 and presented on Figure 17. The 2015 VRP program includes sampling from wells previously sampled for the 2008-2009 VRP program, as well as collecting samples from some existing MOC wells in place south of the STI. MOC wells MH-9 and MH-10 will be added to the 2015 VRP program to provide water quality information south of the STI, as indicated on Figure 17, to address ADEQ comment number 10 (ADEQ 2014). Note that the groundwater flow in the vicinity of the STI is from west to east due to the effect of groundwater extraction activities related to the MOC. Therefore, in reference to ADEQ comments regarding the need for sampling upgradient of the STI, the proposed sampling activity would accomplish this objective, as wells south of the STI would not be located hydrologically downgradient of mine activities.

4.3 Central Investigation Area - Former CLEAR Plant

Supplemental characterization activities in the Former CLEAR Plant area within the Central Investigation Area include hydrogeological assessment, groundwater monitoring, and soil analysis.

4.3.1 Groundwater Assessment Activities

The specific objectives of the supplemental groundwater assessment activities in this area are to:

- Provide downgradient characterization of COIs from the Former CLEAR Plant for both the alluvial and bedrock formations.
- Assess the hydraulic characteristics of both the alluvium and bedrock formations including vertical hydraulic gradient.
- Assess the hydraulic connection between the alluvium and bedrock formations and response to precipitation events.

The planned assessment will include installation of two new wells (TW-2014-01 and MW-2014-01), as shown on Figure 5 and cross section C-C' on Figure 11. TW-2014-01 will be screened in the lower portion of the quaternary alluvial sediments, and MW-2014-01 will be screened in the upper portion of the underlying bedrock, anticipated to be the Ruby Star Granodiorite formation.

The anticipated well construction details are presented in Table 6. The alluvial well will be drilled to the base of the alluvial deposits, screened across the saturated interface, and used to assess the saturated thickness and hydraulic characteristics of the alluvium. The bedrock well will be drilled and screened across into the upper portion of the bedrock, the exact screen interval will be dependent on the conditions encountered in the field, but a screen length of 50 ft is anticipated.

After installation and well development, if sufficient water is available in each of the two new wells, hydraulic testing will be conducted. Hydraulic testing will include 2- to 4-hour pumping test(s) in each of the newly installed wells, followed by recovery testing and/or slug testing, with the exact tests dependent on the saturated thickness and well yields.

The hydraulic method(s) to be employed will be determined during development activities, which will give an approximation of the respective well yield. Step testing will be performed to determine the potential well yield and the pumping rate to be used for a constant rate test.

The constant rate pumping test will include both formations being pumped to enable the assessment of formation hydraulic parameters and the hydraulic interaction. As part of testing activities, pressure transducers will be deployed in both wells. Manual water level readings will also be collected during testing as a backup and for cross-reference. Hydraulic testing will follow SOPs contained in the SAP Addendum (Appendix A).

Following the hydraulic testing described above, pressure transducers will be deployed in both wells for a period of 1 year to determine long-term water level changes and

potential connections between precipitation events and alluvium-bedrock hydraulic interaction. Proposed groundwater well monitoring in this area is summarized in Table 4 and presented on Figure 17.

4.3.2 Soil Assessment Activities

Two soil samples exceeded the antimony GPL in the Former CLEAR Plant area. These samples (CP-1 and CP-2, both at a depth of 0.25 ft bgs) are shown on Figure 18. Two confirmation samples will be collected from the vicinity of each area (four samples total) to a depth of 0.25 ft bgs and analyzed for total antimony and SPLP in order to calculate a site-specific GPL. Planned sample coordinates are presented in the SAP Addendum.

4.4 Central Investigation Area - Former Raffinate Pond/Amargosa Wash Areas

Supplemental characterization activities in the Former Raffinate Pond and Amargosa Wash areas within the Central Investigation Area include hydrogeological assessment, groundwater monitoring, and soil analysis.

4.4.1 Groundwater Assessment Activities

The specific objectives of the supplemental groundwater assessment activities in this area are to:

- Provide downgradient characterization of COIs in both the alluvium and bedrock formations.
- Assess the hydraulic characteristics of both the alluvium and bedrock formations including vertical hydraulic gradient.
- Assess the hydraulic connection between the alluvium and bedrock formations and response to precipitation events.

The planned assessment will include installation of two new bedrock wells (MW-2014-02 and MW-2014-03), as shown on Figure 6. The anticipated well construction details are presented in Table 6. The wells will be drilled and screened into the upper portion of the bedrock; the exact screen interval will be dependent on the conditions encountered, but the installation depths are anticipated to be in the region of 80 to 150 ft bgs.

After installation and well development, if sufficient water is available in each of the two new wells, hydraulic testing will be conducted. Hydraulic testing will include recovery testing and/or slug testing, with the exact testing depending on the saturated thickness and well yields. The hydraulic method(s) to be employed will be determined during the development activities, which will give an approximation of the respective well yield.

As part of hydraulic testing activities, pressure transducers will be deployed in the wells. Manual water level readings will also be collected during testing as a backup and for cross-reference. Hydraulic testing will follow SOPs contained in the SAP Addendum (Appendix A).

Pressure transducers will be deployed to the alluvium/bedrock well pairs MW-22/MW-23 and TW-2008-13/MW-2008-08 for a period of 1 year to determine long-term water level changes and potential connections between precipitation events and alluvium-bedrock hydraulic interaction. Proposed groundwater well monitoring in this area is summarized in Table 4 and presented on Figure 17.

4.4.2 Soil Assessment Activities

One soil sample exceeded the antimony GPL in the Central Investigation Area. This sample (EM-17, at a depth of 0.25 ft bgs) is shown on Figure 19. Two confirmation samples will be collected from this vicinity at a depth of 0.25 ft bgs and analyzed for total antimony and SPLP in order to calculate a site-specific GPL. Planned sample coordinates are presented in the SAP Addendum.

4.5 West Investigation Area

The specific objectives of the supplemental groundwater assessment activities in this area are to:

- Provide downgradient characterization of COIs in both the alluvium and bedrock formations.
- Assess the hydraulic connection between the alluvium and bedrock formations and response to precipitation events.

Pressure transducers will be deployed to the alluvium/bedrock well pair TW-2008-05/BW-02 for a period of 1 year to determine long-term water level changes and potential connections between precipitation events and alluvium-bedrock hydraulic

interaction. Proposed groundwater well monitoring in this area is summarized in Table 4 and presented on Figure 20.

5. References

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Tables

Table 1
2013 Analyte List for Sierrita APP and MOC Wells
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

Parameter	Units	APP	MOC	2008-2009 VRP Program
Depth to water level	feet	x		x
Water level elevation	feet amsl	x		x
Temperature - field	ºF	x	x	x
pH - field	SU	x	x	x
pH - lab	SU	x		x
Specific conductance - field	µmhos/cm	x	x	x
Total Dissolved Solids - lab	mg/L	x		x
Total Alkalinity	mg/L	x		x
Bicarbonate	mg/L	x		x
Carbonate	mg/L	x		x
Sulfate	mg/L	x	x	x
Chloride	mg/L	x		x
Fluoride	mg/L	x		x
Nitrate + nitrite	mg/L	x		x
Calcium	mg/L	x		x
Magnesium	mg/L	x		x
Potassium	mg/L	x		x
Sodium	mg/L	x		x
Aluminum	mg/L	x		x
Antimony	mg/L	x		x
Arsenic	mg/L	x		x
Barium	mg/L	x		x
Beryllium	mg/L	x		x
Cadmium	mg/L	x		x
Chromium (total)	mg/L	x		x
Cobalt	mg/L	x		x
Copper	mg/L	x		x
Iron	mg/L	x		x
Lead	mg/L	x		x
Manganese	mg/L	x		x
Mercury	mg/L	x		x
Molybdenum	mg/L	x		x
Nickel	mg/L	x		x
Selenium	mg/L	x		x
Thallium	mg/L	x		x
Uranium	mg/L	x		x
Zinc	mg/L	x		x
Free Cyanide	mg/L	x		
Gross Alpha particle activity	pCi/L	x		x
Gross Beta particle activity	pCi/L			x
Gross Alpha - adjusted	pCi/L	x		x
Radium 226	pCi/L	x		x
Radium 228	pCi/L	x		x
Uranium isotopes (U-234, U-235, U-238)	pCi/L	x		x
Carbon disulfide	mg/L	x		
Benzene	mg/L	x		
Toluene	mg/L	x		
Ethylbenzene	mg/L	x		
Total xylenes	mg/L	x		

Notes:
APP - Aquifer Protection Permit
MOC - Mitigation Order on Consent
VRP - Voluntary Remediation Program
COI - constituent of interest
mg/L - milligrams per liter
µmhos/cm - micromhos per centimeter
SU - standard units
amsl - above mean sea level
pCi/L - picoCuries per liter
°F - degrees Fahrenheit

Table 2
2008-2009 VRP Program Objectives, Findings and Conclusions
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

Feature ID	Type of Feature	Screened Interval Lithology	Associated Wash	2008 VRP Work Plan Objective	Summary of Findings	Conclusions/Recommendations
Background Areas						
MH-17	Permanent Monitoring Well	Harris Ranch Quartz Monzonite	N/A - Background areas	Represents background groundwater conditions in the Harris Ranch Quartz Monzonite.	Low but variable concentrations of metal and radionuclide COIs were found in background bedrock wells. This variability reflects the different bedrock formations that contribute naturally occurring concentrations of COIs, including radionuclides. Radionuclide activity exceeded AWQS in almost all wells. Some background wells exhibited high TDS, sulfate, and/or other cation/anion concentrations, reflecting the geology of the formation that the well is screened in.	Monitoring events for the VRP should include these background wells as a means to assess contribution of natural background to groundwater concentrations of COIs.
MH-21	Permanent Monitoring Well	Ruby Star Intrusives	N/A - Background areas	Verify background COI concentrations in the Ruby Star Granodiorite and compare results to newly installed background wells.		
MW-2008-12	Permanent Monitoring Well	Ruby Star Granodiorite	N/A - Background areas	Evaluate background concentrations in hornblende rich Ruby Star Granodiorite.		
MW-2008-13	Permanent Monitoring Well	Ruby Star Granodiorite	N/A - Background areas	Evaluate background concentrations in hornblende rich Ruby Star Granodiorite.		
MW-2008-14	Permanent Monitoring Well	Tinaja Peak Formation	N/A - Background areas	Evaluate background concentrations in Tinaja Peak Formation.		
MW-2008-15	Permanent Monitoring Well	Harris Ranch Quartz Monzonite	N/A - Background areas	Evaluate background concentrations in Harris Ranch Quartz Monzonite.		
PZ-01	Permanent Monitoring Well	Tinaja Peak Formation	N/A - Background areas	Represents background conditions in the Tinaja Peak Formation.		
Central Investigation Area						
Amargosa East Sump	Active Facility	N/A - Not a well	Amargosa Wash	Not specified	The general chemical characteristics of the active facilities reflect leaching and flotation operations. Leaching solutions exhibit low pH, high sulfate, and other major cations and anions. The flotation process for copper and molybdenum uses an alkaline process, and the solutions from these operations exhibit comparatively higher pH, alkalinity, and lower TDS. Both flotation and leaching solutions contain relatively higher concentrations of trace metals, especially divalent cations, and concentrated radionuclide activity relative to background as a result of processing operations.	No further investigation of processing solutions is recommended. Data collected to date have adequately characterized these potential sources.
Amargosa Pond	Active Facility	N/A - Not a well	Amargosa Wash	Not specified		
Amargosa West Sump	Active Facility	N/A - Not a well	Amargosa Wash	Not specified		
B Pond	Active Facility	N/A - Not a well	Amargosa Wash	Not specified		
B Seepage Silo	Active Facility	N/A - Not a well	Amargosa Wash	Not specified		
Bailey Lake	Active Facility	N/A - Not a well	Amargosa Wash	Characterize COIs in process solution.		
Bailey Sump	Active Facility	N/A - Not a well	Amargosa Wash	Not specified		
C Seepage Silo	Active Facility	N/A - Not a well	Amargosa Wash	Not specified		
Decant Solution (Molybdenum)	Active Facility	N/A - Not a well	Amargosa Wash	Not specified		
Headwall No. 1	Active Facility	N/A - Not a well	Amargosa Wash	Characterize COIs in process solution.		
Raffinate Pond No. 2	Active Facility	N/A - Not a well	Amargosa Wash	Characterize COIs in process solution.		
SX-Sump 1	Active Facility	N/A - Not a well	Amargosa Wash	Not specified		
SX-Sump 2	Active Facility	N/A - Not a well	Amargosa Wash	Not specified		
SX-Sump 3	Active Facility	N/A - Not a well	Amargosa Wash	Not specified		
BW-03	Permanent Monitoring Well	Ruby Star Granodiorite	Amargosa Wash	Evaluate potential releases from upgradient process areas along the west side of Demetrie Wash and potential influence from Amargosa Wash.	Metal COIs < AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Chloride, calcium, hardness, and TDS higher than north background wells. Concentrations of radionuclide COIs consistent with background.	Further investigation proposed to assess source and transport potential of COIs in the alluvial aquifer in this area.
BW-04	Permanent Monitoring Well	Bedrock Complex	Amargosa Wash	Evaluate potential releases from B Pond and Amargosa Wash area in general. May assist with determining effectiveness of B Sump.	Cadmium and nickel > AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Chloride, calcium, hardness, and TDS concentrations are higher than north background wells. Concentrations of radionuclide COIs consistent with background.	Further investigation proposed to assess source and transport potential of COIs in the bedrock aquifer in this area.
MH-22	Permanent Monitoring Well	Alluvium	Amargosa Wash	Evaluate alluvial groundwater in Demetrie Wash to identify potential releases from Demetrie and Amargosa Washes.	This well is only periodically saturated. One sample collected, showing Metal COIs < AWQS; Gross alpha and Gross beta > AWQS. Note that this well is a POC well; the APP establishes specific Action Levels for constituents in groundwater for these wells.	Continue to monitor per APP program. Assess alluvial-bedrock groundwater interaction downgradient of Central Investigation Area.

Table 2
2008-2009 VRP Program Objectives, Findings and Conclusions
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

Feature ID	Type of Feature	Screened Interval Lithology	Associated Wash	2008 VRP Work Plan Objective	Summary of Findings	Conclusions/Recommendations
MH-23	Permanent Monitoring Well	Demetrie Volcanics	Amargosa Wash	Evaluate potential influence of alluvial water with underlying bedrock groundwater (collocated with MH-22).	Metal COIs < AWQS; Gross alpha and Gross beta > AWQS. Chloride, calcium, hardness, and TDS were higher than the north background wells. Note that this well is a POC well; the APP establishes specific Action Levels for constituents in groundwater for these wells.	Continue to monitor per APP program. Assess alluvial-bedrock groundwater interaction downgradient of Central Investigation Area.
MW-2008-01	Permanent Monitoring Well	Ruby Star Granodiorite	Demetrie Wash	Evaluate groundwater quality upgradient of the Former CLEAR Plant Area.	Metal COIs < AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Radionuclide and general chemistry concentrations are consistent with background.	The Former CLEAR Plant is a source of general chemistry COIs to groundwater. Additional characterization proposed to characterize this source.
MW-2008-02	Permanent Monitoring Well	Ruby Star Granodiorite	Demetrie Wash	Evaluate groundwater quality immediately downgradient of the Former CLEAR Plant.	Metal COIs < AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Calcium, chloride, hardness, and TDS were greater than upgradient well concentrations. Radionuclide concentrations are consistent with background.	The Former CLEAR Plant is a source of general chemistry COIs to groundwater. Additional characterization proposed to characterize this source.
MW-2008-03	Permanent Monitoring Well	Ruby Star Granodiorite	Demetrie Wash	Evaluate groundwater quality immediately downgradient of the Former E Pond.	Metal COIs < AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Calcium, chloride, hardness, and TDS were greater than north background and upgradient groundwater concentrations. Radionuclide concentrations are consistent with background.	Further investigation proposed to assess source and transport potential of COIs in the bedrock aquifer in this area.
MW-2008-04	Permanent Monitoring Well	Ruby Star Granodiorite	Demetrie Wash	Evaluate groundwater quality immediately downgradient of the Former Evaporation Pond.	Only one monitoring quarter indicated nickel > AWQS. Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Calcium, chloride, hardness, and TDS were greater than north background and upgradient groundwater concentrations. Radionuclide concentrations are consistent with background.	Further investigation proposed to assess source and transport potential of COIs in the bedrock aquifer in this area.
MW-2008-05	Permanent Monitoring Well	Ruby Star Granodiorite	Demetrie Wash	Evaluate groundwater quality immediately downgradient of the Old D Pond.	Only one monitoring quarter indicated selenium > AWQS. Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Calcium, chloride, hardness, and TDS are consistent with, or lower than, the well upgradient of Old D Pond. Radionuclide and general chemistry concentrations are consistent with background. Soil samples in Old D Pond did not indicate that selenium has the potential to migrate to groundwater from this source.	Old D Pond is not a source of COIs to groundwater. Further investigation of this source is not needed.
MW-2008-06	Permanent Monitoring Well	Ruby Star Granodiorite	Demetrie Wash	Evaluate groundwater quality upgradient of the Old D Pond.	Se > AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Calcium, chloride, hardness, and TDS were greater than north background wells or groundwater upgradient of the former CLEAR Plant. Radionuclide concentrations are consistent with background. Soil samples in Old D Pond did not indicate that selenium has the potential to migrate to groundwater from this source.	Old D Pond is not a source of COIs to groundwater. Further investigation of this source is not needed.
MW-2008-07	Permanent Monitoring Well	Ruby Star Intrusives	Amargosa Wash	Evaluate groundwater quality immediately upgradient of the Former C Pond.	Ni, Be, Cd > AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Hardness, calcium, and magnesium are greater than north background wells. Radionuclide concentrations are consistent with background.	Former C Pond is not a source of COIs to groundwater. Further investigation of this source is not needed. However, bedrock groundwater is subject to fracture-flow, hence inclusion of this well is recommended during VRP investigation to characterize nature and extent from Former Raffinate Pond.

Table 2
2008-2009 VRP Program Objectives, Findings and Conclusions
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

Feature ID	Type of Feature	Screened Interval Lithology	Associated Wash	2008 VRP Work Plan Objective	Summary of Findings	Conclusions/Recommendations
MW-2008-08	Permanent Monitoring Well	Ruby Star Granodiorite	Amargosa Wash	Evaluate groundwater quality immediately downgradient of the Former C Pond.	Metal COIs < AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. General chemistry parameters are consistent with the well upgradient of Former C Pond. Radionuclide concentrations are consistent with background.	Former C Pond is not a source of COIs to groundwater. Further investigation of this source is not needed. However, this is one of the four alluvial-bedrock well pairs in the Central Investigation Area, and provides information as to the dynamic of water and COI transport from alluvial to bedrock groundwater. Recommended for additional sampling to address VRP data gap with respect to this transport mechanism.
MW-2008-09	Permanent Monitoring Well	Ruby Star Intrusives	Amargosa Wash	Evaluate groundwater quality immediately downgradient of the Former Raffinate Pond.	Be, Cd, Pb, Ni > AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Magnesium, hardness, TDS, sulfate, and potassium are greater than the background. Radionuclide concentrations are consistent with background. Although COIs in upgradient sources (measured at MW-2008-11) are above background and/or AWQS, concentrations appear to increase downgradient of the Former Raffinate Pond.	Former Raffinate Pond is a source of COIs to groundwater. Additional characterization in this area is proposed.
MW-2008-10	Permanent Monitoring Well	Ruby Star Granodiorite	Amargosa Wash	Evaluate groundwater quality immediately downgradient of the Former Raffinate Pond.	Be, Cd, Ni > AWQS, although soil results do not indicate a potential for these COIs to migrate to groundwater. Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Magnesium, hardness, TDS, sulfate, and potassium are greater than the background. Radionuclide concentrations are consistent with background. Although COIs in upgradient sources (measured at MW-2008-11) are above background and/or AWQS, concentrations appear to increase downgradient of the Former Raffinate Pond.	Former Raffinate Pond is a source of COIs to groundwater. Additional characterization in this area is proposed.
MW-2008-11	Permanent Monitoring Well	Ruby Star Granodiorite	Amargosa Wash	Evaluate groundwater quality upgradient of the Former Raffinate Pond.	Be, Cd, Ni > AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Magnesium, hardness, TDS, sulfate, and potassium are greater than the 95th percentile of the north background wells. Radionuclide concentrations are consistent with background.	VRP investigation of groundwater contributions from the Former Raffinate Pond should include this location to understand COI concentrations upgradient of this facility. Additionally, this is one of the four alluvial-bedrock well pairs in the Central Investigation Area, and provides information as to the dynamic of water and COI transport from alluvial to bedrock groundwater. Recommended for additional sampling to address VRP data gap with respect to this transport mechanism.
PZ-02	Permanent Monitoring Well	Demetrie Volcanics	Amargosa Wash	Evaluate quality of bedrock groundwater downgradient of sulfide leach stockpile and in vicinity of Headwall No. 1 and Bailey Lake.	Cd, Ni, Se > AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Calcium, magnesium, sodium, nitrate, and TDS are greater than north background wells. Radionuclide concentrations are consistent with background. pH is circumneutral and sulfate concentration matches background.	Further investigation proposed to assess source and transport potential of COIs in the bedrock aquifer in this area.
PZ-03	Permanent Monitoring Well	Ruby Star Intrusives	Amargosa Wash	Evaluate bedrock groundwater quality in Amargosa Wash and possibly part of the Esperanza Mill area. Provides an additional Ruby Star Granodiorite monitoring point.	Metal COIs < AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Chloride, magnesium, calcium, hardness, sulfate, and TDS are greater than the 95th percentile of north background wells. Radionuclide concentrations are consistent with background.	Further investigation proposed to assess source and transport potential of COIs in the bedrock aquifer in this area.
PZ-05	Permanent Monitoring Well	Ruby Star Intrusives	Demetrie Wash	Evaluate bedrock groundwater quality in the general mill area and provides an additional Ruby Star Granodiorite monitoring point.	As > AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. TDS, sodium, potassium, magnesium, hardness, chloride, and calcium are greater than north background wells. Radionuclide concentrations are consistent with background.	Water quality upgradient of Central Investigation Area shows concentrations are greater than AWQS and/or background. Monitoring events for the VRP should include this well as a means to assess contribution of upgradient groundwater to COIs in the Central Investigation Area.
PZ-06	Permanent Monitoring Well	Ruby Star Intrusives	Demetrie Wash	Evaluate bedrock groundwater quality upgradient of the general mill area.	As, Be, Cd, Cr, Ni > AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Potassium, nitrate, magnesium, chloride, calcium, and hardness are greater than north background wells. Sulfate and TDS are increasing over time. Radionuclide concentrations are consistent with background.	Water quality upgradient of Central Investigation Area shows concentrations are greater than AWQS and/or background. Monitoring events for the VRP should include this well as a means to assess contribution of upgradient groundwater to COIs in the Central Investigation Area.

Table 2
2008-2009 VRP Program Objectives, Findings and Conclusions
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

Feature ID	Type of Feature	Screened Interval Lithology	Associated Wash	2008 VRP Work Plan Objective	Summary of Findings	Conclusions/Recommendations
PZ-04	Permanent Monitoring Well	Ruby Star Intrusives	Demetrie Wash	Evaluate bedrock groundwater quality in the general mill area and provides an additional Ruby Star Granodiorite monitoring point.	Metal COIs < AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. TDS, sulfate, sodium, magnesium, hardness, fluoride, chloride, and calcium are greater than north background wells. Radionuclide concentrations are consistent with background.	Water quality upgradient of Central Investigation Area shows concentrations are greater than AWQS and/or background. Monitoring events for the VRP should include this well as a means to assess contribution of upgradient groundwater to COIs in the Central Investigation Area.
TW-2008-08	Temporary Monitoring Well	Alluvium	Amargosa Wash	Confirm that the pond (Launders Facility) has not released elevated concentrations of COIs from process solutions to groundwater.	This well was dry.	Further investigation proposed to assess source and transport potential of COIs in the alluvial aquifer in this area.
TW-2008-09	Temporary Monitoring Well	Alluvium	Amargosa Wash	Confirm that the ponds (Headwall No. 1 and Bailey Lake) have not released elevated concentrations of COIs from process solutions to groundwater.	Be, Cd, Cr, Ni, Se > AWQS; Gross alpha and Gross beta > AWQS. Most general chemistry parameters are greater than north background.	Further investigation proposed to assess source and transport potential of COIs in the alluvial aquifer in this area.
TW-2008-10	Temporary Monitoring Well	Alluvium	Amargosa Wash	Confirm that the pond (Raffinate Pond No. 2) has not released elevated concentrations of COIs from process solutions to groundwater.	Sb, As, Be, Cd, Cr, Pb, Ni, Se > AWQS; Gross alpha and Gross beta > AWQS. Most general chemistry parameters are greater than north background.	Further investigation proposed to assess source and transport potential of COIs in the alluvial aquifer in this area.
TW-2008-11	Temporary Monitoring Well	Alluvium	Amargosa Wash	Confirm that the pond (former A Pond) has not released elevated concentrations of COIs from process solutions to groundwater.	Be, Cd, Cr, Ni, Se > AWQS; Gross alpha and Gross beta > AWQS. Most general chemistry parameters are greater than north background wells.	Further investigation proposed to assess source and transport potential of COIs in the alluvial aquifer in this area.
TW-2008-12	Temporary Monitoring Well	Alluvium	Amargosa Wash	Confirm that the pond (B Pond) has not released elevated concentrations of COIs from process solutions to groundwater.	Be, Cd, Ni > AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Most general chemistry parameters are greater than north background wells.	Further investigation proposed to assess source and transport potential of COIs in the alluvial aquifer in this area.
TW-2008-13	Temporary Monitoring Well	Alluvium	Amargosa Wash	Not specified.	Metal COIs < AWQS; Gross alpha, Gross beta, and Ra226+Ra228 > AWQS. Radionuclide concentrations are consistent with bedrock background wells. Most general chemistry parameters are consistent with north background wells.	Former C Pond is not a source of COIs to groundwater. Further investigation of this source is not needed. However, this is one of the four alluvial-bedrock well pairs in the Central Investigation Area, and provides information as to the dynamic of water and COI transport from alluvial to bedrock groundwater. Recommended for additional sampling to address VRP data gap with respect to this transport mechanism.
TW-2008-14	Temporary Monitoring Well	Alluvium	Amargosa Wash	Not specified.	This well was dry.	No further monitoring recommended.
TW-2008-15	Temporary Monitoring Well	Alluvium	Amargosa Wash	Not specified.	This well was dry.	This is one of the four alluvial-bedrock well pairs in the Central Investigation Area, and provides information as to the dynamic of water and COI transport from alluvial to bedrock groundwater. Recommended for additional sampling to address VRP data gap with respect to this transport mechanism.
West Investigation Area						
Headwall No. 2	Active Facility	N/A - Not a well	Esperanza Wash	Characterize COIs in process solution.	See note above for active facilities.	No further investigation is needed. See above for active facilities.
Headwall No. 3	Active Facility	N/A - Not a well	Esperanza Wash	Characterize COIs in process solution.		
Headwall No. 5	Active Facility	N/A - Not a well	Esperanza Wash/Unnamed Wash	Characterize COIs in process solution.		
SX-3 Stormwater Pond	Active Facility	N/A - Not a well	Esperanza Wash	Characterize COIs in process solution		

Table 2
2008-2009 VRP Program Objectives, Findings and Conclusions
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

Feature ID	Type of Feature	Screened Interval Lithology	Associated Wash	2008 VRP Work Plan Objective	Summary of Findings	Conclusions/Recommendations
BW-02	Permanent Monitoring Well	Demetrie Volcanics	Esperanza Wash	Confirm no releases have occurred from process solution ponds located in Esperanza Wash.	Be, Cd, Ni > AWQS. Detection limits for Gross alpha and Gross beta are > AWQS. TDS, sulfate, calcium, chloride, hardness, nitrate, and magnesium are greater than west background wells.	Further investigation proposed to assess source and transport potential of COIs in the bedrock aquifer in this area.
MH-18	Permanent Monitoring Well	Tinaja Peak Formation	Tinaja Wash	Evaluate impacts from waste rock stockpile and possibly represent groundwater conditions generally upgradient of Sierrita.	Metal and radionuclide COIs < AWQS. TDS, sulfate, nitrate, hardness, chloride, and calcium are greater than west background wells. Note that this well is a POC well; the APP establishes specific Action Levels for constituents in groundwater for these wells.	Continue to monitor per APP program.
MH-19	Permanent Monitoring Well	Tinaja Peak Formation	Esperanza Wash	Evaluate shallower aquifer impacts from sulfide leach area and Headwall No. 5.	Metal COIs < AWQS; Gross alpha > AWQS. TDS, sulfate, nitrate, hardness, chloride and calcium are greater than west background wells. Note that this well is a POC well; the APP establishes specific Action Levels for constituents in groundwater for these wells.	Continue to monitor per APP program.
MH-20	Permanent Monitoring Well	Demetrie Volcanics	Esperanza Wash	This well is screened at a deeper elevation than well BW-02. Evaluate deeper aquifer impacts.	Metal and Radionuclide COIs < AWQS. TDS and sulfate are greater than west background wells. Note that this well is a POC well; the APP establishes specific Action Levels for constituents in groundwater for these wells.	Continue to monitor per APP program.
MH-27	Permanent Monitoring Well	Demetrie Volcanics	Esperanza Wash	Evaluate quality of bedrock groundwater in vicinity of Headwall No. 2.	Metal COIs < AWQS; detection limits for Gross alpha and Gross beta are > AWQS. TDS, sulfate, sodium, magnesium, hardness, chloride, and calcium are greater than west background wells. Note that this well is a POC well; the APP establishes specific Action Levels for constituents in groundwater for these wells.	Continue to monitor per APP program.
PZ-16	Permanent Monitoring Well	Demetrie Volcanics	Esperanza Wash	Evaluate quality of bedrock groundwater in vicinity of Headwall No. 5.	Metal COIs < AWQS; Gross alpha > AWQS and detection limits for Gross beta are > AWQS. TDS, sulfate, sodium, magnesium, hardness, chloride, and calcium are greater than west background wells.	Further investigation proposed to assess source and transport potential of COIs in the bedrock aquifer in this area.
TW-2008-02	Temporary Monitoring Well - Destroyed	Alluvium	Esperanza Wash	Confirm that the plant (SX Plant No. 3) has not released elevated concentrations of COIs from process solutions to groundwater.	This well was dry.	This well has been destroyed and cannot be monitored.
TW-2008-03	Temporary Monitoring Well	Alluvium	Esperanza Wash	Confirm that the pond (Headwall No. 3) has not released elevated concentrations of COIs from process solutions to groundwater.	This well was dry.	Include in data gaps investigation of this investigation area to confirm/provide updated data for alluvial aquifer saturation and COI concentrations.
TW-2008-04	Temporary Monitoring Well	Alluvium	Esperanza Wash	Confirm that the pond (Raffinate Pond No. 3) has not released elevated concentrations of COIs from process solutions to groundwater.	This well had water during only 1 quarter of monitoring due to dry conditions, and only radionuclides were measured. Radionuclide concentrations were > AWQS but consistent with background.	Include in data gaps investigation of this investigation area to confirm/provide updated data for alluvial aquifer saturation and COI concentrations.
TW-2008-05	Temporary Monitoring Well	Alluvium	Esperanza Wash	Confirm that the pond (SX-3 Stormwater Pond) has not released elevated concentrations of COIs from process solutions to groundwater.	This well was dry.	Include in data gaps investigation of this investigation area to confirm/provide updated data for alluvial aquifer saturation and COI concentrations.
TW-2008-07	Temporary Monitoring Well	Alluvium	Esperanza Wash	Confirm that the pond (Headwall No. 2) has not released elevated concentrations of COIs from process solutions to groundwater.	This well had water during only 1 quarter of monitoring due to dry conditions, and only radionuclides were measured. Radionuclide concentrations were > AWQS but consistent with background.	Include in data gaps investigation of this investigation area to confirm/provide updated data for alluvial aquifer saturation and COI concentrations.
East Investigation Area						
Reclaim Pond Settling Basin	Active Facility	N/A - Not a well	N/A - East of washes	Gather data to characterize COI concentrations in reclaim water.	See note above for active facilities.	No further sampling is recommended. See above for active facilities.
MH-14	Permanent Monitoring Well	Basin Fill Deposits	N/A - East of washes	Evaluate basin fill deposits groundwater quality in northern portion of well field.	Metal COIs < AWQS; Gross alpha > AWQS. Radionuclide concentrations are consistent with background. Note that this well is a POC well; the APP establishes specific Action Levels for constituents in groundwater for these wells.	Continue monitoring per APP program.
MH-15W	Permanent Monitoring Well	Basin Fill Deposits	N/A - East of washes	Evaluate basin fill deposits groundwater quality in central portion of well field.	Metal COIs < AWQS; Gross alpha > AWQS. Radionuclide concentrations are consistent with background. Note that this well is a POC well; the APP establishes specific Action Levels for constituents in groundwater for these wells.	Continue monitoring per APP program.

Table 2
2008-2009 VRP Program Objectives, Findings and Conclusions
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

Feature ID	Type of Feature	Screened Interval Lithology	Associated Wash	2008 VRP Work Plan Objective	Summary of Findings	Conclusions/Recommendations
MH-16W	Permanent Monitoring Well	Basin Fill Deposits	N/A - East of washes	Evaluate basin fill deposits groundwater quality in southern portion of well field.	Metal COIs < AWQS; Gross alpha > AWQS. Radionuclide concentrations are consistent with background. Note that this well is a POC well; the APP establishes specific Action Levels for constituents in groundwater for these wells.	Continue monitoring per APP program.
MH-28	Permanent Monitoring Well	Basin Fill Deposits	N/A - East of washes	Evaluate basin fill deposits groundwater quality in northern portion of well field.	Metal COIs < AWQS; Gross alpha > AWQS. Radionuclide concentrations are consistent with background. Note that this well is a POC well; the APP establishes specific Action Levels for constituents in groundwater for these wells.	Continue monitoring per APP program.
MH-29	Permanent Monitoring Well	Basin Fill Deposits	N/A - East of washes	Evaluate basin fill deposits groundwater quality in southern portion of well field.	Metal COIs < AWQS; Gross alpha > AWQS. Radionuclide concentrations are consistent with background. Note that this well is a POC well; the APP establishes specific Action Levels for constituents in groundwater for these wells.	Continue monitoring per APP program.
MH-30	Permanent Monitoring Well	Basin Fill Deposits (20 ft), Mesozoic Sedimentary Rocks (80 ft)	N/A - East of washes	Evaluate basin fill deposits groundwater quality in northern portion of well field.	Metal COIs < AWQS; Gross alpha > AWQS.	Continue monitoring per APP program.
PZ-07	Permanent Monitoring Well	Basin Fill Deposits (8 feet), Ruby Star Intrusives (42 feet)	Demetrie Wash	Evaluate groundwater quality at northern edge of basin fill deposits and northern Sierrita property boundary.	Metal COIs < AWQS; Gross alpha and Ra226+Ra228 > AWQS.	Further characterization is proposed to confirm upgradient concentrations of COIs in basin fill.
PZ-09	Permanent Monitoring Well	Basin Fill Deposits (82 feet), Ruby Star Intrusives (18 feet)	N/A - East of washes	Not specified	This well was dry.	No further monitoring recommended.
PZ-08	Permanent Monitoring Well	Demetrie Volcanics	Demetrie Wash	Evaluate southern portion Sierrita property boundary and groundwater quality before it flows beneath Sierrita Tailing Impoundment.	Metal and Radionuclide COIs < AWQS. General chemistry COIs are consistent with background.	STI is not a source of COIs to groundwater (sulfate addressed through MOC). Further investigation of this source is not needed for the VRP.
PZ-2007-05	Permanent Monitoring Well	Basin Fill Deposits	N/A - East of washes	Evaluate basin fill deposits groundwater quality immediately downgradient of the Esperanza Tailing Impoundment and near the Sierrita Tailing Impoundment reclaim pond.	Metal COIs < AWQS; Gross alpha > AWQS.	STI is not a source of COIs to groundwater (sulfate addressed through MOC). Further investigation of this source is not needed for the VRP.
PZ-2008-19	Permanent Monitoring Well (well buried)	Tailings	N/A - East of washes	Not specified.	Metal COIs < AWQS; Gross alpha and Gross beta > AWQS.	STI is not a source of COIs to groundwater (sulfate addressed through MOC). Further investigation of this source is not needed for the VRP.
PZ-2008-20	Permanent Monitoring Well (well buried)	Tailings	N/A - East of washes	Not specified.	Metal COIs < AWQS; Gross alpha and Gross beta > AWQS.	STI is not a source of COIs to groundwater (sulfate addressed through MOC). Further investigation of this source is not needed for the VRP.
PZ-2008-16	Permanent Monitoring Well (well buried)	Tailings	N/A - East of washes	Not specified.	Metal COIs < AWQS; Gross alpha and Gross beta > AWQS.	STI is not a source of COIs to groundwater (sulfate addressed through MOC). Further investigation of this source is not needed for the VRP.

Notes:
Wells are generally ordered in this table upgradient to downgradient per area or feature.
N/A = not applicable
* - denotes that well construction diagrams unavailable; assumed lithology
APP - Aquifer Protection Permit
AWQS - Arizona Aquifer Water Quality Standards
CLEAR - Copper Leach Electrowinning and Regeneration
COIs - constituents of interest
POC - Point of Compliance
STI - Sierrita Tailings Impoundment
TDS - Total Dissolved Solids
VRP - Voluntary Remediation Program

Table 3
Summary of Data Gaps and Actions
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

Objective	Source	Comment or Data Gap Identified	Response Summary	Action or Proposed Sampling
Site Wide				
Incorporate soil and sediment data into the CSM.	ADEQ 4/14	ADEQ Comment No. 3: VRP suggests that Sierrita include soil and sediment data into the site's conceptual site model and subsequent groundwater investigation.	Sierrita responded that the findings of the soil investigation, which showed a lack of connection between soil and groundwater (this was done by comparison to GPLs), would be included in the Work Plan to support Sierrita' s rationale for proposed data collection.	Text description of soil/sediment connection to groundwater is provided in the Work Plan (see Section 2). Site-specific GPLs for antimony in the CLEAR Plant and Esperanza Mill subarea need to be determined. Four samples in the CLEAR Plant subarea and two samples in the Esperanza Mill subarea will be collected for total and SPLP antimony analysis.
Provide an all-inclusive data set for groundwater.	ADEQ 4/14	ADEQ Comment No. 4: VRP requests that Sierrita provide an all-inclusive data set for any and all groundwater wells installed before, during, and after the Work Plan period.	Sierrita responded that monitoring data at the site collected since 2009 will be considered to assist in further development of the VRP CSM and data gaps Work Plan.	A comprehensive well map is provided in the Work Plan, as well as the data collected for the APP and MOC during the period 2009-2014.
Conduct groundwater monitoring events semi-annually in January and July, coinciding with the site's wet season. Use the new monitoring data to provide groundwater contours of alluvial and basin fill aquifers in addition to the bedrock aquifer.	ADEQ 4/14	ADEQ Comment No. 6: VRP requests that additional site-wide groundwater monitoring be conducted to provide a more complete data set of current groundwater conditions. VRP suggests that the monitoring events be conducted semi-annually in January and July, coinciding with the site's wet season. a. With the additional monitoring data, VRP suggests contouring the groundwater elevations for the alluvial and basin fill aquifers in addition to the bedrock aquifer. b. VRP also suggests that Sierrita utilize the additional data collected to re-assess aquifer characteristics calculated by URS such as: hydraulic conductivity and horizontal and vertical hydraulic gradients.	Sierrita responded that a groundwater collection program will be proposed in the Work Plan for wells within VRP-defined site boundaries. The program will incorporate the VRP requests made in comment #6.	Additional sampling is proposed in the Work Plan (see Section 4.1). Groundwater contours of each aquifer/unit will be made following the monitoring events.
Revise Table 17 in the Groundwater investigation report.	ADEQ 4/14	ADEQ Comment No. 12: Table 17: VRP suggests that this table include a preliminary outcome/conclusion and recommendations column.	Sierrita responded that the Work Plan will contain a table of wells proposed for further monitoring and the rationale as to why each well was included as a monitoring point for the VRP.	A table summarizing the preliminary outcome/conclusion and recommendations column following the groundwater investigation is provided in the Work Plan (see Table 2).
Provide additional geologic cross sections.	ADEQ 4/14	ADEQ Comment No. 15: Figures 5 and 6: VRP would like to remind Sierrita of the commitment made in their February 22, 2012 letter titled Voluntary Remediation Program - Soil and Sediment Characterization Report in regards to developing "updated geologic cross-sections" based upon new information obtained during any soil and groundwater work. As such, VRP recommends including at least two updated cross-sections (north-south and east-west, or best-fit based on well locations) for each of the investigation areas (background, west, central, and east). Please include applicable wells and respective information such as: total depth, screening interval, groundwater elevation, known faults, and a legend that matches the formations discussed in the report.	Sierrita responded that additional cross sections will be forthcoming in the Work Plan.	Additional cross sections are provided in the Work Plan (see Section 2 and Figures 9 through 16).
Central Investigation Area - Active Facility Area in Amargosa Wash				
Additional characterization of the extent of impacts in the alluvial and bedrock aquifer is needed in the active facility area in Amargosa Wash.	ADEQ 4/14	ADEQ Comment No. 9: Page 58, Section 4.3.4 "Active Facilities in the Central Investigation Area", 1st paragraph: VRP suggests installing groundwater monitoring wells alongside Amargosa Wash.	Migration potential in alluvium and bedrock in proximity to the active facilities warrants further investigation in the Amargosa Wash.	Additional wells are proposed in this area in the bedrock aquifer (Figure 6).
	ADEQ 4/14	ADEQ Comment No 10: Page 67, Section 6.5 "Data Gaps and Recommendations for Further Data Collection": VRP concurs with the recommendations and data gaps presented here. However, VRP requests that Sierrita also include the following: • Monitoring wells south of the Sierrita Tailings Impoundment. • Monitoring wells within, or adjacent to, the major washes. • Install well pairs in alluvium and bedrock in areas where alluvium is present at the surface. • Continue the investigation/analysis of background water quality. VRP notes that Sierrita' s background water quality analysis is the basis for most of the data analysis, preliminary conclusions, and proposed data gaps. With the data set currently presented in the Report, VRP does not concur with the proposed background water quality. VRP requests that Sierrita collect additional alluvial (if applicable), basin fill, bedrock, and groundwater samples from several areas that are not down-gradient or cross-gradient of current or historical mining operations and/or disturbed land areas.	Sierrita responded that it will incorporate data collection requests in the Work Plan. Data collection and well installation will coincide with specific areas identified for further investigation.	
	GIR	Section 5, pg. 60: Groundwater COIs greater than background and/or AWQS were observed in samples from wells screened in the alluvial aquifer in Amargosa Wash, near SX-Sump-2, Raffinate Pond No. 2, and Amargosa Pond. There are no wells installed in the bedrock hydrostratigraphic unit in this immediate area, so the extent of impacts to the bedrock hydrostratigraphic unit cannot be ascertained. Additionally, limited alluvial wells are installed in this area, such that characterization of the nature and extent in the alluvial aquifer is also limited.	Sierrita will investigate the extent of COI presence in the alluvial and bedrock units in the Amargosa Wash area, extending from Bailey Lake to Former A pond.	

Table 3
Summary of Data Gaps and Actions
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

Objective	Source	Comment or Data Gap Identified	Response Summary	Action or Proposed Sampling
Understand precipitation-driven surface water-groundwater system interactions.	ADEQ 4/14	ADEQ Comment No. 6: VRP requests that additional site-wide groundwater monitoring be conducted to provide a more complete data set of current groundwater conditions. VRP suggests that the monitoring events be conducted semi-annually in January and July, coinciding with the site's wet season. a. With the additional monitoring data, VRP suggests contouring the groundwater elevations for the alluvial and basin fill aquifers in addition to the bedrock aquifer. b. VRP also suggests that Sierrita utilize the additional data collected to re-assess aquifer characteristics calculated by URS such as: hydraulic conductivity and horizontal and vertical hydraulic gradients.	Sierrita responded that a hydraulic testing program will be proposed in the Work Plan for wells within VRP-defined site boundaries.	Pressure transducers are proposed to be installed in MH-22 and MH-23 (Figure 6).
	GIR	Section 5, pg. 61: During groundwater quality sampling events, it was noted that rainfall patterns varied substantially between quarters, as did, at times, groundwater quality concentrations of COIs. Additionally, wells installed in the alluvial aquifer were often dry, suggesting that movement of COIs within the alluvial aquifer and from the alluvial aquifer into the bedrock hydrostratigraphic unit may occur only over short durations, driven by high precipitation events. Therefore, a hydrological investigation of surface water-groundwater system interaction, particularly with respect to response to precipitation events, would aid in further interpretation of source-distribution dynamics of groundwater COIs and connectivity (or lack thereof) between facility operations, alluvial groundwater quality, and bedrock groundwater quality. Concurrent measurements of precipitation, groundwater elevation, and solution pond pump/seepage rates are recommended to facilitate further interpretation.	Sierrita will investigate the migration potential from alluvium to bedrock in the Amargosa Wash area, extending from Bailey Lake to Former A pond.	
Re-assess aquifer characteristics such as: hydraulic conductivity and horizontal and vertical hydraulic gradients.	ADEQ 4/14	ADEQ Comment No. 6: VRP requests that additional site-wide groundwater monitoring be conducted to provide a more complete data set of current groundwater conditions. VRP suggests that the monitoring events be conducted semi-annually in January and July, coinciding with the site's wet season. a. With the additional monitoring data, VRP suggests contouring the groundwater elevations for the alluvial and basin fill aquifers in addition to the bedrock aquifer. b. VRP also suggests that Sierrita utilize the additional data collected to re-assess aquifer characteristics calculated by URS such as: hydraulic conductivity and horizontal and vertical hydraulic gradients.	Sierrita responded that a groundwater collection program will be proposed in the Work Plan for wells within VRP-defined site boundaries. The program will incorporate the VRP requests made in comment #6.	Pumping tests (if sufficient water is available), or else aquifer yield tests, are proposed in TW-2014-01 and MH-2014-01, which are alluvium-bedrock wells in the former CLEAR Plant Area. Slug tests will be performed on MH-2014-02 and MH-2014-03 wells, which are bedrock wells in the Central Investigation area. Field mapping of exposed formation outcrops will also be completed, which can also be useful to identify areas of fracture.
	GIR	Section 5, pg. 61: Additionally, the potential influence of fracturing in the bedrock on COI distribution is not well understood throughout the Central Investigation Area. Geophysics analysis and/or aquifer testing in this area is suggested as a means to measure fracturing influence on groundwater COI distribution in areas of interest. Deployment of this type of instrumentation, will aid in the analysis of other transient hydraulic conditions, such as storm events, and also support interpretation of subsequent aquifer tests (i.e., pumping tests) in this area; [...]	Sierrita will conduct aquifer testing in the Amargosa Wash area, extending from Bailey Lake to Former A pond.	
Determine extent of downgradient effects.	GIR	Section 5, pg. 60: MH-22 and MH-23 were identified in the Work Plan as downgradient monitoring wells, in the alluvial aquifer and bedrock hydrostratigraphic unit, respectively, for Amargosa Wash and Demetrie Wash. Further characterization of the extent of potential downgradient effects is recommended.	Sierrita will investigate the migration potential from alluvium to bedrock in the Amargosa Wash and Demetrie Wash areas.	Additional sampling is proposed at MH-22 and MH-23 (Figure 6 and Table 4).
Central Investigation Area - Former Raffinate Pond				
Additional characterization of the extent of COI impacts related to the former Raffinate Pond is needed.	GIR	Section 5, pg. 61: The nature and extent of groundwater COI impacts of former operations needs additional characterization.	Sierrita will develop a monitoring program for downgradient wells and determine the COI migration potential from alluvial to bedrock aquifer by review of soil data and alluvial aquifer data collection.	Additional sampling at MW-2008-09, MW-2008-10, and PZ-03 is proposed. There is no alluvial aquifer in this area; therefore, additional well installation is not proposed.
Central Investigation Area - Former CLEAR Plant				
Additional characterization of the extent of COI impacts related downgradient from the CLEAR Plant area is needed.	GIR	Section 5 pg. 61: Understanding the hydrologic regime in the bedrock hydrostratigraphic unit in the vicinity of former CLEAR Plant area, and in the interface between the bedrock hydrostratigraphic unit and the basin fill aquifer, is recommended to help interpret COI impacts to groundwater in this area.	Sierrita will investigate the downgradient COI migration from the former CLEAR Plant area.	An alluvium and bedrock well pair is proposed in the former CLEAR Plant area (Figure 5). Additional sampling is proposed for downgradient wells.
Re-assess aquifer characteristics such as: hydraulic conductivity and horizontal and vertical hydraulic gradients.	ADEQ 4/14	ADEQ Comment No. 6: VRP requests that additional site-wide groundwater monitoring be conducted to provide a more complete data set of current groundwater conditions. VRP suggests that the monitoring events be conducted semi-annually in January and July, coinciding with the site's wet season. a. With the additional monitoring data, VRP suggests contouring the groundwater elevations for the alluvial and basin fill aquifers in addition to the bedrock aquifer. b. VRP also suggests that Sierrita utilize the additional data collected to re-assess aquifer characteristics calculated by URS such as: hydraulic conductivity and horizontal and vertical hydraulic gradients.	Sierrita responded that a groundwater collection program will be proposed in the Work Plan for wells within VRP-defined site boundaries. The program will incorporate the VRP requests made in comment #6.	Pumping tests (if sufficient water is available), or else aquifer yield tests, are proposed in TW-2014-01 and MH-2014-01, which are alluvium-bedrock wells in the former CLEAR Plant Area. Slug tests will be performed on MH-2014-02 and MH-2014-03 wells, which are bedrock wells in the Central Investigation area. Field mapping of exposed formation outcrops will also be completed, which can also be useful to identify areas of fracture.
	GIR	Section 5, pg. 61: The current hydraulic conductivity estimates for the bedrock hydrostratigraphic unit are subject to uncertainties, due to potential micro and macro structural controls on groundwater flow, and limitations of the current slug test data set. Therefore, hydraulic conductivity estimates should be viewed at this time as preliminary estimates, and further refinements in these areas of interest would be warranted to assist with further interpretation of controls on COI distribution in the alluvial aquifer and bedrock hydrostratigraphic unit. Longer term aquifer performance tests would assist in understanding the transmissivity of the bedrock and connectedness of the fractures, and provide more than a “near well” estimate of hydraulic conductivity.	Sierrita will refine hydraulic conductivity estimates in the former CLEAR Plant area.	

Table 3
Summary of Data Gaps and Actions
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

Objective	Source	Comment or Data Gap Identified	Response Summary	Action or Proposed Sampling
West Investigation Area				
Further monitoring of wells in this investigation area is recommended.	ADEQ 4/14	ADEQ Comment No 10: Page 67, Section 6.5 "Data Gaps and Recommendations for Further Data Collection": VRP concurs with the recommendations and data gaps presented here. However, VRP requests that Sierrita also include the following: • Monitoring wells south of the Sierrita Tailings Impoundment. • Monitoring wells within, or adjacent to, the major washes. • Install well pairs in alluvium and bedrock in areas where alluvium is present at the surface. • Continue the investigation/analysis of background water quality.	Sierrita responded that it will incorporate data collection requests in the Work Plan. Data collection and well installation will coincide with specific areas identified for further investigation.	Additional sampling of bedrock wells in this area is proposed in the Work Plan (see Section 4 and Table 4).
	GIR	Section 5, pg. 62: Data collection recommendations include additional monitoring of the bedrock hydrostratigraphic unit in the vicinity of each of the active facilities in this area to assess potential impacts of the active facilities to groundwater COI concentrations.	Sierrita will develop a monitoring program for existing bedrock wells.	
Understand precipitation driven surface water-groundwater system interactions.	ADEQ 4/14	ADEQ Comment No. 6: VRP requests that additional site-wide groundwater monitoring be conducted to provide a more complete data set of current groundwater conditions. VRP suggests that the monitoring events be conducted semi-annually in January and July, coinciding with the site's wet season. a. With the additional monitoring data, VRP suggests contouring the groundwater elevations for the alluvial and basin fill aquifers in addition to the bedrock aquifer. b. VRP also suggests that Sierrita utilize the additional data collected to re-assess aquifer characteristics calculated by URS such as: hydraulic conductivity and horizontal and vertical hydraulic gradients.	Sierrita responded that a hydraulic testing program will be proposed in the Work Plan for wells within VRP-defined site boundaries.	Pressure transducers are proposed to be installed in alluvial-bedrock wells in TW-2008-05 and BW-02, respectively (Figure 4).
East Investigation Area				
Install wells south of STI.	ADEQ 4/14	ADEQ Comment No 10: Page 67, Section 6.5 "Data Gaps and Recommendations for Further Data Collection": VRP concurs with the recommendations and data gaps presented here. However, VRP requests that Sierrita also include the following: • Monitoring wells south of the Sierrita Tailings Impoundment. • Monitoring wells within, or adjacent to, the major washes. • Install well pairs in alluvium and bedrock in areas where alluvium is present at the surface. • Continue the investigation/analysis of background water quality. VRP notes that Sierrita' s background water quality analysis is the basis for most of the data analysis, preliminary conclusions, and proposed data gaps. With the data set currently presented in the Report, VRP does not concur with the proposed background water quality. VRP requests that Sierrita collect additional alluvial (if applicable), basin fill, bedrock, and groundwater samples from several areas that are not down-gradient or cross-gradient of current or historical mining operations and/or disturbed land areas.	Sierrita responded that it will incorporate data collection requests in the Work Plan. Data collection and well installation will coincide with specific areas identified for further investigation.	Wells in the south and west of the STI currently exist and are proposed for sampling in the Work Plan (see Section 4).
Background Areas				
Continue to investigate background water quality.	ADEQ 4/14	ADEQ Comment No 10: Page 67, Section 6.5 "Data Gaps and Recommendations for Further Data Collection": VRP concurs with the recommendations and data gaps presented here. However, VRP requests that Sierrita also include the following: • Monitoring wells south of the Sierrita Tailings Impoundment. • Monitoring wells within, or adjacent to, the major washes. • Install well pairs in alluvium and bedrock in areas where alluvium is present at the surface. • Continue the investigation/analysis of background water quality. VRP notes that Sierrita' s background water quality analysis is the basis for most of the data analysis, preliminary conclusions, and proposed data gaps. With the data set currently presented in the Report, VRP does not concur with the proposed background water quality. VRP requests that Sierrita collect additional alluvial (if applicable), basin fill, bedrock, and groundwater samples from several areas that are not down-gradient or cross-gradient of current or historical mining operations and/or disturbed land areas.	Sierrita responded that it will incorporate data collection requests in the Work Plan. Data collection and well installation will coincide with specific areas identified for further investigation.	A basin fill background well has been identified to supplement bedrock background wells in north and west areas; these wells are proposed for sampling in the Work Plan (see Section 4).

Notes:
ADEQ - Arizona Department of Environmental Quality
APP - Aquifer Protection Permit
CLEAR - Copper Leach Electrowinning and Regeneration
COIs - Constituents of interest
CSM - Conceptual Site Model
GPL - Groundwater Protection Level
MOC - Mitigation Order on Consent
SPLP - Synthetic Precipitate Leaching Procedure
VRP - Voluntary Remediation Program
URS - URS Corporation

Table 4
Planned 2015 VRP Groundwater Sampling Program
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

VRP Well ID	Well Status	2008-2009 VRP Program	APP Well	MOC Well	2008 VRP Work Plan Objective	Conclusion/Recommendation from 2008-2009 VRP Program	2015 VRP Data Gaps Objective
Background Areas							
MH-17	Active	x			Represents background groundwater conditions in the Harris Ranch Quartz Monzonite.	Monitoring events for the VRP should include these background wells as a means to assess contribution of natural background to groundwater concentrations of COIs.	Provide current concentrations of background COIs for groundwater associated with Harris Ranch Quartz Monzonite.
MH-21	Active	x	x		Verify background COI concentrations in the Ruby Star Granodiorite and compare results to newly installed background wells.	Monitoring events for the VRP should include these background wells as a means to assess contribution of natural background to groundwater concentrations of COIs.	Provide current concentrations of background COIs for groundwater associated with Ruby Star Granodiorite.
MW-2008-12	Active	x			Evaluate background concentrations in hornblende rich Ruby Star Granodiorite.	Monitoring events for the VRP should include these background wells as a means to assess contribution of natural background to groundwater concentrations of COIs.	Provide current concentrations of background COIs for groundwater associated with hornblend rich Ruby Star Granodiorite.
MW-2008-13	Active	x			Evaluate background concentrations in hornblende rich Ruby Star Granodiorite.	Monitoring events for the VRP should include these background wells as a means to assess contribution of natural background to groundwater concentrations of COIs.	Provide current concentrations of background COIs for groundwater associated with hornblend rich Ruby Star Granodiorite.
MW-2008-14	Active	x			Evaluate background concentrations in Tinaja Peak Formation.	Monitoring events for the VRP should include these background wells as a means to assess contribution of natural background to groundwater concentrations of COIs.	Provide current concentrations of background COIs for groundwater associated with Tinaja Peak Formation.
MW-2008-15	Active	x			Evaluate background concentrations in Harris Ranch Quartz Monzonite.	Monitoring events for the VRP should include these background wells as a means to assess contribution of natural background to groundwater concentrations of COIs.	Provide current concentrations of background COIs for groundwater associated with Harris Ranch Quartz Monzonite.
MW-2014-04	New - TBD				N/A - new well proposed for Basin Fill Aquifer	N/A - new well	Evaluate background COI concentrations in basin fill deposits.
PZ-01	Active	x			Represents background conditions in the Tinaja Peak Formation.	Monitoring events for the VRP should include these background wells as a means to assess contribution of natural background to groundwater concentrations of COIs.	Provide current concentrations of background COIs for groundwater associated with Tinaja Peak Formation.
Central Investigation Area							
BW-03	Active	x			Evaluate potential releases from upgradient process areas along the west side of Demetrie Wash and potential influence from Amargosa Wash.	Further investigation proposed to assess source and transport potential of COIs in the alluvial aquifer in this area.	Provide current concentrations of COIs in alluvium/bedrock groundwater downgradient of the Central Investigation Area.
BW-04	Active	x			Evaluate potential releases from B Pond and Amargosa Wash area in general. May assist with determining effectiveness of B Sump.	Further investigation proposed to assess source and transport potential of COIs in the bedrock aquifer in this area.	Provide current concentrations of COIs in alluvium/bedrock groundwater downgradient of B Pond and the Central Investigation Area.
MH-22	Active	x	x		Evaluate alluvial groundwater in Demetrie Wash to identify potential releases from Demetrie and Amargosa Washes.	Continue to monitor per APP program. Assess alluvial-bedrock groundwater interaction downgradient of Central Investigation Area.	Evaluate transport mechanism of COIs from alluvium to bedrock for the Site. Provide current concentrations of COIs in bedrock groundwater downgradient of the Central Investigation Area.
MH-23	Active	x	x		Evaluate potential influence of alluvial water with underlying bedrock groundwater (collocated with MH-22).	Continue to monitor per APP program. Assess alluvial-bedrock groundwater interaction downgradient of Central Investigation Area.	Evaluate transport mechanism of COIs from alluvium to bedrock for the Site. Provide current concentrations of COIs in alluvial groundwater downgradient of the Central Investigation Area.
MW-2008-01	Active	x			Evaluate groundwater quality upgradient of the Former CLEAR Plant Area.	The Former CLEAR Plant is a source of general chemistry COIs to groundwater. Additional characterization proposed to characterize this source.	Provide current concentrations of bedrock COIs in groundwater upgradient of the Former CLEAR Plant area.
MW-2008-02	Active	x			Evaluate groundwater quality immediately downgradient of the Former CLEAR Plant.	The Former CLEAR Plant is a source of general chemistry COIs to groundwater. Additional characterization proposed to characterize this source.	Provide current concentrations of bedrock COIs in groundwater downgradient of the Former CLEAR Plant area.
MW-2008-03	Active	x			Evaluate groundwater quality immediately downgradient of the Former E Pond.	Further investigation proposed to assess source and transport potential of COIs in the bedrock aquifer in this area.	Provide current concentrations of bedrock COIs in groundwater downgradient of the Former CLEAR Plant area.
MW-2008-04	Active	x			Evaluate groundwater quality immediately downgradient of the Former Evaporation Pond.	Further investigation proposed to assess source and transport potential of COIs in the bedrock aquifer in this area.	Provide current concentrations of bedrock COIs in groundwater downgradient of the Former CLEAR Plant area.

Table 4
Planned 2015 VRP Groundwater Sampling Program
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

VRP Well ID	Well Status	2008-2009 VRP Program	APP Well	MOC Well	2008 VRP Work Plan Objective	Conclusion/Recommendation from 2008-2009 VRP Program	2015 VRP Data Gaps Objective
MW-2008-07	Active	x			Evaluate groundwater quality immediately upgradient of the Former C Pond.	Former C Pond is not a source of COIs to groundwater. Further investigation of this source is not needed. However, bedrock groundwater is subject to fracture-flow, hence inclusion of this well is recommended during VRP investigation to characterize nature and extent from Former Raffinate Pond.	Provide current concentrations of COIs in bedrock groundwater downgradient of Former Raffinate Pond.
MW-2008-08	Active	x			Evaluate groundwater quality immediately downgradient of the Former C Pond.	Former C Pond is not a source of COIs to groundwater. Further investigation of this source is not needed. However, this is one of the four alluvial-bedrock well pairs in the Central Investigation Area, and provides information as to the dynamic of water and COI transport from alluvial to bedrock groundwater. Recommended for additional sampling to address VRP data gap with respect to this transport mechanism.	Evaluate transport mechanism of COIs from alluvium to bedrock for the Site. Provide current concentrations of COIs in bedrock groundwater in the Central Investigation Area.
MW-2008-09	Active	x			Evaluate groundwater quality immediately downgradient of the Former Raffinate Pond.	Former Raffinate Pond is a source of COIs to groundwater. Additional characterization in this area is proposed.	Provide current concentrations of COIs in bedrock groundwater downgradient of Former Raffinate Pond.
MW-2008-10	Active	x			Evaluate groundwater quality immediately downgradient of the Former Raffinate Pond.	Former Raffinate Pond is a source of COIs to groundwater. Additional characterization in this area is proposed.	Provide current concentrations of COIs in bedrock groundwater downgradient of Former Raffinate Pond.
MW-2008-11	Active	x			Evaluate groundwater quality upgradient of the Former Raffinate Pond.	VRP investigation of groundwater contributions from the Former Raffinate Pond should include this location to understand COI concentrations upgradient of this facility. Additionally, this is one of the four alluvial-bedrock well pairs in the Central Investigation Area, and provides information as to the dynamic of water and COI transport from alluvial to bedrock groundwater. Recommended for additional sampling to address VRP data gap with respect to this transport mechanism.	Provide current concentrations of bedrock COIs in bedrock groundwater upgradient of Former Raffinate Pond, and characterize alluvial-bedrock groundwater COI relationship.
MW-2014-01	New - TBD				N/A - new well proposed for bedrock aquifer	N/A - new well	Evaluate transport mechanisms of COIs from alluvial to bedrock groundwater for the Site. Provide update on extent of COIs downgradient of Former CLEAR Plant. Provide current concentrations of COIs in bedrock groundwater downgradient of the Former CLEAR Plant area.
MW-2014-02	New - TBD				N/A - new well proposed for bedrock aquifer	N/A - new well	Assess extent of COIs in bedrock downgradient of the Central Investigation Area.
MW-2014-03	New - TBD				N/A - new well proposed for bedrock aquifer	N/A - new well	Assess extent of COIs in bedrock downgradient of the Central Investigation Area.
PZ-02	Active	x			Evaluate quality of bedrock groundwater downgradient of sulfide leach stockpile and in vicinity of Headwall No. 1 and Bailey Lake.	Further investigation proposed to assess source and transport potential of COIs in the bedrock aquifer in this area.	Provide current concentrations of COIs in bedrock groundwater in this area.
PZ-03	Active	x			Evaluate bedrock groundwater quality in Amargosa Wash and possibly part of the Esperanza Mill area. Provides an additional Ruby Star Granodiorite monitoring point.	Further investigation proposed to assess source and transport potential of COIs in the bedrock aquifer in this area.	Provide current concentrations of COIs in bedrock groundwater in the Central Investigation Area.
PZ-04	Active	x			Evaluate bedrock groundwater quality in the general mill area and provides an additional Ruby Star Granodiorite monitoring point.	Water quality upgradient of Central Investigation Area shows concentrations are greater than AWQS and/or background. Monitoring events for the VRP should include this well as a means to assess contribution of upgradient groundwater to COIs in the Central Investigation Area.	Provide current concentrations of COIs in bedrock groundwater entering the Central Investigation Area.

Table 4
Planned 2015 VRP Groundwater Sampling Program
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

VRP Well ID	Well Status	2008-2009 VRP Program	APP Well	MOC Well	2008 VRP Work Plan Objective	Conclusion/Recommendation from 2008-2009 VRP Program	2015 VRP Data Gaps Objective
PZ-05	Active	x			Evaluate bedrock groundwater quality in the general mill area and provides an additional Ruby Star Granodiorite monitoring point.	Water quality upgradient of Central Investigation Area shows concentrations are greater than AWQS and/or background. Monitoring events for the VRP should include this well as a means to assess contribution of upgradient groundwater to COIs in the Central Investigation Area.	Provide current concentrations of COIs in bedrock groundwater entering the Central Investigation Area.
PZ-06	Active	x			Evaluate bedrock groundwater quality upgradient of the general mill area.	Water quality upgradient of Central Investigation Area shows concentrations are greater than AWQS and/or background. Monitoring events for the VRP should include this well as a means to assess contribution of upgradient groundwater to COIs in the Central Investigation Area.	Provide current concentrations of COIs in bedrock groundwater entering the Central Investigation Area.
TW-2008-08	Active	x			Confirm that the pond (Launders Facility) has not released elevated concentrations of COIs from process solutions to groundwater.	Further investigation proposed to assess source and transport potential of COIs in the alluvial aquifer in this area.	Provide confirmation/current concentrations of COIs in alluvial groundwater in this area.
TW-2008-09	Active	x			Confirm that the ponds (Headwall No. 1 and Bailey Lake) have not released elevated concentrations of COIs from process solutions to groundwater.	Further investigation proposed to assess source and transport potential of COIs in the alluvial aquifer in this area.	Provide confirmation/current concentrations of COIs in alluvial groundwater in this area.
TW-2008-10	Active	x			Confirm that the pond (Raffinate Pond No. 2) has not released elevated concentrations of COIs from process solutions to groundwater.	Further investigation proposed to assess source and transport potential of COIs in the alluvial aquifer in this area.	Provide confirmation/current concentrations of COIs in alluvial groundwater in this area.
TW-2008-11	Active	x			Confirm that the pond (former A Pond) has not released elevated concentrations of COIs from process solutions to groundwater.	Further investigation proposed to assess source and transport potential of COIs in the alluvial aquifer in this area.	Provide confirmation/current concentrations of COIs in alluvial groundwater in this area.
TW-2008-12	Active	x			Confirm that the pond (B Pond) has not released elevated concentrations of COIs from process solutions to groundwater.	Further investigation proposed to assess source and transport potential of COIs in the alluvial aquifer in this area.	Provide current concentrations of COIs in alluvial groundwater downgradient of B Pond and the Central Investigation Area.
TW-2008-13	Active	x			Not specified.	Former C Pond is not a source of COIs to groundwater. Further investigation of this source is not needed. However, this is one of the four alluvial-bedrock well pairs in the Central Investigation Area, and provides information as to the dynamic of water and COI transport from alluvial to bedrock groundwater. Recommended for additional sampling to address VRP data gap with respect to this transport mechanism.	Evaluate transport mechanism of COIs from alluvium to bedrock for the Site. Provide current concentrations of COIs in alluvial groundwater in the Central Investigation Area.
TW-2008-15	Active	x			Not specified.	This is one of the four alluvial-bedrock well pairs in the Central Investigation Area, and provides information as to the dynamic of water and COI transport from alluvial to bedrock groundwater. Recommended for additional sampling to address VRP data gap with respect to this transport mechanism.	Provide confirmation/current concentrations of COIs in alluvial groundwater upgradient of the Central Investigation Area.
TW-2014-01	New - TBD				N/A - new well proposed for alluvial aquifer	N/A - new well	Evaluate transport mechanisms of COIs from alluvium to bedrock for the Site. Provide update on extent of COIs downgradient of Former CLEAR Plant. Provide current concentrations of COIs in alluvial groundwater downgradient of the Former CLEAR Plant.
East Investigation Area							
MH-9	Active	x	x	x	N/A - APP-MOC well proposed for VRP monitoring for basin fill deposits	N/A - new well	Provide COI concentration data in the basin fill deposits to the south of the STI.
MH-10	Active	x	x	x	N/A - APP-MOC well proposed for VRP monitoring for basin fill deposits	N/A - new well	Provide COI concentration data in the basin fill deposits to the south of the STI.
MH-14	Active	x	x	x	Evaluate basin fill deposits groundwater quality in northern portion of well field.	Continue monitoring per APP program.	Provide COI concentration data in the basin fill deposits to the east of the STI.
MH-15W	Active	x		x	Evaluate basin fill deposits groundwater quality in central portion of well field.	Continue monitoring per APP program.	Provide COI concentration data in the basin fill deposits to the east of the STI.

Table 4
Planned 2015 VRP Groundwater Sampling Program
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

VRP Well ID	Well Status	2008-2009 VRP Program	APP Well	MOC Well	2008 VRP Work Plan Objective	Conclusion/Recommendation from 2008-2009 VRP Program	2015 VRP Data Gaps Objective
MH-16W	Active	x	x	x	Evaluate basin fill deposits groundwater quality in southern portion of well field.	Continue monitoring per APP program.	Provide COI concentration data in the basin fill deposits to the east of the STI.
MH-28	Active	x	x	x	Evaluate basin fill deposits groundwater quality in northern portion of well field.	Continue monitoring per APP program.	Provide COI concentration data in the basin fill deposits to the east of the STI.
MH-29	Active	x	x	x	Evaluate basin fill deposits groundwater quality in southern portion of well field.	Continue monitoring per APP program.	Provide COI concentration data in the basin fill deposits to the east of the STI.
MH-30	Active	x		x	Evaluate basin fill deposits groundwater quality in northern portion of well field.	Continue monitoring per APP program.	Provide COI concentration data in the basin fill deposits to the northeast of the STI.
PZ-07	Active	x			Evaluate groundwater quality at northern edge of basin fill deposits and northern Sierrita property boundary.	Further characterization is proposed to confirm upgradient concentrations of COIs in basin fill.	Provide current COI concentrations for the East Investigation Area to confirm upgradient concentrations of COIs in basin fill.
West Investigation Area							
BW-02	Active	x			Confirm no releases have occurred from process solution ponds located in Esperanza Wash.	Further investigation proposed to assess source and transport potential of COIs in the bedrock aquifer in this area.	Provide current concentrations of COIs in bedrock downgradient of solution ponds in the Esperanza Wash, for the West Investigation Area.
MH-18	Active	x	x		Evaluate impacts from waste rock stockpile and possibly represent groundwater conditions generally upgradient of Sierrita.	Continue to monitor per APP program.	Provide current concentrations of COIs in bedrock, in the West Investigation Area.
MH-19	Active	x	x		Evaluate shallower aquifer impacts from sulfide leach area and Headwall No. 5.	Continue to monitor per APP program.	Provide current concentrations of COIs in bedrock downgradient of the sulfide leach area and Headwall No. 5, for the West Investigation Area.
MH-20	Active	x	x		This well is screened at a deeper elevation than well BW-02. Evaluate deeper aquifer impacts.	Continue to monitor per APP program.	Provide current concentrations of COIs in bedrock downgradient of the West Investigation Area.
MH-27	Active	x	x		Evaluate quality of bedrock groundwater in vicinity of Headwall No. 2.	Continue to monitor per APP program.	Provide current concentrations of COIs in bedrock downgradient of Headwall No. 2 for the West Investigation Area.
PZ-16	Active	x			Evaluate quality of bedrock groundwater in vicinity of Headwall No. 5.	Further investigation proposed to assess source and transport potential of COIs in the bedrock aquifer in this area.	Provide current concentrations of COIs in bedrock downgradient of process solution ponds and Headwall No. 5 for the West Investigation Area.
TW-2008-03	Active	x			Confirm that the pond (Headwall No. 3) has not released elevated concentrations of COIs from process solutions to groundwater.	Include in data gaps investigation of this investigation area to confirm/provide updated data for alluvial aquifer saturation and COI concentrations.	Provide current concentrations of COIs in alluvium downgradient of Headwall No. 3 for the West Investigation Area.
TW-2008-04	Active	x			Confirm that the pond (Raffinate Pond No. 3) has not released elevated concentrations of COIs from process solutions to groundwater.	Include in data gaps investigation of this investigation area to confirm/provide updated data for alluvial aquifer saturation and COI concentrations.	Provide current concentrations of COIs in alluvium downgradient of Raffinate Pond No. 3 and Headwall No. 3 for the West Investigation Area.
TW-2008-05	Active	x			Confirm that the pond (SX-3 Stormwater Pond) has not released elevated concentrations of COIs from process solutions to groundwater.	Include in data gaps investigation of this investigation area to confirm/provide updated data for alluvial aquifer saturation and COI concentrations.	Provide current concentrations of COIs in alluvium downgradient of SX-3 Stormwater Pond for the West Investigation Area.
TW-2008-07	Active	x			Confirm that the pond (Headwall No. 2) has not released elevated concentrations of COIs from process solutions to groundwater.	Include in data gaps investigation of this investigation area to confirm/provide updated data for alluvial aquifer saturation and COI concentrations.	Provide current concentrations of COIs in alluvium downgradient of Headwall No. 2 for the West Investigation Area.

Notes:
Wells are generally ordered in this table upgradient to downgradient per area or feature.
N/A = not applicable
APP - Aquifer Protection Permit
AWQS - Arizona Aquifer Water Quality Standards
CLEAR - Copper Leach Electrowinning and Regeneration
COIs - constituents of interest
MOC - Mitigation Order on Consent
STI - Sierrita Tailings Impoundment
TBD - To Be Determined
VRP - Voluntary Remediation Program

Table 5
2008-2009 Wells Omitted from the 2015 VRP Groundwater Sampling Program
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

VRP Well ID	Well Status	2008-2009 VRP Program	APP Well	MOC Well	Associated Wash	Screened Lithology	2008 objective	Conclusion/Recommendation from 2008-2009 VRP Program	2015 Groundwater Monitoring Plan
MW-2008-05	Active	X			Demetrie Wash	Ruby Star Granodiorite/In	Evaluate groundwater quality immediately downgradient of the Old D Pond.	Old D Pond is not a source of COIs to groundwater. Further investigation of this source is not needed.	Remove from VRP groundwater monitoring program.
MW-2008-06	Active	X			Demetrie Wash	Ruby Star Granodiorite/Intrusives	Evaluate groundwater quality upgradient of the Old D Pond.	Old D Pond is not a source of COIs to groundwater. Further investigation of this source is not needed.	Remove from VRP groundwater monitoring program.
PZ-08	Active	X			Demetrie Wash	Demetrie Volcanics	Evaluate southern portion Sierrita property boundary and groundwater quality before it flows beneath Sierrita Tailing Impoundment.	STI is not a source of COIs to groundwater (sulfate addressed through MOC). Further investigation of this source is not needed for the VRP.	Remove from VRP groundwater monitoring program.
PZ-09	Active	X			N/A - East Investigation Area	Other	Not specified	No further monitoring recommended.	Remove from VRP groundwater monitoring program.
PZ-2007-05	Abandoned	X			N/A - East Investigation Area	Basin Fill Deposits	Evaluate basin fill deposits groundwater quality immediately downgradient of the Esperanza Tailing Impoundment and near the Sierrita Tailing Impoundment reclaim pond.	STI is not a source of COIs to groundwater (sulfate addressed through MOC). Further investigation of this source is not needed for the VRP.	Well previously abandoned and has been removed from the program.
PZ-2008-16	Permanent Monitoring Well (well buried)	X			N/A - East of washes	Tailings	Metal COIs < AWQS; Gross alpha and Gross beta > AWQS.	STI is not a source of COIs to groundwater (sulfate addressed through MOC). Further investigation of this source is not needed for the VRP.	Remove from VRP groundwater monitoring program.
PZ-2008-19	Permanent Monitoring Well (well buried)	X			N/A - East of washes	Tailings	Metal COIs < AWQS; Gross alpha and Gross beta > AWQS.	STI is not a source of COIs to groundwater (sulfate addressed through MOC). Further investigation of this source is not needed for the VRP.	Remove from VRP groundwater monitoring program.
PZ-2008-20	Permanent Monitoring Well (well buried)	X			N/A - East of washes	Tailings	Metal COIs < AWQS; Gross alpha and Gross beta > AWQS.	STI is not a source of COIs to groundwater (sulfate addressed through MOC). Further investigation of this source is not needed for the VRP.	Remove from VRP groundwater monitoring program.
TW-2008-02	Temporary Monitoring Well - Destroyed	X			Esperanza Wash	Alluvium	Confirm that the plant (SX Plant No. 3) has not released elevated concentrations of COIs from process solutions to groundwater.	This well was dry.	This well has been destroyed and cannot be monitored.
TW-2008-14	Active	x			Amargosa Wash	Alluvium	Not specified.	No further monitoring recommended.	Remove from VRP groundwater monitoring program.

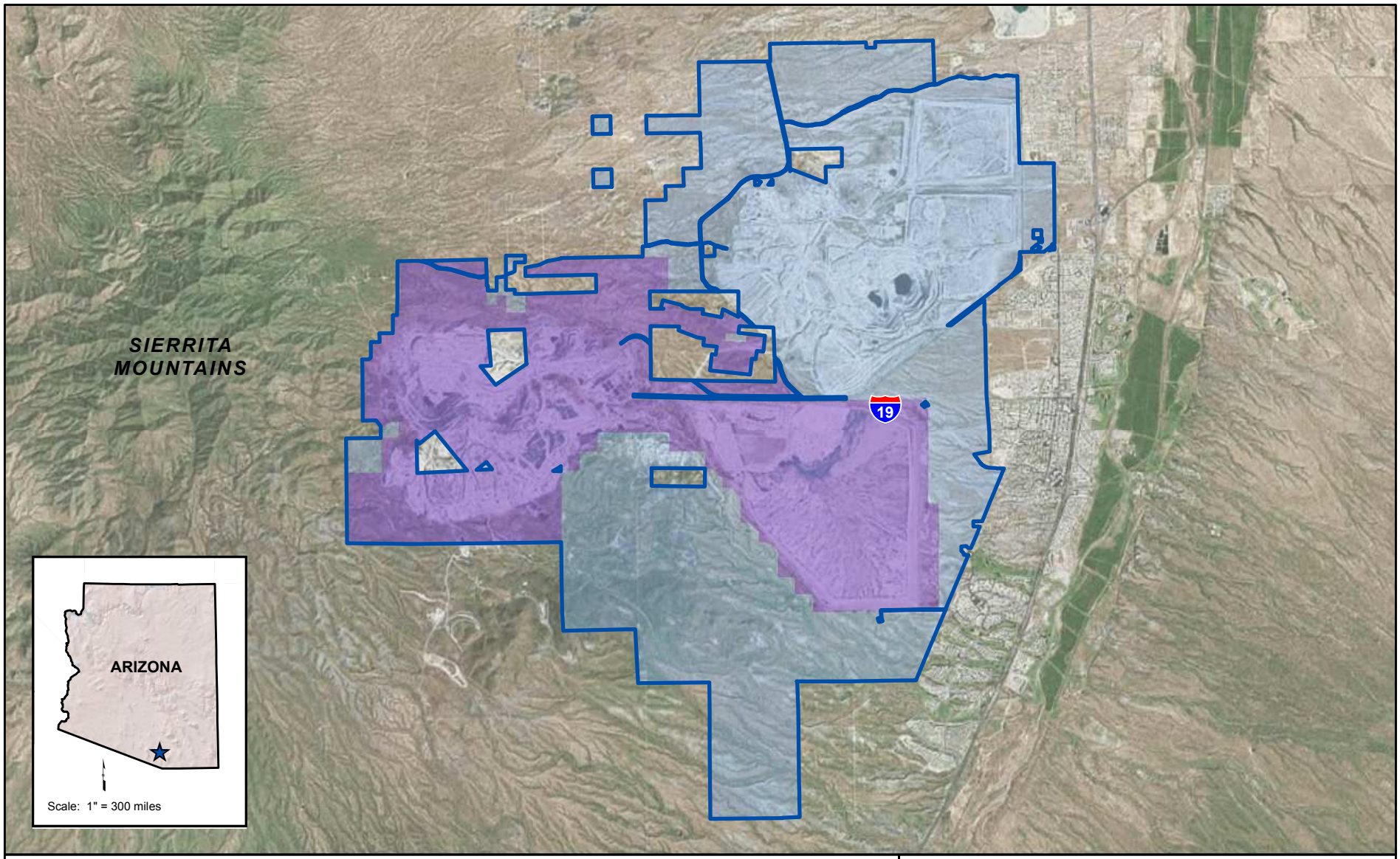
Notes:
N/A = not applicable
APP - Aquifer Protection Permit
AWQS - Arizona Aquifer Water Quality Standards
COIs - constituents of interest
MOC - Mitigation Order on Consent
STI - Sierrita Tailings Impoundment
VRP - Voluntary Remediation Program

Table 6
Anticipated Well Construction Details
Freeport-McMoRan Sierrita Inc.
Green Valley, Arizona

VRP Well ID	Investigation Area	Site Feature	Anticipated Screened Lithology[1]	Northing	Easting	Ground Elevation (ft)	Approximate Borehole Depth (ft bgs)	Borehole Diameter (inches)	Casing Diameter (inches)	Approximate Screen Top (ft bgs)	Approximate Screen Bottom (ft bgs)	Screen Length (ft)
TW-2014-01	Central Investigation Area (North)	Demetrie Wash	Alluvium	955395.0656	319021.2421	3605	50	8	4	20	50	30
MW-2014-01	Central Investigation Area (North)	Demetrie Wash	Bedrock	955395.0656	319021.2421	3605	100	8	4	50	100	50
MW-2014-02	Central Investigation Area (South)	Bedrock South of CIA	Bedrock	952010.1906	314441.2464	3690	80	8	4	50	80	30
MW-2014-03	Central Investigation Area (South)	Bedrock South of CIA	Bedrock	954507.0214	314663.1319	3660	150	8	4	100	150	50
MW-2014-04	Background Area (South)	Background West of STI	Basin Fill Deposits	964724.2840	301936.2289	3315	500	8	4	400	450	50

Notes:
All depths are approximated and will be determined in the field based on conditions encountered
1 - Lithology is predicted from the present geological interpretation, but differing field conditions may result in a different screened lithology for bedrock wells
CIA - Central Investigation Area
ft bgs - feet below ground surface
STI - Sierrita Tailings Impoundment
VRP - Voluntary Remediation Program

Figures



LEGEND

- Approximate property boundary
- Approximate VRP site definition

NOTES

· Topographic map source: ESRI USA Topo Maps.

N

0 2.5 5 Miles

Scale: 1" = 5 mi

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA

VOLUNTARY REMEDIATION PROGRAM DATA GAPS WORKPLAN

SITE LOCATION MAP

ARCADIS

FIGURE
1

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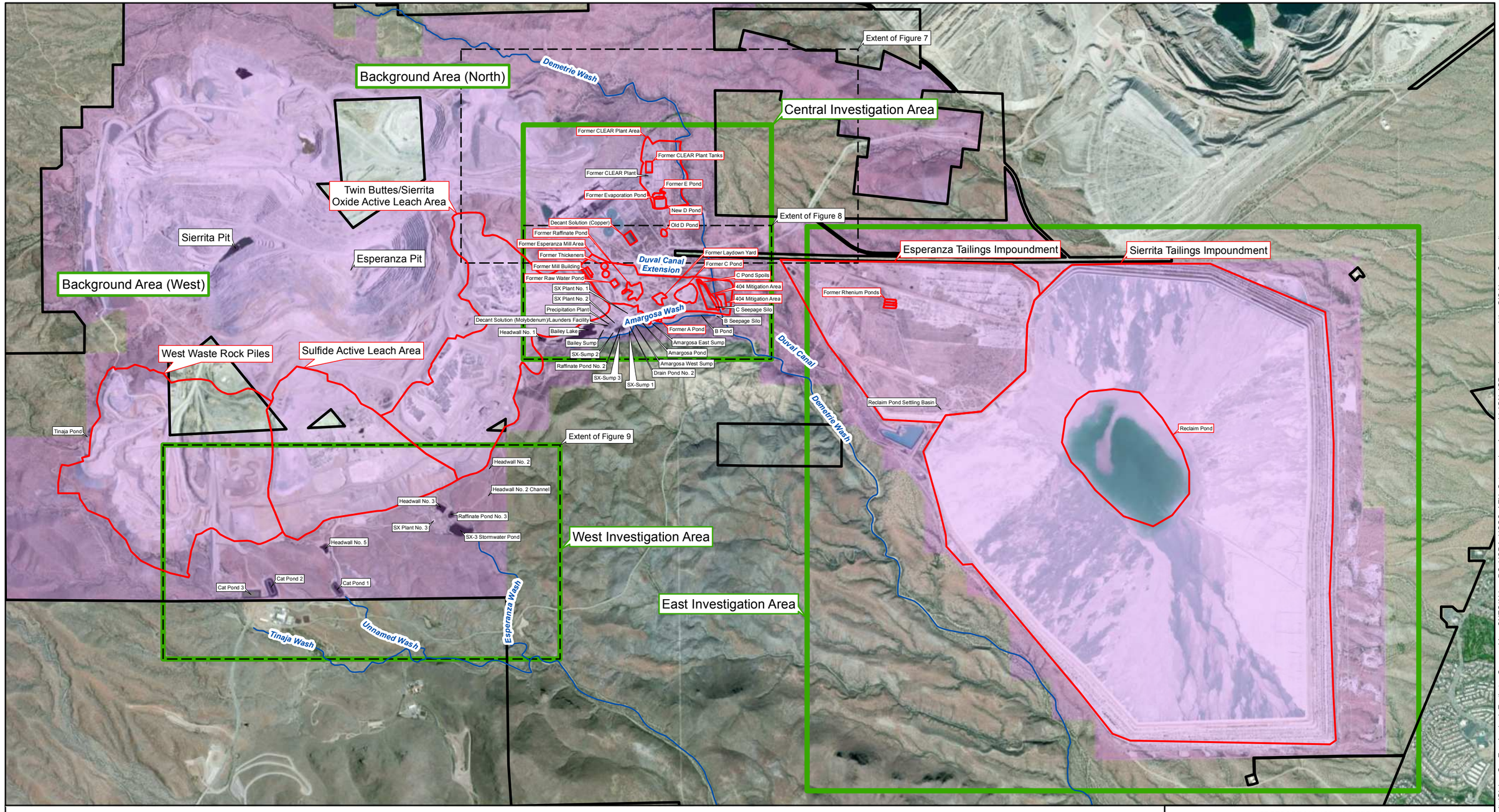


LEGEND

- Property boundary
- VRP site definition
- VRP investigation area
- Site feature
- Wash
- Figure extent

0 1,500 3,000 6,000 Feet

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA

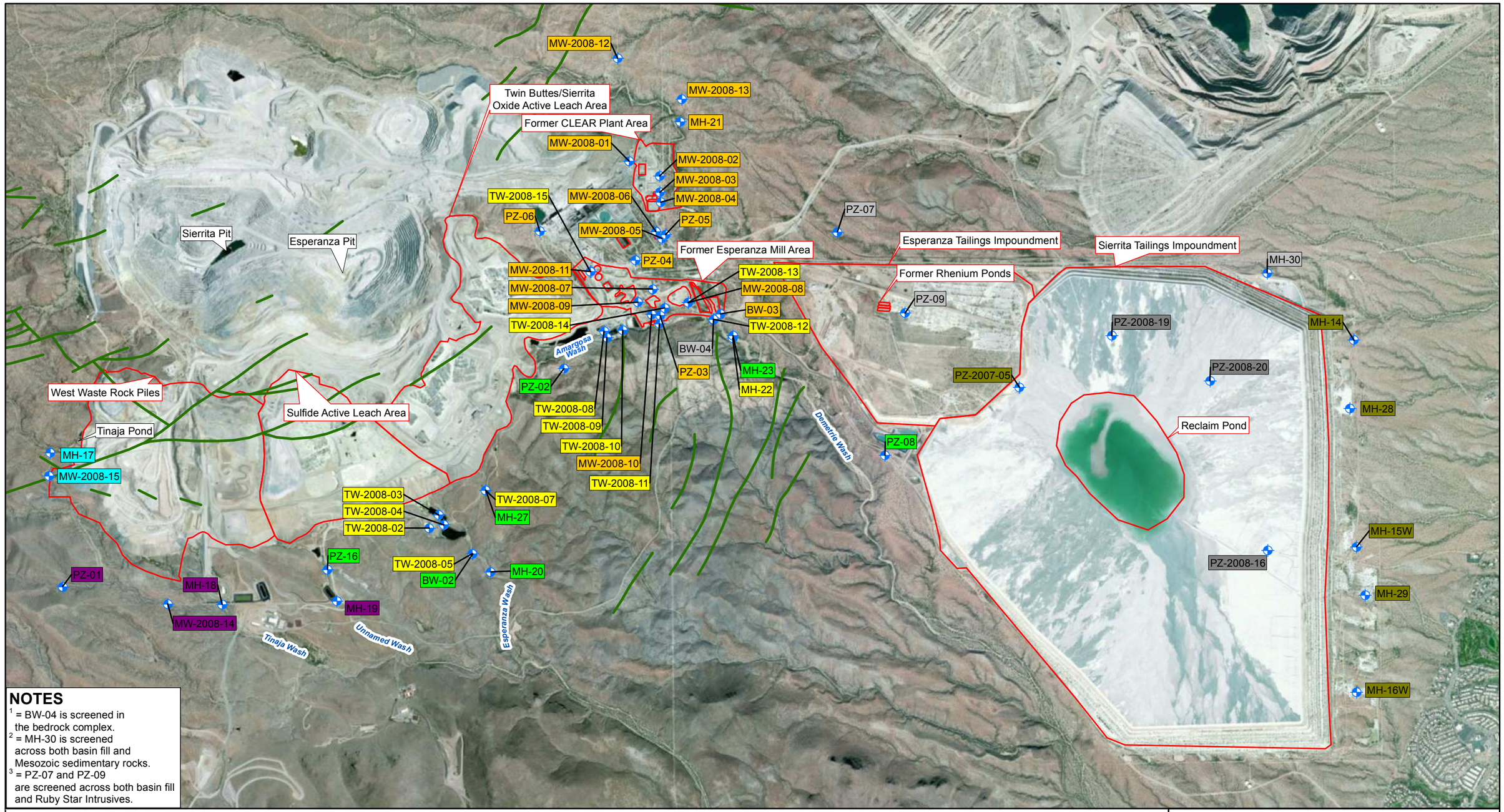
VOLUNTARY REMEDIATION PROGRAM DATA GAPS WORKPLAN

SITE FEATURES MAP

ARCADIS

FIGURE **2**

G:\Project\Sierrita\GIS\Projects\VRP GW characterization report\Final 05-19-2014\Figure 02 site features map.mxd 5/15/2014



NOTES

[1] = BW-04 is screened in the bedrock complex.
[2] = MH-30 is screened across both basin fill and Mesozoic sedimentary rocks.
[3] = PZ-07 and PZ-09 are screened across both basin fill and Ruby Star Intrusives.

GROUNDWATER WELL LITHOLOGIC UNITS

- BW-04 Other
- PZ-2008-16 Tailings
- MH-17 Quaternary Alluvium
- BW-02 Basin Fill Deposits
- MH-28 Tinaja Peak Formation
- BW-03 Ruby Star Granodiorite/ Intrusives
- MH-22 Demetrie Volcanics
- MH-17 Harris Ranch Quartz Monzonite

LEGEND

- Site Feature
- 2008 - 2009 VRP Groundwater Monitoring Location
- Inferred Fault (source: Titley, et al (1986), adapted from Cooper (1973))

N

0 1,500 3,000 6,000 Feet

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA

VOLUNTARY REMEDIATION PROGRAM DATA GAPS WORKPLAN

2008 - 2009 VRP SITE
GOUNDWATER MONITORING WELL NETWORK

ARCADIS

FIGURE 3

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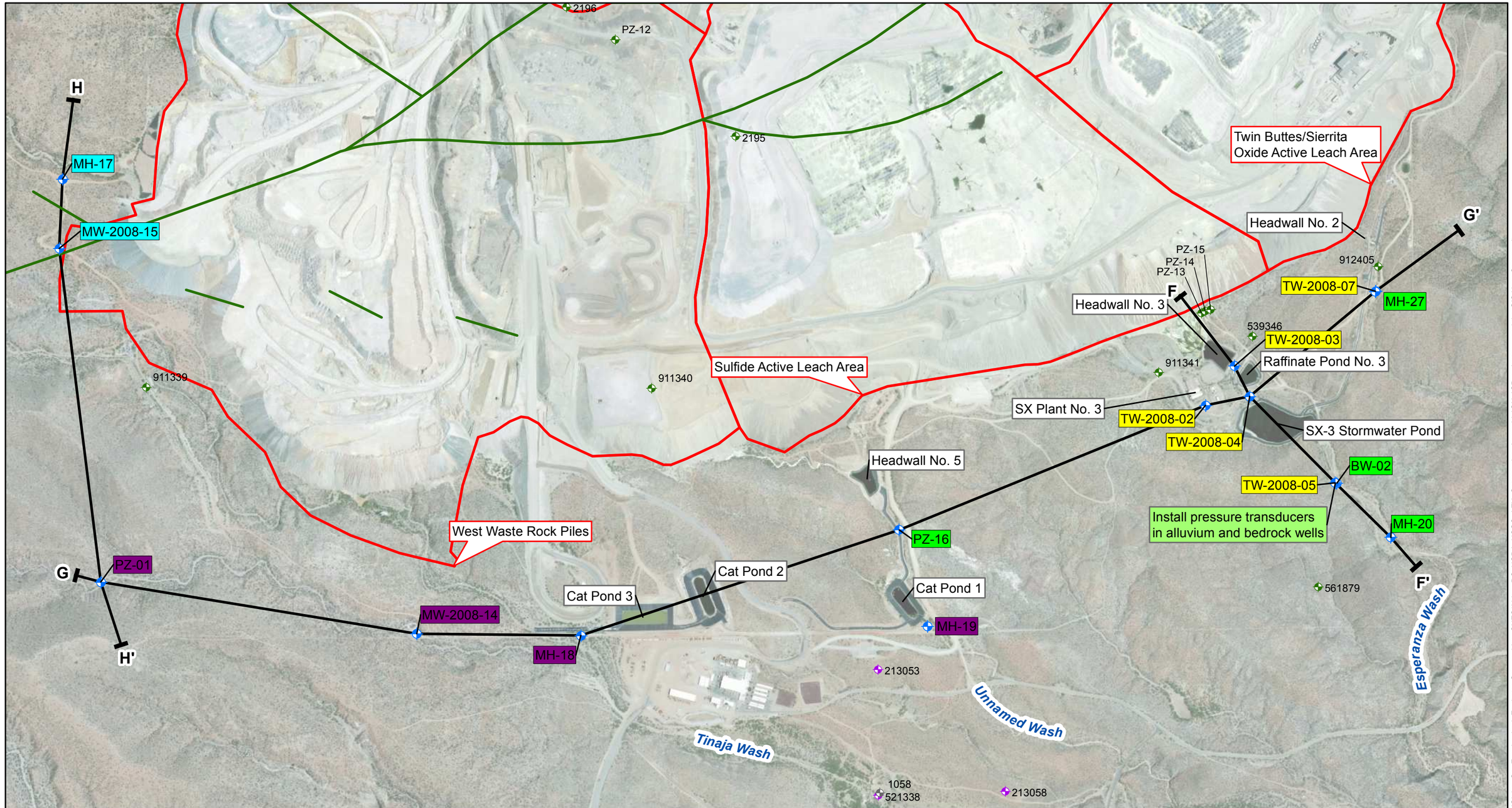
Service Layer Credits: Source: Esri, DigitalGlobe, GeoEye, i-cubed, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community



GROUNDWATER WELL LITHOLOGIC UNITS

- MH-17 Quaternary Alluvium
- MH-28 Tinaja Peak Formation
- MH-22 Demetrie Volcanics
- MH-17 Harris Ranch Quartz Monzonite

LEGEND

- Site Feature
- Cross-Section Location
- Inferred Fault (source: Titley, et al (1986), adapted from Cooper (1973))
- 2008 - 2009 VRP Groundwater Monitoring Location
- Mine
- Commercial
- No-Owner Defined

0 500 1,000 2,000 Feet

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA

VOLUNTARY REMEDIATION PROGRAM DATA GAPS WORKPLAN

WEST INVESTIGATION AREA, BACKGROUND AREA AND PLANNED ASSESSMENT

ARCADIS

FIGURE 4

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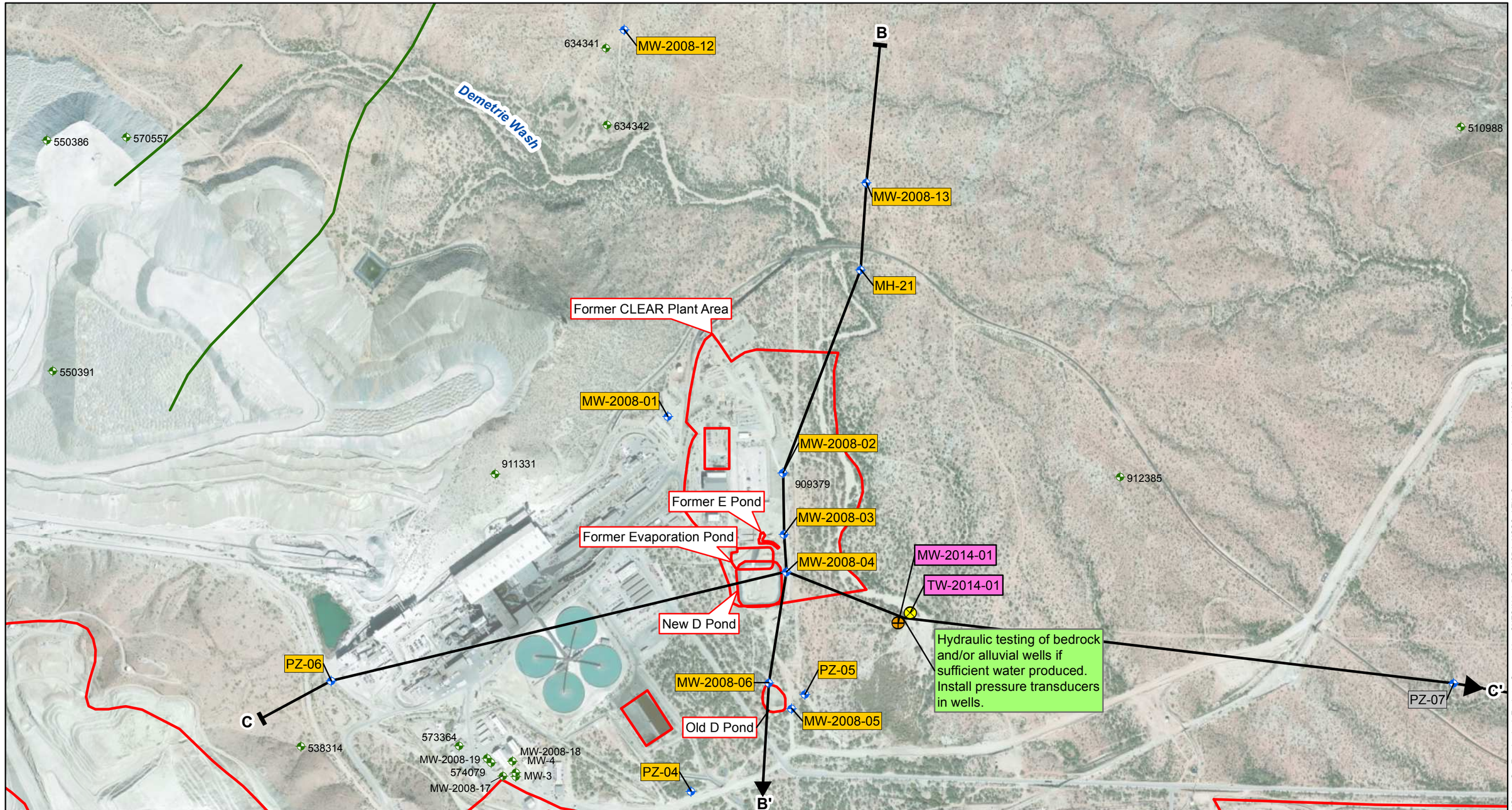

GROUNDWATER WELL LITHOLOGIC UNITS

- BW-04 Other
- MH-17 Quaternary Alluvium
- BW-03 Ruby Star Granodiorite/ Intrusives
- TW-2014-01 Proposed Well Location

LEGEND

- Site Feature
- 2008 - 2009 VRP Groundwater Monitoring Location
- Mine
- Proposed Alluvium Well
- Proposed Bedrock Well
- Inferred Fault (source: Titley, et al (1986), adapted from Cooper (1973)
- Cross-Section Location
- Cross-Section Location That Extends Beyond Map Extent

NOTES

[3] = PZ-07 is screened across both basin fill and Ruby Star Intrusives.

0 400 800 1,600 Feet

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA

VOLUNTARY REMEDIATION PROGRAM DATA GAPS WORKPLAN

CENTRAL INVESTIGATION AREA (NORTH), BACKGROUND AREA AND PLANNED ASSESSMENT

ARCADIS

FIGURE 5

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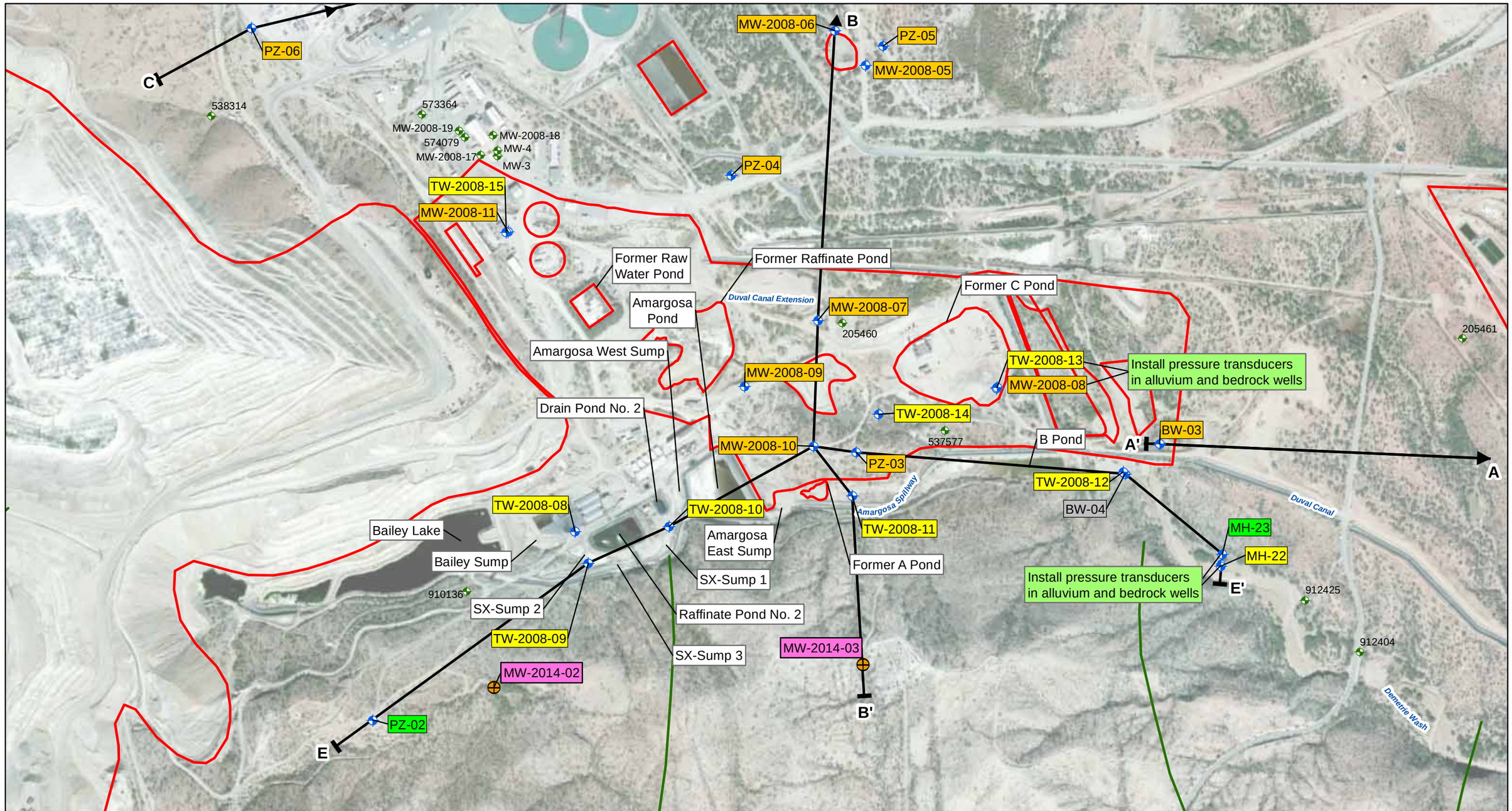


GROUNDWATER WELL LITHOLOGIC UNITS

- BW-04 — Other
- MH-17 — Quaternary Alluvium
- BW-03 — Ruby Star Granodiorite/ Intrusives
- MH-22 — Demetrie Volcanics
- MW-2014-02 — Proposed Well Locations

LEGEND

- Site Feature
- 2008 - 2009 VRP Groundwater Monitoring Location
- Mine
- Proposed Bedrock Well
- Inferred Fault (source: Titley, et al (1986), adapted from Cooper (1973)
- Cross-Section Location
- Cross-Section Location That Extends Beyond Map Extent

NOTES

[1] = BW-04 is screened in the bedrock complex.

0 300 600 1,200 Feet

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA

VOLUNTARY REMEDIATION PROGRAM DATA GAPS WORKPLAN

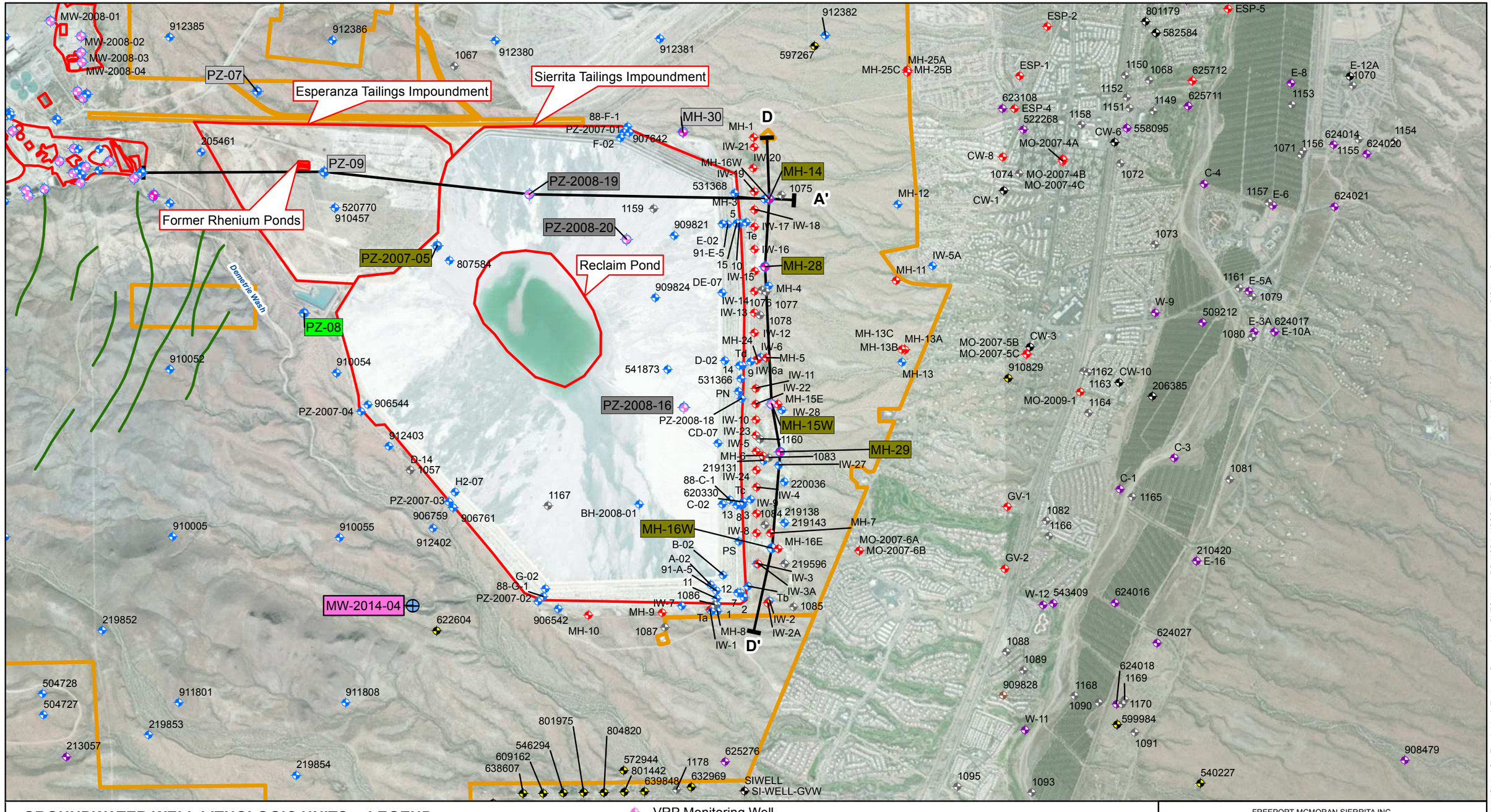
CENTRAL INVESTIGATION AREA (SOUTH) AND PLANNED ASSESSMENT

ARCADIS

FIGURE 6

CITY:(DEN-TECH) DIV/GROUP:(ENV/GIS) DB: GMCKINNEY LD: PIC: PM: TM:
PROJECT: PATH: Z:\GISPROJECTS_ENV\SierritaGIS\ArcMap_MXD\2014\Fig6_CentralInvestigationAreaSouth.mxd

Service Layer Credits: Source: Esri, DigitalGlobe, GeoEye, i-cubed, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community



GROUNDWATER WELL LITHOLOGIC UNITS

- BW-04 Other
- PZ-2008-16 Tailings
- MH-17 Quaternary Alluvium
- BW-02 Basin Fill Deposits
- BW-03 Ruby Star Granodiorite/ Intrusives
- MH-22 Demetrie Volcanics
- MW-2014-04 Proposed Well Location

LEGEND

- Site Feature
- Property Boundary
- 2008 - 2009 VRP Groundwater Monitoring Location
- Proposed Basin Fill Well
- VRP Monitoring Well
- VRP/APP-POC
- VRP/Mitigation/APP-POC
- Mitigation
- Mine
- Commercial
- State
- Municipal/Utility
- Private
- No-Owner Defined
- Inferred Fault (source: Titley, et al (1986), adapted from Cooper (1973)
- Cross-Section Location

3,000 1,500 0 3,000 Feet

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA

VOLUNTARY REMEDIATION PROGRAM DATA GAPS WORKPLAN

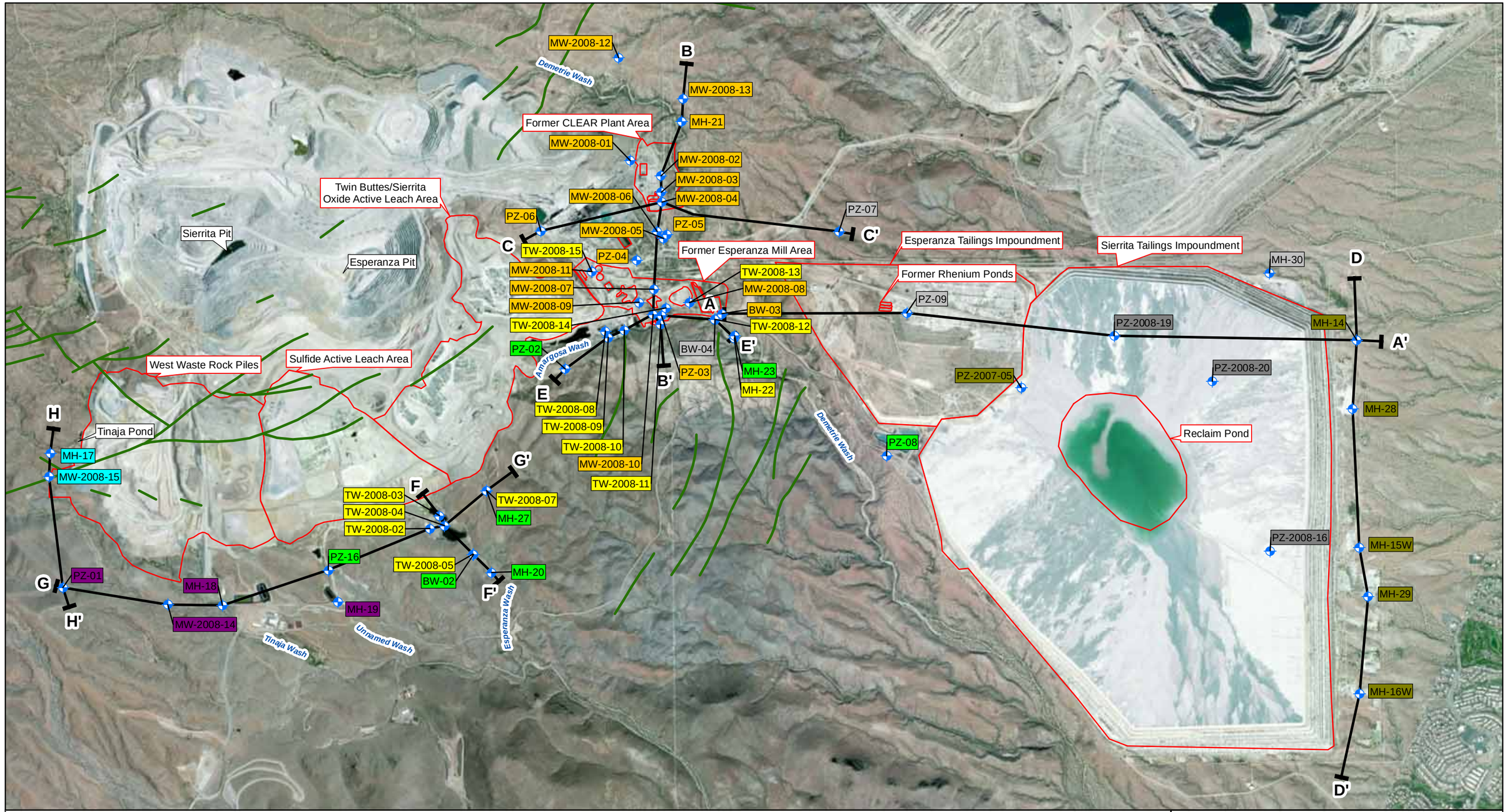
EAST INVESTIGATION AREA AND PLANNED ASSESSMENT

ARCADIS

FIGURE 7

Document Path: Z:\GISPROJECTS_ENV\SierritaGIS\ArcMap_MXD\2014\Fig7_EastInvestigation_v2.mxd

Service Layer Credits: Source: Esri, DigitalGlobe, GeoEye, i-cubed, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community



GROUNDWATER WELL LITHOLOGIC UNITS

- BW-04 Other
- PZ-2008-16 Tailings
- MH-17 Quaternary Alluvium
- BW-02 Basin Fill Deposits
- MH-28 Tinaja Peak Formation
- BW-03 Ruby Star Granodiorite/ Intrusives
- MH-22 Demetrie Volcanics
- MH-17 Harris Ranch Quartz Monzonite

LEGEND

- Site Feature
- 2008 - 2009 VRP Groundwater Monitoring Location
- Cross-Section Location
- Inferred Fault (source: Titley, et al (1986), adapted from Cooper (1973))

NOTES

[1] = BW-04 is screened in the bedrock complex.
[2] = MH-30 is screened across both basin fill and Mesozoic sedimentary rocks.
[3] = PZ-07 and PZ-09 are screened across both basin fill and Ruby Star Intrusives.

0 1,500 3,000 6,000 Feet

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA

VOLUNTARY REMEDIATION PROGRAM DATA GAPS WORKPLAN

CROSS SECTION LOCATION MAP

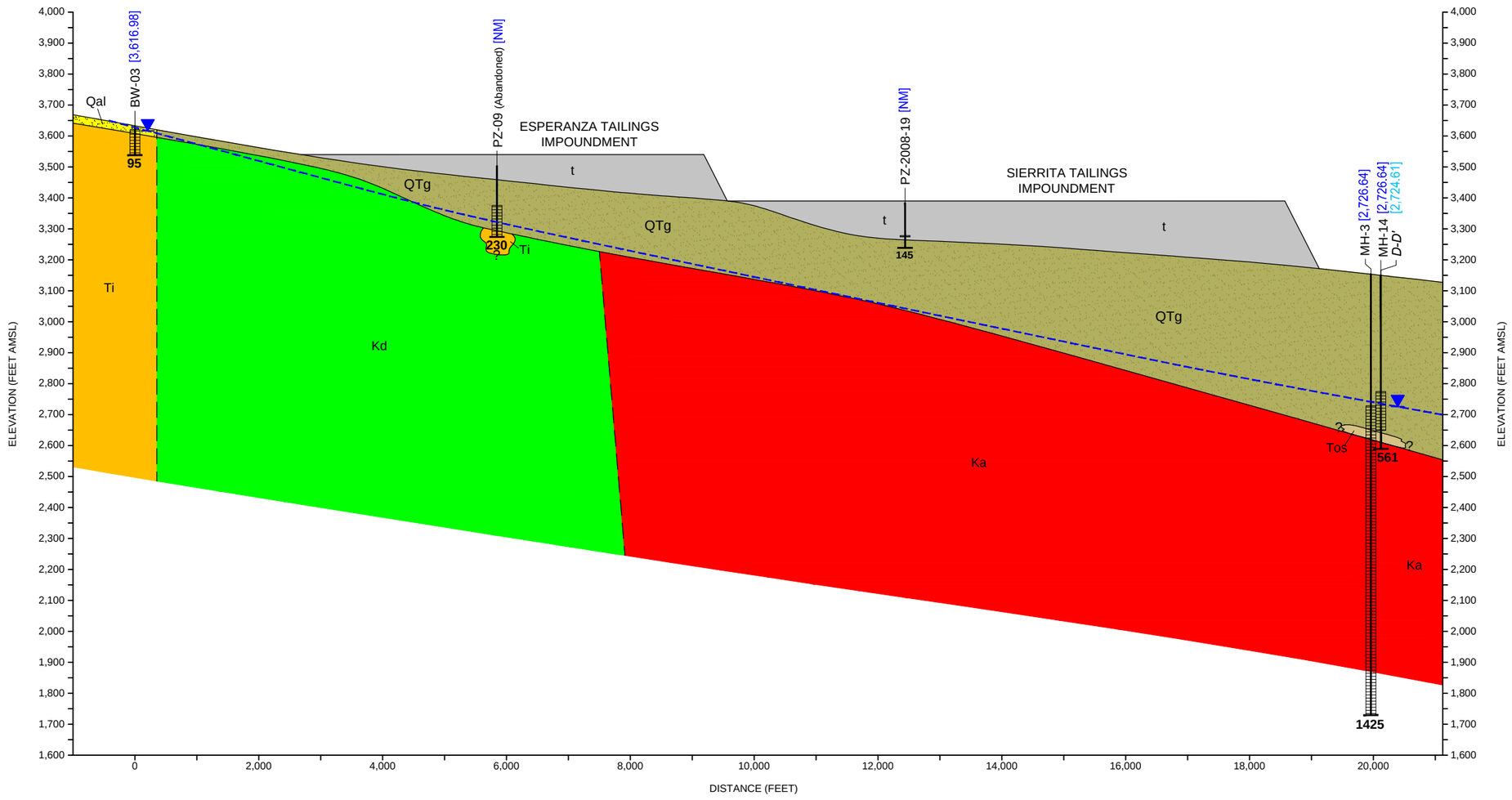
ARCADIS

FIGURE **8**

CITY:(DEN-TECH) DIV/GROUP:(ENV/GIS) DB: GMCKINNEY LD: PIC: PM: TM:
PROJECT: PATH: Z:\GISPROJECTS_ENV\SierritaGIS\ArcMap_MXD\2014Fig8_CrossSectionMap.mxd

A
Northwest

A'
East



LEGEND:

WATER LEVEL (FEET AMSL) [2009], [2013]

MH-14 [2,726.64] [2,724.61]

WELL/BORING ID

GROUND SURFACE

LITHOLOGIC CONTACT (DASHED WHERE INFERRED)

WELL SCREEN INTERVAL

561 TOTAL DEPTH

t	FILL / TAILINGS
Qal	QUATERNARY ALLUVIUM
QTg	BASIN-FILL DEPOSITS
Tos	PANTANO FORMATION
Ti	RUBY STAR GRANODIORITE / INTRUSIVES
Ka	ANGELICA ARKOSE
Kd	DEMETRIE VOLCANICS

AMSL	ABOVE MEAN SEA LEVEL
NM	NOT MEASURED

0 2,000 4,000
HORIZONTAL SCALE IN FEET

0 400 800
VERTICAL SCALE IN FEET

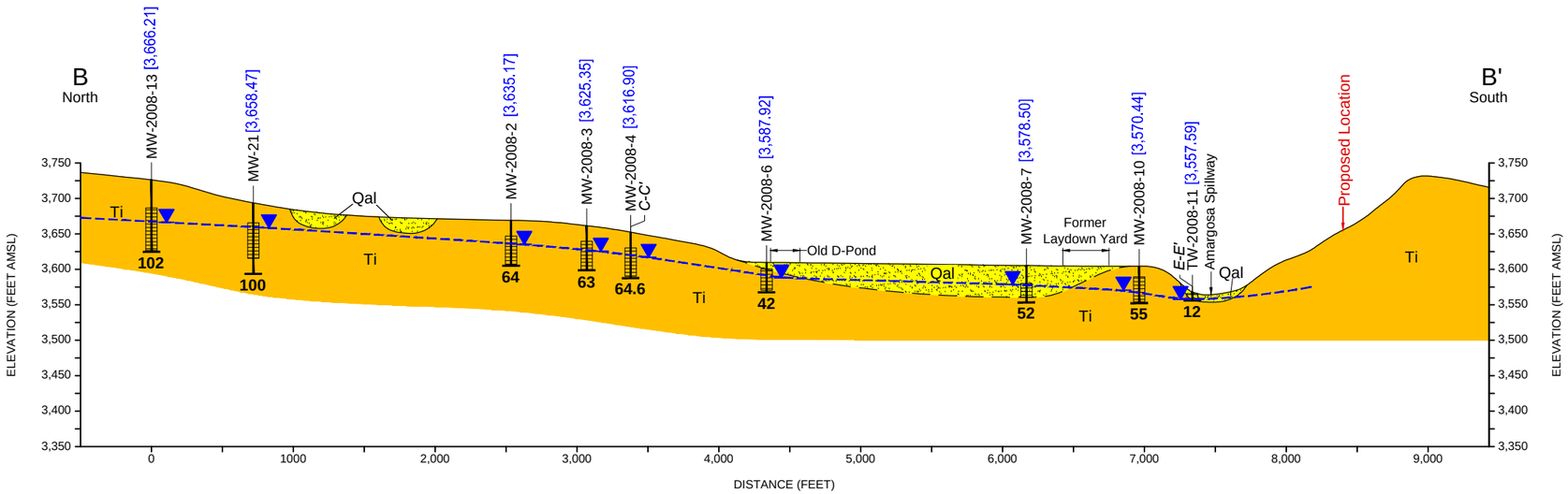
FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA
VOLUNTARY REMEDIATION PROGRAM
DATA GAPS WORKPLAN

CROSS-SECTION A-A' THROUGH EAST INVESTIGATION AREA

ARCADIS

FIGURE
9

CITY: SAN RAFAEL, CA (PETALUMA) DIV/GROUP: ENVCAD DB: J. HARRIS
C:\Users\jharris\Desktop\ENVCADVAZ001233\001400001\DWG\VAZ1233V01.dwg LAYOUT: 9 SAVED: 8/11/2014 7:37 AM ACADVER: 18.1S (LMS TECH) PAGESETUP: ---- PLOTSTYLETABLE: ARCADIS.CTB PLOTTED: 8/20/2014 9:56 AM BY: HARRIS, JESSICA
XREFS: PROJECTNAME: SIERRITA MINE



LEGEND:

MW-21 [3,658.47] — WATER LEVEL (FEET AMSL) [2009]

WELL/BORING ID

GROUND SURFACE

LITHOLOGIC CONTACT (DASHED WHERE INFERRED)

WELL SCREEN INTERVAL

100 — TOTAL DEPTH

Qal — QUATERNARY ALLUVIUM

Ti — RUBY STAR GRANODIORITE / INTRUSIVES

AMSL — ABOVE MEAN SEA LEVEL

0 1,000 2,000
HORIZONTAL SCALE IN FEET

0 200 400
VERTICAL SCALE IN FEET

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA
VOLUNTARY REMEDIATION PROGRAM
DATA GAPS WORKPLAN

CROSS-SECTION B-B' THROUGH CENTRAL INVESTIGATION AREA AND NORTH BACKGROUND AREA

ARCADIS

FIGURE
10

CITY: SAN RAFAEL, CA (PETALUMA) DIV/GROUP: ENVCAD DB: J. HARRIS
C:\Users\jharris\Desktop\ENVCAD\A2001233\00140000\1DWG\A21233V01.dwg LAYOUT: 10 SAVED: 8/20/2014 8:59 AM ACADVER: 18.1S (LMS TECH) PAGESETUP: ---- PLOTSTYLETABLE: ARCADIS.CTB PLOTTED: 11/3/2014 12:33 PM BY: HARRIS, JESSICA
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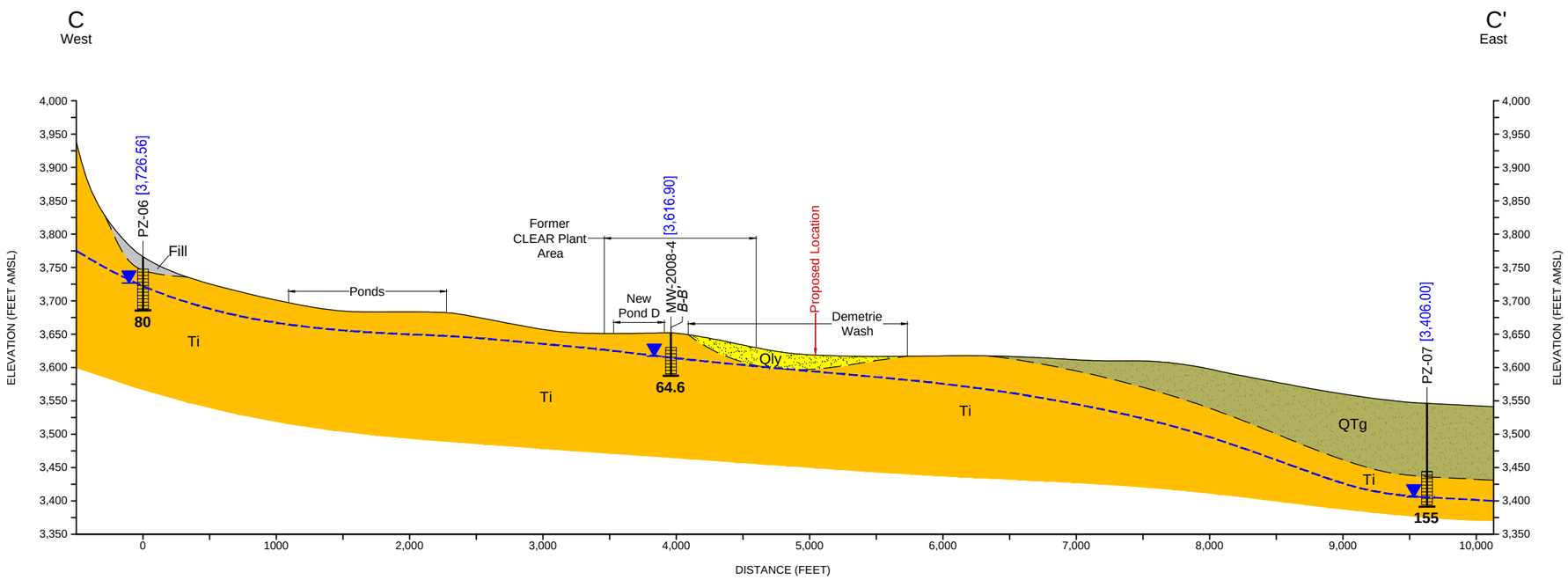
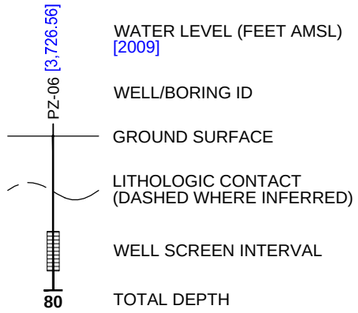
PROJECTNAME: SIERRITA MINE



LEGEND:



WATER LEVEL (FEET AMSL) [2009]

WELL/BORING ID

GROUND SURFACE

LITHOLOGIC CONTACT (DASHED WHERE INFERRED)

WELL SCREEN INTERVAL

TOTAL DEPTH

Fill	FILL
Qly	QUATERNARY ALLUVIUM
QTg	BASIN-FILL DEPOSITS
Ti	RUBY STAR GRANODIORITE / INTRUSIVES

AMSL ABOVE MEAN SEA LEVEL

HORIZONTAL SCALE IN FEET: 0 1,000 2,000

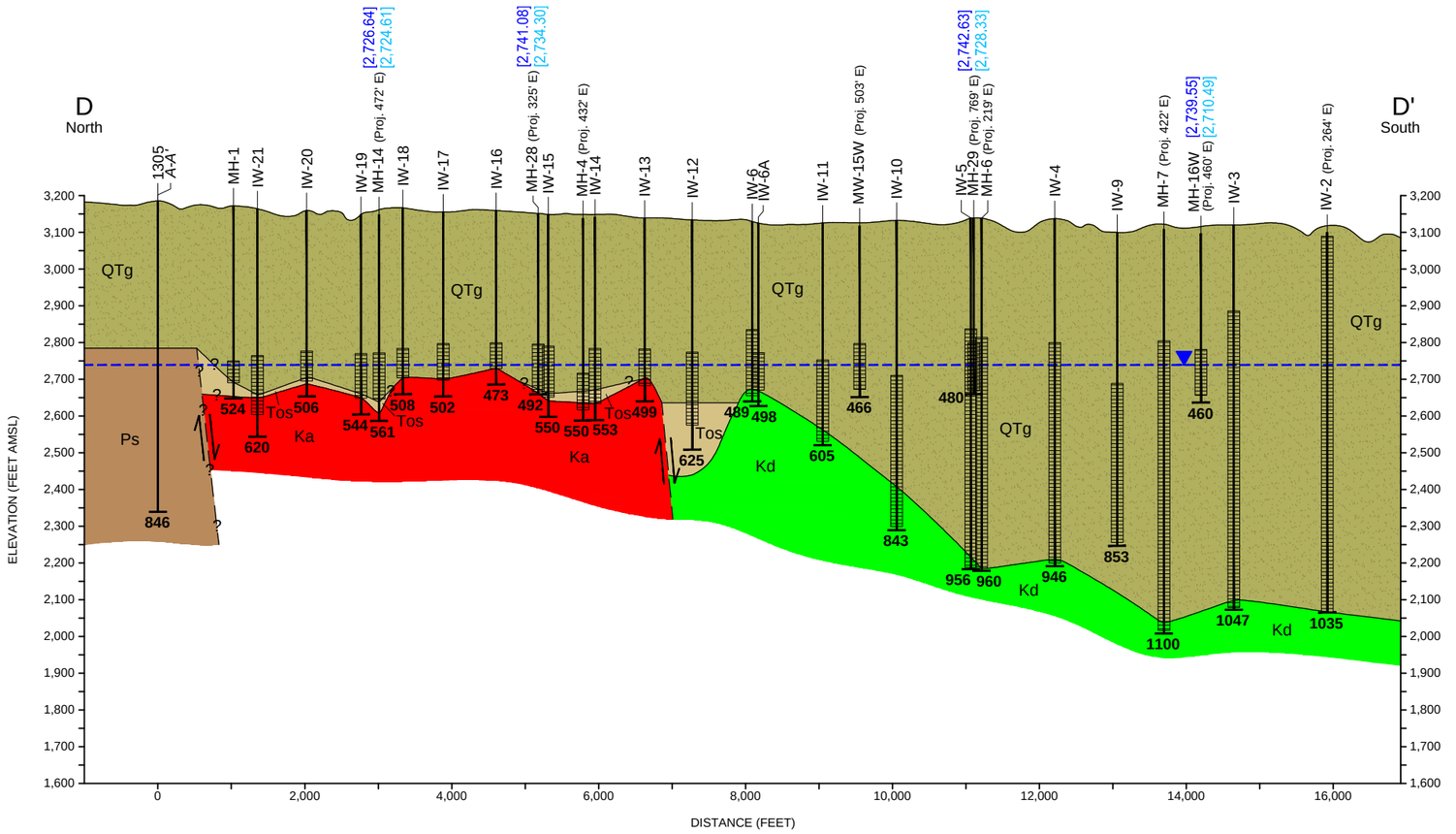
VERTICAL SCALE IN FEET: 0 200 400

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA
VOLUNTARY REMEDIATION PROGRAM
DATA GAPS WORKPLAN

CROSS-SECTION C-C' THROUGH CENTRAL INVESTIGATION AREA (NORTH)

ARCADIS

FIGURE
11



LEGEND:

[2,739.55] MH-16W [2,710.49] — WATER LEVEL (FEET AMSL) [2009], [2013]

WELL/BORING ID

GROUND SURFACE

LITHOLOGIC CONTACT (DASHED WHERE INFERRED)

WELL SCREEN INTERVAL

460 — TOTAL DEPTH

QTg	BASIN-FILL DEPOSITS
Tos	PANTANO FORMATION
Ka	ANGELICA ARKOSE
Kd	DEMETRIE VOLCANICS
Ps	PALEOZOIC SEDIMENTARY ROCKS

FAULT; ARROWS SHOW RELATIVE DIRECTION OF MOVEMENT; DASHED WHERE UNCERTAIN

AMSL ABOVE MEAN SEA LEVEL

SOURCE: ERROL L. MONTGOMERY AND ASSOCIATES (ELMA). 2001. ADDITIONAL CHARACTERIZATION OF HYDROGEOLOGIC CONDITIONS AQUIFER PROTECTION PERMIT APPLICATION NO. 101679, SIERRITA MINE, PHELPS DODGE SIERRITA, INC. PIMA COUNTY, ARIZONA. JANUARY.

0 2,000 4,000
HORIZONTAL SCALE IN FEET

0 400 800
VERTICAL SCALE IN FEET

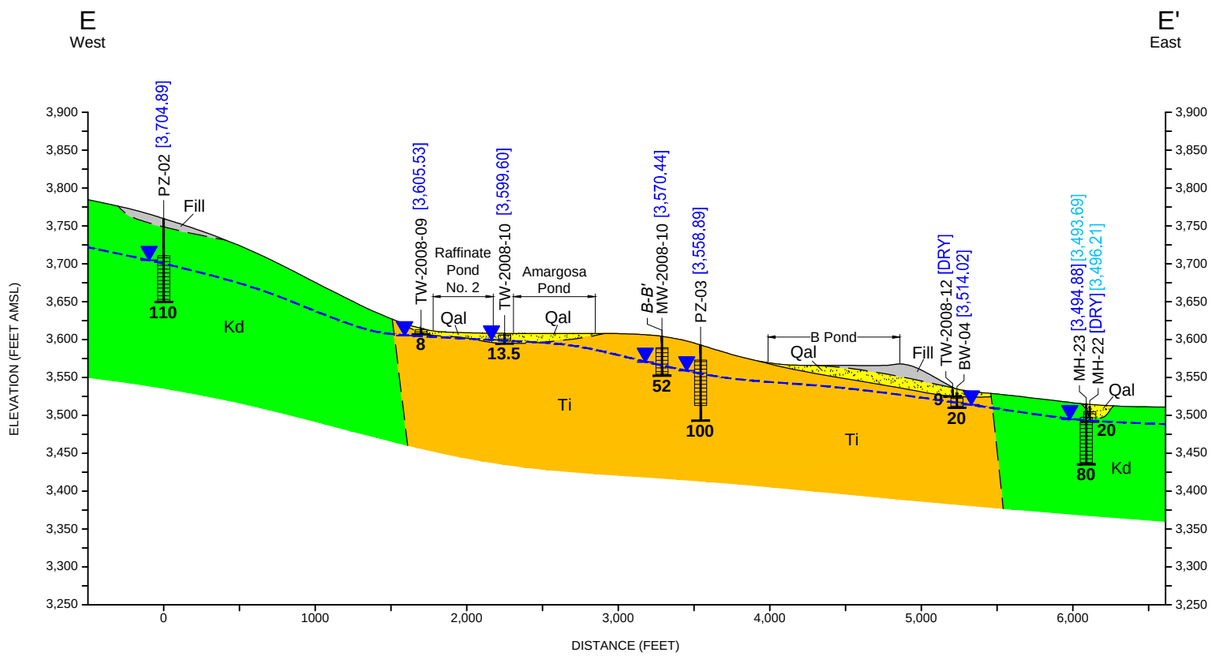
FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA
VOLUNTARY REMEDIATION PROGRAM
DATA GAPS WORKPLAN

CROSS-SECTION D-D' THROUGH EAST INVESTIGATION AREA

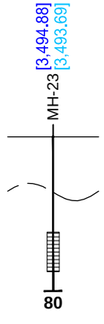
ARCADIS

FIGURE
12

CITY: SAN RAFAEL, CA (PETALUMA) DIV/GROUP: ENVCAD DB: J. HARRIS
C:\Users\jharris\Desktop\ENVCADAZ0012233\00140000\1DWG\A21233V01.dwg LAYOUT: 12 SAVED: 8/20/2014 9:57 AM ACADVER: 18.1S (LMS TECH) PAGESETUP: ---- PLOTSTYLETABLE: ARCADIS.CTB PLOTTED: 8/20/2014 9:58 AM BY: HARRIS, JESSICA
XREFS: PROJECTNAME: SIERRITA MINE



LEGEND:



WATER LEVEL (FEET AMSL) [2009], [2013]

WELL/BORING ID

GROUND SURFACE

LITHOLOGIC CONTACT (DASHED WHERE INFERRED)

WELL SCREEN INTERVAL

TOTAL DEPTH

Fill	FILL
Qal	QUATERNARY ALLUVIUM
Ti	RUBY STAR GRANODIORITE / INTRUSIVES
Kd	DEMETRIE VOLCANICS

AMSL	ABOVE MEAN SEA LEVEL
DRY	WELL REPORTED DRY FROM THE FIELD

0 1,000 2,000
HORIZONTAL SCALE IN FEET

0 200 400
VERTICAL SCALE IN FEET

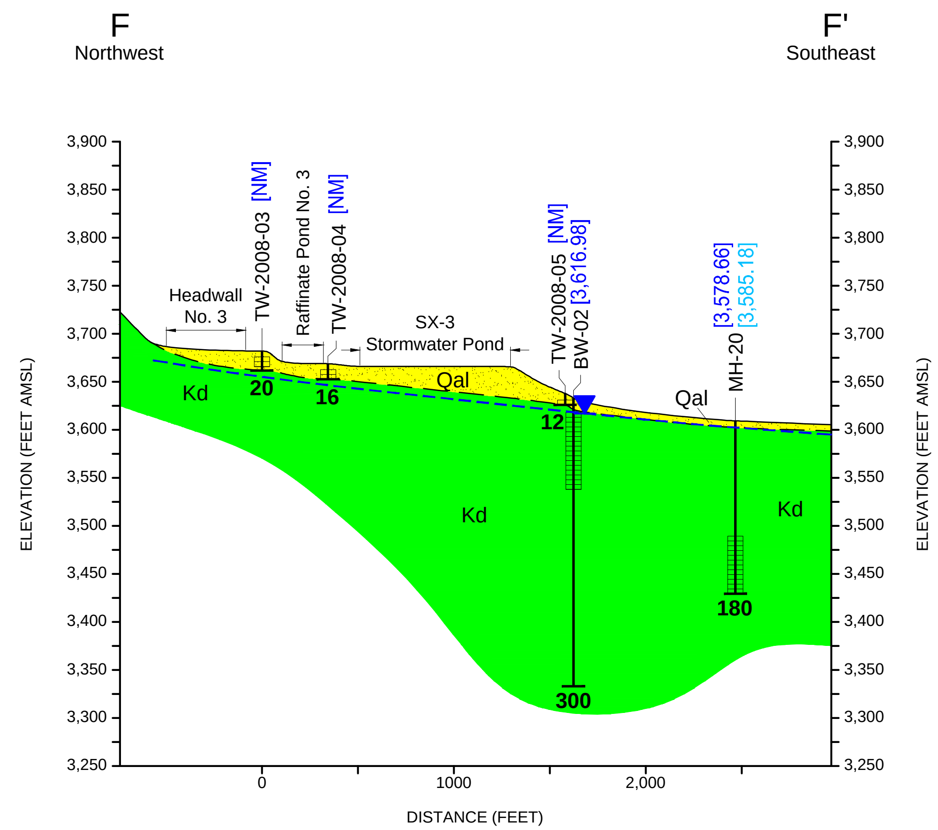
FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA
VOLUNTARY REMEDIATION PROGRAM
DATA GAPS WORKPLAN

CROSS-SECTION E-E' THROUGH CENTRAL INVESTIGATION AREA (SOUTH)

ARCADIS

FIGURE
13

CITY: SAN RAFAEL, CA (PETALUMA) DIV/GROUP: ENV/CAD DB: J. HARRIS
C:\Users\jharris\Desktop\ENV\CAD\A2001233\001400001\DWG\A21233V01.dwg LAYOUT: 13 SAVED: 8/20/2014 9:57 AM ACADVER: 18.1S (LMS TECH) PAGESETUP: ---- PLOTSTYLETABLE: ARCADIS.CTB PLOTTED: 8/20/2014 9:58 AM BY: HARRIS, JESSICA
XREFS: PROJECTNAME: SIERRITA MINE



LEGEND:

[3,578.66] [3,585.18] WATER LEVEL (FEET AMSL) [2009], [2013]

MH-20 WELL/BORING ID

GROUND SURFACE

LITHOLOGIC CONTACT (DASHED WHERE INFERRED)

WELL SCREEN INTERVAL

180 TOTAL DEPTH

Qal QUATERNARY ALLUVIUM

Kd DEMETRIE VOLCANICS

AMSL ABOVE MEAN SEA LEVEL

NM NOT MEASURED

0 1,000 2,000
HORIZONTAL SCALE IN FEET

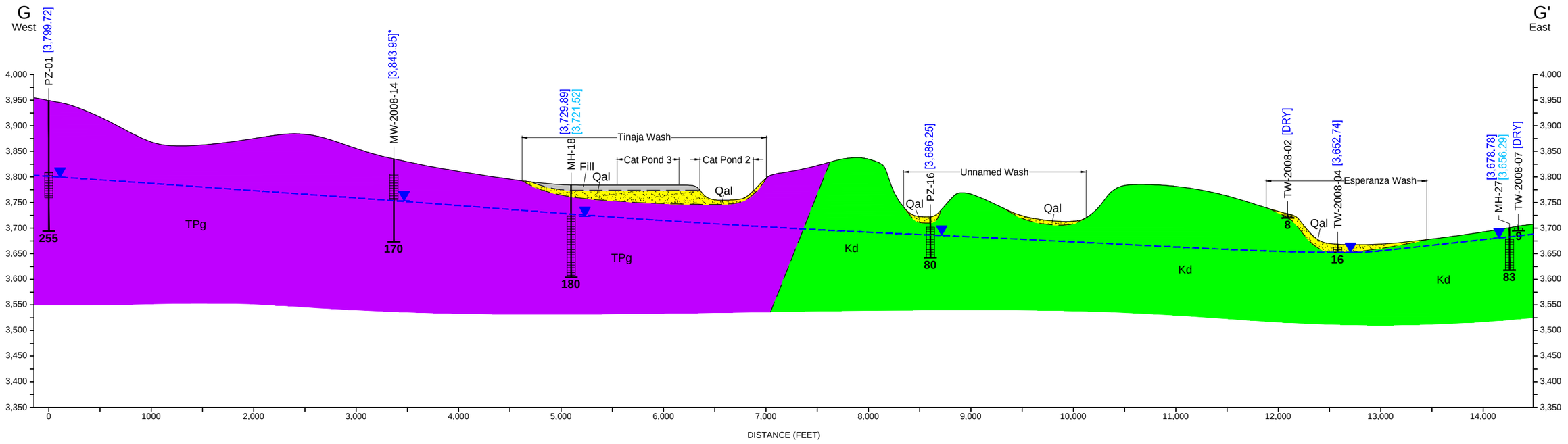
0 200 400
VERTICAL SCALE IN FEET

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA
VOLUNTARY REMEDIATION PROGRAM
DATA GAPS WORKPLAN

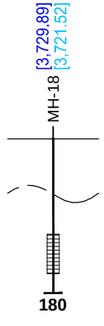
CROSS-SECTION F-F' THROUGH WEST INVESTIGATION AREA

ARCADIS

FIGURE
14



LEGEND:



- WATER LEVEL (FEET AMSL) [2009], [2013]
- WELL/BORING ID
- GROUND SURFACE
- LITHOLOGIC CONTACT (DASHED WHERE INFERRED)
- WELL SCREEN INTERVAL
- TOTAL DEPTH

Fill	FILL
Qal	QUATERNARY ALLUVIUM
TPg	TINAJA PEAK FORMATION
Kd	DEMETRIE VOLCANICS

AMSL	ABOVE MEAN SEA LEVEL
DRY	WELL DRY
*	DEPTH TO WATER SHOWN

0 1,000 2,000
HORIZONTAL SCALE IN FEET

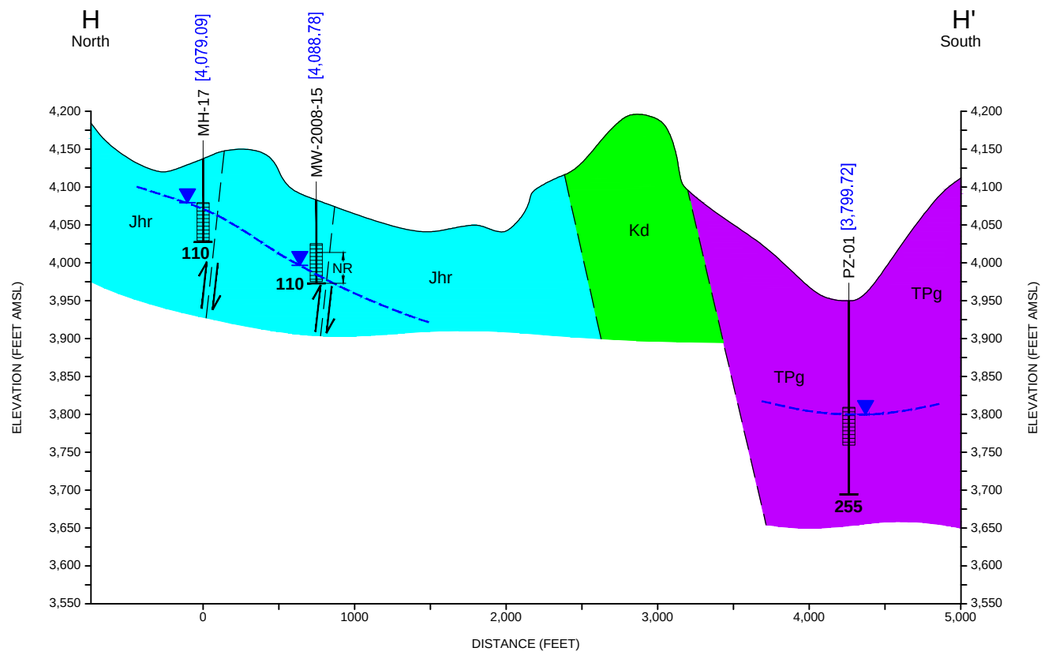
0 200 400
VERTICAL SCALE IN FEET

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA
VOLUNTARY REMEDIATION PROGRAM
DATA GAPS WORKPLAN

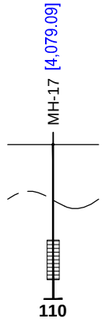
CROSS-SECTION G-G' THROUGH WEST INVESTIGATION AREA

ARCADIS

FIGURE
15



LEGEND:



WATER LEVEL (FEET AMSL) [2009]

WELL/BORING ID

GROUND SURFACE

LITHOLOGIC CONTACT (DASHED WHERE INFERRED)

WELL SCREEN INTERVAL

TOTAL DEPTH

TPg	TINAJA PEAK FORMATION
Kd	DEMETRIE VOLCANICS
Jhr	HARRIS RANCH QUARTZ MANZONITE

FAULT; ARROWS SHOW RELATIVE DIRECTION OF MOVEMENT; DASHED WHERE UNCERTAIN

AMSL	ABOVE MEAN SEA LEVEL
NR	NO RECOVERY

0 1,000 2,000
HORIZONTAL SCALE IN FEET

0 200 400
VERTICAL SCALE IN FEET

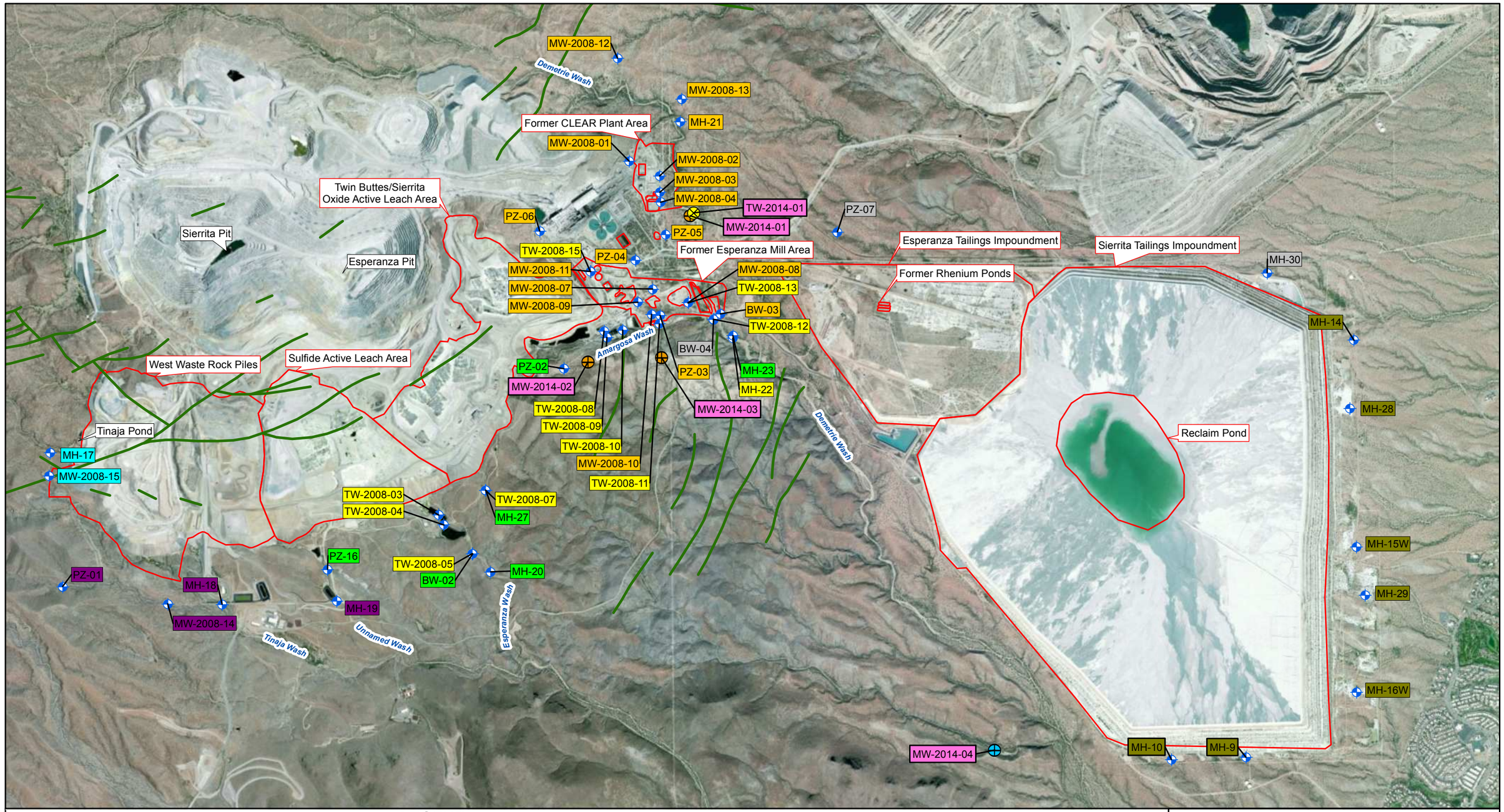
FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA
VOLUNTARY REMEDIATION PROGRAM
DATA GAPS WORKPLAN

CROSS-SECTION H-H' THROUGH WEST BACKGROUND AREA

ARCADIS

FIGURE
16

CITY: SAN RAFAEL, CA (PETALUMA) DIV/GROUP: ENVCAD DB: J. HARRIS
C:\Users\jharris\Desktop\ENVCAD\AZ00123300140000\DWG\AZ1233V01.dwg LAYOUT: 16 SAVED: 8/20/2014 9:59 AM ACADVER: 18.1S (LMS TECH) PAGESETUP: ---- PLOTSTYLETABLE: ARCADIS.CTB PLOTTED: 8/20/2014 9:59 AM BY: HARRIS, JESSICA
XREFS:
PROJECTNAME: SIERRITA MINE



GROUNDWATER WELL LITHOLOGIC UNITS

- BW-04 Other
- PZ-2008-16 Tailings
- MH-17 Quaternary Alluvium
- BW-02 Basin Fill Deposits
- MH-28 Tinaja Peak Formation
- BW-03 Ruby Star Granodiorite/ Intrusives
- MH-22 Demetrie Volcanics
- MH-17 Harris Ranch Quartz Monzonite
- MW-2014-04 Tinaja Peak Formation

LEGEND

- Site Feature
- 2015 VRP Groundwater Monitoring Location
- Proposed Alluvium Well
- Proposed Bedrock Well
- Proposed Basin Fill Well
- Cross-Section Location
- Inferred Fault (source: Titley, et al (1986), adapted from Cooper (1973)

NOTES

[1] = BW-04 is screened in the bedrock complex.
[2] = MH-30 is screened across both basin fill and Mesozoic sedimentary rocks.
[3] = PZ-07 and PZ-09 are screened across both basin fill and Ruby Star Intrusives.

0 1,500 3,000 6,000 Feet

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA

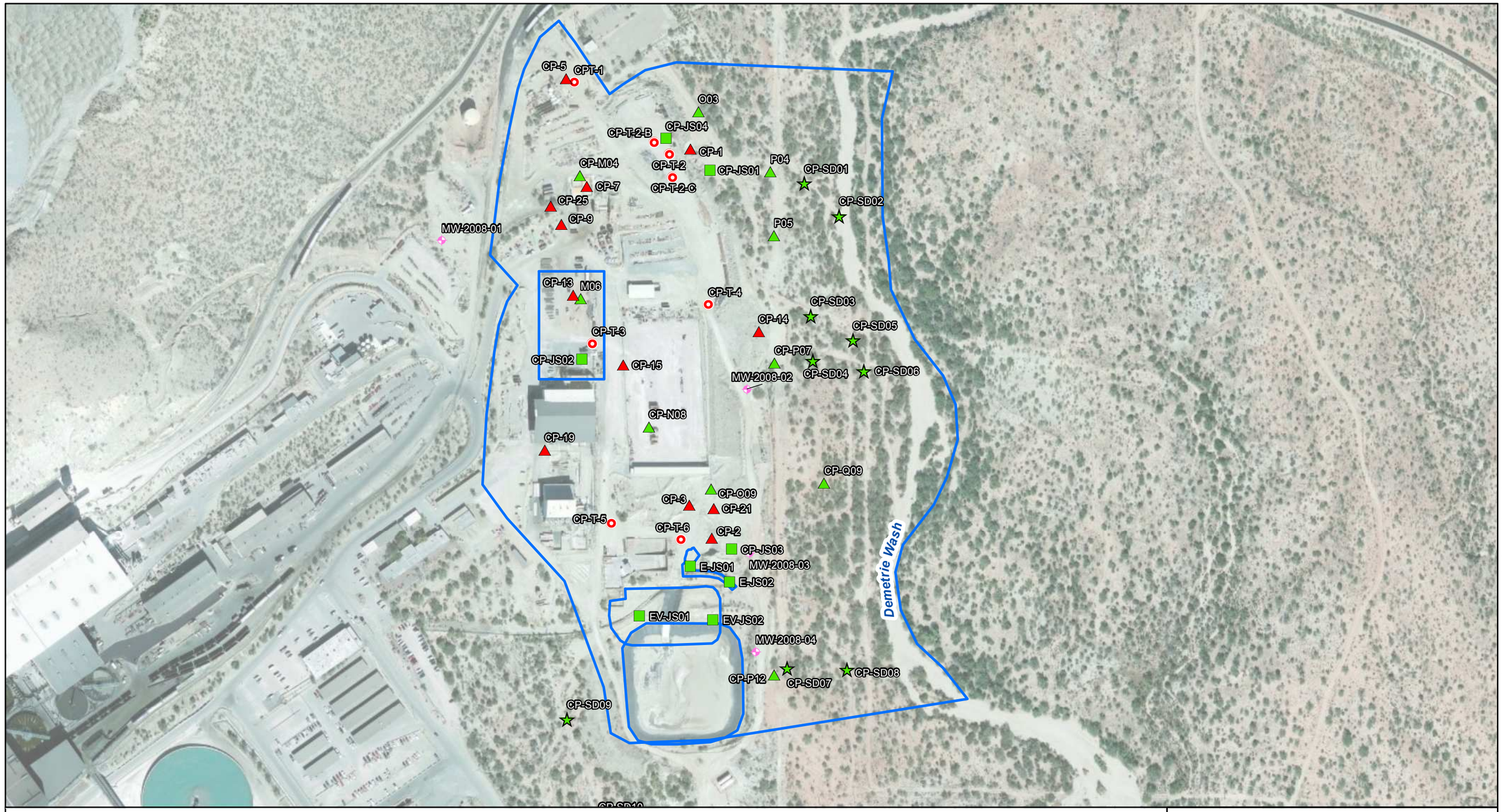
VOLUNTARY REMEDIATION PROGRAM DATA GAPS WORKPLAN

VRP GROUNDWATER MONITORING PROGRAM FOR 2015

ARCADIS

FIGURE 17

CITY:(DEN-TECH) DIV/GROUP:(ENV/GIS) DB: GMCKINNEY LD: PIC: PM: TM:
PROJECT: PATH: Z:\GISPROJECTS_ENV\Sierrita\GIS\ArcMap_MXD\2014\Fig17_VRP_GW_Monitoring2015_v3.mxd



Legend

Soil Sample Locations

- Judgment Soil Boring
- Random Soil Boring
- Sediment Sample
- Surface Soil Sample
- Trench Location
- VRP Monitoring Well
- Former CLEAR Plant Sub Areas

N

0 150 300 600 Feet

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA

VOLUNTARY REMEDIATION PROGRAM DATA GAPS WORKPLAN

FORMER CLEAR PLANT SUBAREA
SOIL SAMPLE LOCATIONS

ARCADIS

FIGURE
18

CITY:(DEN-TECH) DIV/GROUP:(ENV/GIS) DB: GMCKINNEY LD: PIC: PM: TM:
PROJECT: PATH: Z:\GISPROJECTS_ENV\Sierrita\GIS\ArcMap_MXD\2014\Fig18_FormerCLEARPlant_SoilLocations.mxd

MW-2008-19
MW-1
MW-2
MW-2008-18
MW-2008-17
MW-4
MW-3
PZ-04
PZ-4
EM-C22
EM-H22
MW-2008-11
EM-E24
EM-K24
EM-13
EM-P24
EM-5
EM-JS01
EM-17
EM-3
EM-18
RA-SD02
TW-2008-15
MW-2008-07
PZ-2008-02
RA-SD01
205460
EM-4
RA-JS02
EM-10
EM-B-1
EM-14
C-JS01
CS-JS01
CS-JS05
EM-X26
RA-JS01
RA-JS03
EM-T-2B
M26
CS-JS06
RA-JS04
RA-JS05
C-JS02
C-JS03
C-JS04
CS-JS02
G27
MW-2008-09
EM-JS02
MW-2008-08
EM-JS08
TW-2008-13
C-JS05
EM-JS07
CS-JS03
EM-JS06
CS-JS04
TW-2008-14
TW-2008-08
PZ-2008-01
537574
537577
537575
EM-N29
MW-2008-10
PZ-03
PZ-3
Sump C
BW-3
BW-03
Former B Pond
Sump B
Amargosa Pond
BW-04
TW-2008-12
BW-4
Amargosa Wash
Amargosa Intercept
TW-2008-11
Raffinate Pond No. 2
Intercept No. 2
TW-2008-10
Bailey Lake
Intercept No. 1
SX Sump-1
SX Sump-2
Demetrie Wash
MH-23
SX Sump-3
MH-22
TW-2008-09

Legend

Soil Sample Locations

- Judgment Soil Boring
- Random Soil Boring
- Sediment Sample
- Surface Soil Sample
- Trench Location
- Process Solution
- Boring Location
- VRP Monitoring Well
- VRP/APP-POC
- Mine
- Former Esperanza Mill Subareas

0 175 350 700 Feet

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA

VOLUNTARY REMEDIATION PROGRAM DATA GAPS WORKPLAN

FORMER ESPERANZA MILL SUBAREA SOIL SAMPLE LOCATIONS

ARCADIS

FIGURE 19

CITY:(DEN-TECH) DIV/GROUP:(ENV/GIS) DB:GMCKINNEY LD: PIC: PM: TM:
PROJECT: PATH: Z:\GISPROJECTS_ENV\SierritaGIS\ArcMap_MXD\2014\Fig19_FormerEsperanza_SoilLocation.mxd

ARCADIS

Appendix A

Sampling and Analysis Plan Addendum

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Freeport-McMoRan Sierrita Inc.

Sampling and Analysis Plan and Field Sampling Plan Addendum

Voluntary Remediation Program Sierrita Mine (VRP Site Code: 100073-03)

Green Valley, Arizona

November 2014

ARCADIS

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Voluntary Remediation Program

Sampling and Analysis Plan and Field Sampling Plan Addendum

Sierrita Mine
Green Valley, Arizona

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Acronyms and Abbreviations

ADEQ	Arizona Department of Environmental Quality
bgs	below ground surface
CLEAR	Copper Leach Electrowinning and Regeneration
COIs	constituents of interest
DQO	data quality objective
FSP	Field Sampling Plan
GPS	Global Positioning System
IDW	Investigation Derived Waste
PPE	personal protective equipment
PVC	polyvinyl chloride
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
SAP	Sampling and Analysis Plan
Sierrita	Freeport-McMoRan Sierrita Inc.
Site	Sierrita Mine
SOP	Standard Operating Procedure
STI	Sierrita Tailings Impoundment
URS	URS Corporation
USEPA	United States Environmental Protection Agency
VRP	Voluntary Remediation Program

1. Introduction

This Sampling and Analysis Plan and Field Sampling Plan (SAP-FSP) Addendum provides guidance for data collection field methods, procedures, and documentation associated with the Freeport-McMoRan Sierrita Inc. (Sierrita) Site, located 6200 West Duval Mine Road, Green Valley, Pima County, Arizona. This SAP-FSP is an addendum to the SAP and FSP contained in the prior Work Plan (URS Corporation [URS] 2008a) and subsequent addendum (URS 2008b), as prepared for previous field activities for the Arizona Department of Environmental Quality's (ADEQ's) Arizona Voluntary Remediation Program (VRP). Training requirements and certifications, and field QC samples, will be consistent with the original SAP-FSP (URS 2008a).

2. Field Activities

This section describes the following field activities, which will be performed for the VRP data gaps assessment:

- Pre-mobilization
- Mobilization
- Borehole drilling, monitoring well construction, development, and hydraulic testing
- Groundwater sampling
- Sample management
- Field analysis
- Decontamination
- Management of investigation-derived waste (IDW)
- Surveying
- Demobilization.

Instructions for performing the field activities are given in standard operating procedures (SOPs), which are included with this FSP as Attachment A.

Approved methods and procedures will be followed during the field investigation. Any deviations from this FSP or SOPs will be documented and described in the reporting phase.

2.1 Pre-mobilization

Prior to the startup of field activities, pre-mobilization activities will be conducted to verify and define sample and/or drill locations, if necessary. Locations will be selected and staked, if necessary, based on the following information:

- Site access
- Local topography
- Data quality objectives (DQOs) for the sample points

The ADEQ will be informed if an alternative location is required to meet related data needs. Prior to the selection of any alternate locations for sampling points, Sierrita will obtain the concurrence of the ADEQ.

Additionally, access agreements with landowners will be initiated for data gap actions to be performed off the Sierrita property, if required. Copies of all access agreements will be provided to ADEQ upon request.

Additional pre-mobilization activities may include identifying appropriate locations for decontamination facilities, IDW storage and disposal, and other logistic considerations. Equipment and supplies will be ordered, and subcontractors will be engaged during pre-mobilization.

2.2 Mobilization

Mobilization activities will prepare field personnel and the field activities support area for the startup of work. Mobilization will involve the following activities:

- Setup of decontamination facilities on the site, if needed

- Receipt, organization, and transport of field supplies and equipment
- Calibration and testing of field equipment
- Setup and checking of site communications
- Kickoff meeting involving field staff
- Site health and safety briefing.

2.3 Borehole Drilling and Logging

Boreholes will be drilled as part of the data gap investigations at the Sierrita Mine. Locations of wells are identified in the VRP Data Gap Work Plan and are summarized below.

Central Investigation Area- Former CLEAR Plant: Two wells will be installed as part of the investigation activities to delineate downgradient migration of constituents of interest (COIs) from the former Copper Leach Electrowinning and Regeneration (CLEAR) Plant area. One well will be screened to the base of the alluvial materials, and the second well will be screened in the upper portion of the underlying bedrock. Total well depths for the alluvial and bedrock wells are anticipated to be 50 and 100 feet below ground surface (bgs), respectively.

Central Investigation Area - Former Raffinate Pond/Amargosa Wash Areas: Two bedrock wells will be installed to the south of the Central Investigation Area as part of the activities to assess the potential migration of COIs from this area. The total well depths are anticipated to be 80 and 150 feet bgs.

East Investigation Area: One well will be installed to assist in the assessment of background COI concentrations for basin fill materials to the southwest of the Sierrita Tailings Impoundment (STI). The total well depth is anticipated to be approximately 450 feet bgs.

Boreholes will be drilled in accordance with SOP 16.0 (Drilling and Sampling of Subsurface Materials). It is anticipated that boreholes will be drilled with dual-wall percussion, air-rotary methods, or other methods as described in the Work Plan (ARCADIS 2014a).

Each borehole will be logged at approximate 5- to10-foot intervals in accordance with SOP 17.0 (Logging). The locations of surface soil samples will be surveyed in accordance with SOP No. 20.0 (Surveying [Conventional and Global Positioning System {GPS}]). Equipment will be documented as described in SOP No. 6.0 (Decontamination of Equipment). Wash water from decontamination and any other IDW will be managed as described in SOP No. 23.0 (Investigation-Derived Waste Management).

2.4 Monitoring Well Construction and Development

Monitoring wells will be installed as part of the data gap investigations at the Sierrita Mine. Monitoring wells will be installed in accordance with SOP 14.0 (Monitoring Well Installation), which includes Schedule 40 or 80 polyvinyl chloride (PVC) casing and well screen, appropriately sized filter pack, bentonite grout, and surface wellhead completions. Screens will be 20 to 50 feet long and will intersect the water table for alluvial wells and the formation of interest for bedrock wells, with additional construction details described in the Work Plan (ARCADIS 2014a). Construction information will be documented as described in SOP 14.0 (Monitoring Well Installation).

After monitoring wells are installed, each will be developed in accordance with SOP 15.0 (Well Development). The SOP provides specifications for the volume of development water to be purged, criteria for assessing development performance, development water disposal, and documentation for development.

The ground surface and top of PVC casing (measuring point) will be surveyed in accordance with SOP No. 20.0 (Surveying [Conventional and GPS]). The northing and easting coordinates will be surveyed using the state plane coordinate system.

2.5 Groundwater Sampling

Groundwater sampling is part of the data gap investigations at the Sierrita Mine. Specific information on sampling is contained in the Work Plan (ARCADIS 2014a) and Quality Assurance Project Plan (QAPP; ARCADIS 2014b). Groundwater samples will be collected in accordance with SOP 2.0 (Monitor Well Groundwater Sampling), and static water level in monitoring wells will be measured prior to sampling as described in SOP 2.1 (Water Elevation Measurements). Well water will then be purged to remove well bore storage so that groundwater samples are representative of the screened formation. Procedures for well purging are described in SOP No. 2.0 (Monitor Well Groundwater Sampling). Wells will be purged using a stainless steel/Teflon®

submersible pump capable of low and high flow rates or disposable Teflon® bailers. Field parameters will be measured during the purging process as described in SOP No. 8.0 (Field Parameter Measurements [including Instrument Calibration]).

Well purging will be attempted at a low flow rate (0.5 liter/minute) using a submersible pump. Water levels will be measured during the purging process. If the water level does not drop significantly (i.e., more than 0.1 meter [0.3 foot]) due to low-flow purging, purging of the well will continue at the low flow rate until field parameters stabilize (per SOP No. 8.0 [Field Parameter Measurements {including Instrument Calibration}]). If the water level drops significantly from the initial static level at the 0.5 liter/minute flow rate, the pump rate will be reduced to as low as 0.1 liter/minute, or lower, if appropriate (USEPA 1996). If the stress (drawdown) on the well continues, low-flow well purging will be discontinued, and the well will be purged at a higher pumping rate or with a bailer. Pumping at the higher flow rate may result in pumping the well dry. If this occurs, the well should be sampled when it has recharged sufficiently to collect the sample. Otherwise, the well should be purged until field parameter stabilization is achieved.

Following well purging, field parameters will be measured and recorded. Groundwater samples will then be collected in accordance with SOP No. 2.0 (Monitor Well Groundwater Sampling). Filtered and unfiltered samples will be collected. Samples will be filtered for dissolved metals analysis in the field in accordance with SOP No. 3.0 (Field Filtration of Water Samples).

Samples will be handled as described in Section 3.0 and SOP No. 9.0 (Sample Management) and submitted to an analytical laboratory for analysis. The specific analytical parameters, analytical methods, required sample containers, and preservatives are presented in the QAPP (ARCADIS 2014b). The details of each groundwater sampling event will be recorded in field logbooks and groundwater sample field data sheets.

Any non-dedicated sampling equipment will be decontaminated as described in SOP No. 6.0 (Decontamination of Equipment). To the degree possible, dedicated sampling equipment, such as tubing, will be used to minimize the need for equipment decontamination and potential for cross-contamination of wells. Wash water from decontamination, purge water, and any other waste water will be managed as described in SOP No. 23.0 (Investigation-Derived Waste Management).

2.6 Groundwater Hydraulic Testing

Hydraulic testing will be performed as part of the VRP data gap assessment at the Former CLEAR Plant Area and on wells to be installed south of the Central Investigation Area. The objective of the testing in the Former CLEAR Plant Area is to assess the potential hydraulic connection between the alluvium and bedrock, and also to determine aquifer hydraulic parameters for each formation (hydraulic conductivity, specific yield). To the south of the Central Investigation Area, the objective will be to determine the hydraulic parameters for bedrock in that area.

Three types of hydraulic testing may be used: 1) pumping testing, 2) slug testing, and 3) specific capacity testing. Procedures for these three types of hydraulic testing are contained in SOPs 31.0 (Pump Testing), 40.0 (Slug Testing), and 41.0 (Specific Capacity Testing), respectively.

Equipment will be decontaminated as described in SOP No. 6.0 (Decontamination of Equipment). Test water and any other waste water will be managed as described in the Overall Site Plan and SOP No. 23.0 (Investigation-Derived Waste Management).

Specific information on the locations and type of testing are contained in the VRP Data Gap Work Plan (ARCADIS 2014a).

2.7 Decontamination

Equipment will be decontaminated during data collection activities for the following purposes:

- Personnel health and safety
- Minimization of cross-contamination of samples and environmental media
- Minimization of migration of contamination to non-impacted areas

Equipment will be decontaminated per SOP No. 6.0 (Decontamination of Equipment).

2.8 Management of Investigation-Derived Waste

IDW will be handled as described in SOP No. 23.0 (Investigation-Derived Waste Management) generated during the field investigation is expected to include:

- Used personal protective equipment (PPE) and other non-soil solid wastes
- Wash and rinse water from decontamination activities
- Soil cuttings and other soil wastes generated during sampling
- Well development and purge water.

2.9 Surveying

Surveying will be performed in accordance with SOP No. 20.0 (Surveying [Conventional and GPS]), which contains a general discussion of methods and surveying criteria. If surveying procedures described in SOP No. 20.0 cannot be conducted (e.g., due to weather constraints), alternate measuring techniques will be employed (e.g., use of a measuring wheel sited from the edges of buildings with known surveying coordinates).

2.10 Demobilization

Demobilization will involve the following:

- Dismantling and removing temporary structures (e.g., decontamination station)
- Completing field documentation
- Final shipping of samples
- Decontaminating site-dedicated vehicles and other equipment to be removed from the site, as necessary
- Returning equipment and supplies
- Cleaning up any areas that may be disturbed
- Departing from the site.

3. Sample Management

Groundwater, surface water, and soil samples will be collected and submitted to an analytical laboratory as part of the VRP data gap assessment. Specific analyses, analytical methods, required containers, and preservatives to be employed are identified in the QAPP (ARCADIS 2014b). Procedures for handling, shipping, and documenting samples are described in SOP No. 9.0 (Sample Management). The SOP describes chain of custody, sample labeling, and sample cooler packing and labeling procedures. Example chain-of-custody forms, sample labels, and sample cooler labels are provided in the SOP.

Each sample will be assigned a unique field sample number to prevent ambiguity in associating sample locations and dates to field measurements and laboratory sample results. The field sample number is the single designation to which laboratory sample analysis results are related. Field crews will be provided with field sample numbers for their planned sampling activities (on pre-printed labels, if possible). Quality assurance/quality control (QA/QC) samples will also be assigned unique field sample numbers.

Field data and activities, including field sample numbers, field parameter measurements, and numerous other types of information, will be documented as described in Section 4.0.

4. Field Documentation

Field documentation will be performed for the following purposes:

- To track samples
- To associate sample location ID numbers with locations, dates, and other sampling event data
- To track the status and completeness of field tasks
- To maintain complete records of sample events and measurements
- To facilitate electronic entry of field data
- To document the reliability of field instruments
- To provide a written record that can be used to reconstruct field events
- To provide a written record of sample collection, shipment, and chain of custody.

Field documentation will include the recording of field events and data in project logbooks and on field forms, and completion of chain-of-custody records. Sample locations will be further documented by taking photographs. The approved procedure for logging photographs is described in SOP No. 9.0 (Sample Management).

Field data will serve the following functions:

- Documentation of field data will be the primary source of information for the creation of the project database.
- The field data will be combined with analytical results from laboratories to complete data records.
- The field data will be the source of information that links the analytical records to the sampling locations and events.
- Field documents are also the original records of measurements and events.

Therefore, it is critical that the field events are recorded accurately and completely.

Field personnel will document all aspects of the investigation activities in project logbooks and/or daily note logs. The logbook/notes documentation will be the key record of field activities. Complete and accurate descriptions of the field activities are critical to the success of the project. Project logbooks/notes will include the following information:

- Date
- Time
- Location (GPS coordinates)
- Weather conditions
- Task
- Personnel present including work crew members and visitors
- Record of events, procedures, and measurements
- Deviations from SOPs (refer to requirements described in the QAPP)
- Other pertinent information.

Field forms will also be used to record field events. The purpose of the field forms is to guide field personnel in collection of field data and to create a complete record of the sampling and field measurement events. Various field forms and their uses are included in the SOPs for each field task and in Attachment B.

8. References

ARCADIS. 2014a. Voluntary Remediation Program Data Gaps Workplan, Sierrita Mine, Green Valley, Arizona. August.

ARCADIS. 2014b. Voluntary Remediation Program Quality Assurance Project Plan Addendum, Freeport Sierrita Mine Green Valley, Arizona. August.

URS Corporation (URS). 2008a. Voluntary Remediation Program (VRP) Investigation Work Plan, Freeport-McMoRan Sierrita Inc., Green Valley, Arizona. Volumes I and II. Prepared for Freeport-McMoRan Sierrita Inc. April.

URS. 2008b. Addendum to Sampling & Analyses Plan (SAP) & Quality Assurance Project Plan (QAPP), Voluntary Remediation Program (VRP), Freeport-McMoRan Sierrita Green Valley, Arizona. Prepared for Freeport-McMoRan Sierrita Inc. September.)

U.S. Environmental Protection Agency (EPA). 1996. Low Stress (low flow) Purging and Sampling Procedures for the Collection of Groundwater Samples from Monitoring Wells; EQASOP-GW-001; revised January 19, 2010.

Attachment A

SOPs

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Environmental Standard Operating Procedures

Sierrita Mine
VRP Data Gaps Assessment

Prepared for:
Freeport-McMoRan Sierrita Inc..

Prepared by:
ARCADIS U.S., Inc.

August 26, 2014
Revision 1
Project No. AZ001233.0014.0001

ARCADIS

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Freeport-McMoRan Sierrita Inc.

VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 2.1

WATER ELEVATION MEASUREMENTS

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1.0 PURPOSE AND SCOPE

The purpose of this document is to define the standard operating procedure (SOP) for measuring water elevations in monitoring wells for Freeport-McMoRan Sierrita Inc. (Sierrita). This procedure describes equipment and field procedures necessary to collect water elevation measurements. The well locations and frequency of measurement are specified in the work plan. SOP No. 6.0, Decontamination of Equipment, describes decontamination procedures that are applicable to this SOP.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Design Contractor has the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate environmental staff to implement this SOP and for ensuring that procedures are followed by all personnel.

All personnel performing these procedures are required to have the appropriate health and safety training. In addition, all personnel are required to have a complete understanding of the procedures described within this SOP and receive specific training regarding these procedures, if necessary.

All environmental and assay laboratory staff are responsible for documenting deviations from this SOP and reporting them to the Design Contractors.

3.0 RELATED STANDARD OPERATING PROCEDURES

The procedures set forth in this SOP are intended for use with the following SOPs:

SOP No. 2.0	Monitor Well Groundwater Sampling
SOP No. 9.0	Sample Management

4.0 EQUIPMENT LIST

The equipment necessary that may be used to measure water levels include:

- Electric water level indicator capable of producing measurements to a precision of 0.01 feet
- 5-gallon buckets or equivalent for decontamination
- Brushes for decontamination
- Field data sheets
- Field notebook
- Chemical-free paper towels for Kimwipes
- Alconox soap
- Potable water

- Garden-type sprayer filled with deionized or distilled water
- Appropriate health and safety equipment

5.0 WATER ELEVATION MEASUREMENT PROCEDURE

5.1 DISCUSSION

Generally, water elevation measurements are used to construct potentiometric surface maps. Therefore, water level measurements at a given site should be collected within a 24-hour period. The device used to measure water levels should be adequate to attain an accuracy of 0.01 feet. Water levels should be allowed to stabilize for a minimum of 48 hours after well construction and development before measurements are taken.

5.2 MEASUREMENT PROCEDURE

This section gives the steps to follow when measuring water levels. Note that appropriate health and safety equipment should be worn during well opening, well measurement, and decontamination.

- Before any measurement is taken, the water level probe shall be decontaminated. Decontamination procedures are discussed in SOP No. 6.0, Decontamination of Equipment.
- Make sure the monitoring well is labeled and the location ID is visible on the protective casing.
- After opening the well cover, measure the depth of the static water level and the total depth of the well using an electric water level indicator. The measuring point for all the wells shall be the top of PVC or steel well casing. The measuring point will be marked by a notch or other mark in the PVC or steel casing. If no mark is present, measure from the top of the north side of the casing.
- The static water level and the depth of the well shall be measured with the indicator, written down on the field data sheet or field notebook, and immediately rechecked before the indicator is removed from the well.
- Care should be taken to verify the readings during each water level measurement period. Note any significant changes in water level, by comparing the most recent measurement with past measurements, if appropriate.
- The water level depth below the measuring point (in feet) will be subtracted from the measuring point elevation to determine the elevation of the static water level. If measuring point elevations are available at the time of water level measurement, the calculated water elevation should be checked in the field to see that it is reasonable and the subtraction was performed correctly. If there is a discrepancy, the well should be measured again.
- All columns of field data sheets shall be completed, including time of measurement. If items on the sheet do not apply to a specific location, the item will be labeled as not applicable (NA). A field data sheet for water elevation measurement is shown as Figure 1. Section 5.3 describes the documentation required.

5.3 DECONTAMINATION

The water level indicator must be decontaminated before using between wells and at the conclusion of measurements. The probe will be decontaminated according to the procedure for decontamination of sampling equipment described in SOP No. 6.0, Decontamination of Equipment. Probe decontamination can be completed at the wells.

6.0 DOCUMENTATION

Documentation of observations and data acquired in the field will provide information on the activities concluded and also provide a permanent record of field activities. The observations and data will be recorded with waterproof ink in a permanently bound weatherproof field logbook with consecutively numbered pages, and on field data sheets.

6.1 FIELD DATA SHEET FOR WATER LEVEL MEASUREMENTS

A field sampling data sheet for groundwater samples (Figure 1) will be completed at each sampling location. The data sheet will be completely filled in. If items on the sheet do not apply to a specific location, the item will be labeled as not applicable (NA). The information on the data sheet includes the following:

- Well number
- Field book reference number
- Field personnel
- Well I.D.
- Date and time of measurements
- Sample identification number
- Water level
- Static Water Elevation Data
- The measurement point elevation should be filled in if it has been determined at the time of measurement. If it is not known, it should be filled in after it is obtained, and the water elevation calculated at that time. Both entries should be initialed and dated if not performed during field activities.
- Any irregularities or problems that may have a bearing on sampling quality
- Comments

6.2 FIELD NOTES

Field notes shall be kept in a bound field book. The following information will be recorded using water proof ink:

- Names of personnel
- Associated field form number for each location sampled.

- Weather conditions
- Date and time of activities
- Location and well number
- Decontamination information
- Sampler's signature
- Other pertinent information (problems, special conditions, etc.)

Figure 1: Field Data Sheet for Water Elevation Measurement

Instrument Number: _____ Date: _____

Sampler's Name: _____ Project No.: _____

Project Name: _____

Well Number	Date/ Time	Measurement and Location Point Elevation (MSL)	Depth of Water	Depth to Well	Water Elevation	Sampler's Initials

Note: BE SURE TO DECONTAMINATE THE PROBE BETWEEN WELLS

Freeport-McMoRan Sierrita Inc.

VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 2.0

MONITOR WELL GROUNDWATER SAMPLING

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1.0 PURPOSE AND SCOPE

The purpose of this document is to define the standard operating procedure (SOP) for collecting groundwater samples from wells for Freeport-McMoRan Sierrita Inc. (Sierrita). This procedure gives descriptions of equipment, field procedures, and quality assurance/quality control (QA/QC) procedures necessary to collect groundwater samples from wells using a bailer and/or submersible pump and use of low stress (low purging) procedures.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Design Contractor has the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate environmental staff to implement this SOP and for ensuring that procedures are followed by all personnel.

All personnel performing these procedures are required to have the appropriate health and safety training. In addition, all personnel are required to have a complete understanding of the procedures described within this SOP and receive specific training regarding these procedures, if necessary.

All environmental and assay laboratory staff are responsible for documenting deviations from this SOP and reporting them to the Design Contractor.

3.0 RELATED STANDARD OPERATING PROCEDURES

The procedures set forth in this SOP are intended for use with the following SOPs:

SOP No. 2.1	Water Elevation Measurements
SOP No. 3.0	Field Filtration of Water Samples
SOP No. 6.0	Decontamination of Equipment
SOP No. 8.0	Field Parameter Measurements (including Instrument Calibration)
SOP No. 9.0	Sample Management
SOP No. 20.0	Surveying (Conventional and GPS)
SOP No. 23.0	Investigation Derived Waste Management

4.0 PROCEDURES FOR GROUNDWATER SAMPLING

Procedures for groundwater sampling from a monitoring well are designed to obtain a sample that is representative of the formation water. Because an estimate of the quality of formation water is desired, standing water within the well must be evacuated before sampling. Also, a measure of the static water elevations is important to determine if horizontal and vertical flow gradients change during site characterization activities.

4.1 BAILER OR SUBMERSIBLE PUMP PROCEDURES

This section gives the step-by-step procedures for well evacuation and collecting water samples with a bailer and or submersible pump. Observations made during sample collection should be recorded in the field logbook and field data sheet as specified in Section 5.0 of this SOP.

4.1.1 Equipment List

Sample bottles with preservatives added will be obtained from the analytical laboratory. Several extra sample bottles will be obtained in case of breakage and for QA/QC samples.

Equipment that may be used during well evacuation/groundwater sample collection:

- Well keys
- Portable generator (or battery) for an electric pump, if used instead of bailers
- Electronic water level measurement probe
- Teflon or stainless steel bailer, or submersible pump
- Nylon rope or twine
- Flow-through cell
- Assorted tools (screwdriver, etc.)
- Thermometer
- Water quality meter that measures:
  - pH meter with a temperature scale
  - Specific conductivity meter
  - Dissolved oxygen meter
  - Oxidation Reduction Potential meter
- Plastic squeeze bottle filled with distilled or deionized water
- Chemical-free paper towels or Kimwipes
- Calculator
- Field logbook
- Field data sheets
- Waterproof pen
- Gloves – latex, vinyl or nitrile (preferably)
- Submersible pump tubing
- Appropriate health and safety equipment
- Sample bottles with preservatives
- Cooler with sufficient ice to cool samples to 4ºC

- Sample labels
- Strapping tape
- Stainless steel bowl
- Disposable in-line 0.45-micron filters (see SOP No. 3.0, Field Filtration of Water Samples)
- Baggies (quart and gallon size)
- Bottle protectors
- Well construction logs
- Historic ground water sampling records
- Bottle for measuring parameters
- Filtering apparatus
- 5 – Gallon buckets
- Clear tape
- Custody seals
- COC's
- Lab contact/ address
- Shipping forms
- Packing materials
- Trash Bags
- Bins for decontamination
- Clipboard
- Graduated Cylinder

4.1.2 Equipment Decontamination

Before any evacuation or sampling begins, all well probes, bailers, submersible pumps, and other sampling devices shall be decontaminated in accordance with SOP No. 6.0, Decontamination of Equipment. If dedicated equipment is used that is not installed inside the well, it should be rinsed with distilled or deionized water. Decontamination supplies will be provided so that equipment can be decontaminated in the field. Each piece of evacuation and/or sampling equipment shall be decontaminated before sampling operations and before sampling subsequent wells. Decontamination water shall be replaced daily or more frequently if necessary (e.g., water is muddy, appears dirty or is likely contaminated). A more in-depth discussion of equipment decontamination is contained in SOP No. 6.0.

4.1.3 Instrument Calibration

Electronic equipment used during sampling includes a water level measurement probe, a pH meter with temperature scale, a specific conductivity meter, dissolved oxygen meter and a

oxidation reduction potential meter or a water quality meter that measures all of these parameters. Before daily field operations and at end of day, the sampler shall verify that all of these are operating properly. The pH and specific conductivity meters, or a water quality meter, require calibration prior to use each day at a minimum. Periodic calibration checks should be performed to ensure that meters are reading consistently. If not, the meters should be recalibrated and the calibration schedule adjusted accordingly. Calibration times and readings will be recorded in a notebook or log sheets to be kept by the field sampler. Specific instructions for calibrating the instruments are given in SOP No. 8.0, Field Parameter Measurements (including Instrument Calibration).

4.1.4 Well Volume Calculations

The following equation shall be used to calculate the volume of water to be removed during well evacuation:

For 2-inch (inside diameter) well:

$$\frac{\text{Evacuation Volume}}{[\text{gal}]} = \frac{\text{Total Depth - Water Level Depth}}{[\text{ft}]} \times \frac{0.16\ \text{gal}}{\text{ft}} = \text{gallons/1 well casing volume}$$

For 4-inch (inside diameter) well:

$$\frac{\text{Evacuation Volume}}{[\text{gal}]} = \frac{\text{Total Depth - Water Level Depth}}{[\text{ft}]} \times \frac{0.65\ \text{gal}}{\text{ft}} = \text{gallons/1 well casing volume}$$

For 6-inch (inside diameter) well:

$$\frac{\text{Evacuation Volume}}{[\text{gal}]} = \frac{\text{Total Depth - Water Level Depth}}{[\text{ft}]} \times \frac{1.47\ \text{gal}}{\text{ft}} = \text{gallons/1 well casing volume}$$

Multiply the volume of one well casing volume by three (3) to obtain the minimum volume of water to be evacuated.

4.1.5 Well Evacuation

The purpose of well evacuation is to remove stagnant water from the well and obtain representative water from the geologic formation being sampled while minimizing disturbance to the collected samples. Before a sample is taken, the well will be evacuated until a minimum of three well casing volumes have been removed and field parameters have stabilized or until the well is bailed/pumped dry. Wells shall be evacuated on the same day that samples are taken. Decontamination and evacuated well water will be disposed of according to SOP 23.0, Investigation Derived Waste Management.

Before well evacuation begins, the following procedures are to be performed at each well:

- Note the condition of the outer well casing, concrete well pad, protective posts (if present), and any other unusual conditions of the area around the well.
- Open the well.
- Note the condition of the inner well cap and casing.
- Measure (to nearest 0.01 foot) and record depth of static water level from the measuring point on the well casing and indicate time as per SOP No. 2.1, Water Elevation

Measurements. Record what the measuring point is (e.g., notch on north side, top of PVC well casing).

- Measure and record total depth of well from the same measuring point on the casing.
- Calculate volume of water in the well casing in gallons based on feet of water and casing diameter (see Section 4.4.3 for calculation of volumes).
- From the above calculation, calculate the three casing volumes to be evacuated.

During well evacuation, the following procedures are to be performed:

- If evacuating the well using a pump, determine flow rate of pump in gallons per minute using the 5-gallon bucket (e.g., 5 gallons in 30 sec. = 10 gallons/min.) Divide the total volume (gallons) by the flowrate (gallons/minute) to obtain the number of minutes to evacuate three casing volumes. If evacuating using a bailer, empty contents of the bailer into a 5-gallon bucket to measure cumulative volume of water bailed.
- Obtain an initial sample from the bailer or discharge tubing of the pump for field measurements (temperature, specific conductivity, dissolved oxygen, oxidation-reduction potential, and pH measurements) and observation of water quality.
- Evacuate three volumes of water in casing. Take and record temperature, specific conductance, and pH measurements after evacuation of each well volume to confirm that the water chemistry has stabilized. Generally, pH values within $\pm$0.2 pH, temperature within 1°C and conductivity within $\pm$10 percent between three consecutive readings indicate good stability of the water chemistry. If the chemistry is not stable after 3 well volumes, continue evacuating, measuring pH and specific conductance after each one-half well volume until adequate stability is reached. If parameters don't stabilize after 5 casing volumes then discontinue purging and obtain sample.
- Field measurement meters (pH/temperature, specific conductivity, dissolved oxygen, and oxidation-reduction potential) must be calibrated each day. Calibration and operation should follow the manufacturer's specific instructions and SOP 8.0, Field Parameter Measurements (including Instrument Calibration).
- Monitor discharge rate and maintain a steady flow if using a pump.
- If the well is pumped or bailed dry during evacuation, it can be assumed that the purpose of removing three well volumes of water has been accomplished, that is, removing all stagnant water that had prolonged contact with the well casing or air. Samples should be obtained after the well has recovered (80%). If recovery is very slow, samples may be obtained as soon as sufficient water is available to collect required parameters.

4.1.6 Collect Groundwater Samples

Collect groundwater samples for chemical analysis within two hours after evacuation is completed. Both filtered and unfiltered samples will be collected (see SOP 3.0, Field Filtration of Water Samples). For slow recovering wells, the sample shall be collected immediately after a sufficient volume is available. Samples should be collected with a decontaminated stainless steel bailer unless a submersible pump is used to sample the well. The first water retrieved from the bailer, if used, should be discarded before collecting samples for chemical analyses.

The following sampling procedure is to be used at each well sampled using a bailer:

- Following purging, measure and record depth of static water level per SOP No. 2.1, Water Elevation Measurements. If the well casing does not have a reference point (usually a V-cut or indelible mark in the well casing), make one. Note that the reference point should be surveyed for correction of ground water elevations to the mean geodesic datum (MSL).
- Use a decontaminated teflon or stainless steel bailer and new nylon rope or twine.
- Use new gloves.
- Lower the bailer to the same depth in the well each time, within the screened interval taking care to avoid hitting the bottom of the well and stirring up particulate matter.
- Retrieve the bailer and empty the water into laboratory containers. All sample containers should be filled with minimal turbulence by allowing the ground water to flow from the tubing gently down the inside of the container. Fill sample bottles completely when possible, but collect at least a sufficient volume for laboratory analysis. Sample bottles for volatile organic analysis (VOCs) will be collected first, filled with minimal agitation to the water, and filled so there is not headspace after sample is capped.
- Label and place samples on ice in a cooler.
- Record time of sampling and record sample identification in field logbook.
- Replace and lock well cap.
- Complete field documentation.

The following sampling procedure is to be used at each well sampled using a submersible pump:

- Decontaminate depth to water meter, submersible pump, and tubing according to SOP No. 6.0, Decontamination of Equipment. Unless using dedicated equipment decontamination is only done where necessary (e.g., depth to water meter).
- Set the pump in the middle of the screened interval.
- Use new gloves.
- After purging of the well, measure and record depth of static water level per SOP No. 2.1, Water Elevation Measurements.
- Fill sample bottles from the pump discharge line completely when possible, but collect at least a sufficient volume for laboratory analysis. All sample containers should be filled with minimal turbulence by allowing the ground water to flow from the tubing gently down the inside of the container. Sample bottles for volatile organic analysis (VOCs) will be collected first, filled with minimal agitation to the water, and filled so there is not headspace after sample is capped.
- Label and place samples on ice in a cooler.
- Record time of sampling and record sample identification in field logbook.
- Replace and lock well cap.
- Complete field documentation

Note that preservation techniques are discussed in detail in SOP No. 9.0, Sample Management.

4.2 LOW STRESS (LOW FLOW) PURGING AND SAMPLING PROCEDURES

The purpose of the low stress purging and sampling procedure is to collect ground water samples from monitoring wells that are representative of ground water conditions in the geological formation with minimal disturbance to the sample. This is accomplished by setting the intake velocity of the sampling pump to a flow rate that limits drawdown inside the well casing.

Sampling at the prescribed (low) flow rate has three primary benefits. First, it minimizes disturbance of sediment in the bottom of the well, thereby producing a sample with low turbidity (i.e., low concentration of suspended particles). Typically, this saves time and analytical costs by eliminating the need for collecting and analyzing an additional filtered sample from the same well. Second, this procedure minimizes aeration of the groundwater during sample collection, which improves the sample quality for VOC analysis. Third, in most cases the procedure significantly reduces the volume of ground water purged from a well and the costs associated with its proper treatment and disposal.

Specify the depth to which the pump intake should be lowered in each well. Generally, the target depth will correspond to the mid-point of the most permeable zone in the screened interval. Borehole geologic and geophysical logs can be used to help select the most permeable zone. However, in some cases, other criteria may be used to select the target depth for the pump intake. Otherwise, the pump should be set at the middle of the screened interval.

Sample bottles with preservatives added will be obtained from the analytical laboratory. Several extra sample bottles will be obtained in case of breakage and for QA/QC samples.

4.2.1 Equipment List

Equipment that may be used during well Low Stress (Low Flow) purging sample collection:

- Well Construction Data
- Location map
- Field data from last sampling event
- Polyethylene sheeting
- Adjustable rate, positive displacement ground water sampling pump (constructed of stainless steel or Teflon)
- Teflon or Teflon – lined polyethylene, PVC, Tygon or polyethylene tubing to collect samples for inorganic analysis.
- Electronic water level measurement probe
- Flow measurement supplies (e.g., graduated cylinder and stop watch or in-line flow meter)
- Power source (generator, nitrogen tank, etc.)
- Water quality meter that measures:
  - pH meter with a temperature scale

  - Specific conductivity meter
  - Dissolved oxygen meter
  - Oxidation Reduction Potential meter
- Plastic squeeze bottle filled with distilled or deionized water
- Flow-through cell
- Chemical-free paper towels or Kimwipes
- Calculator
- Field logbook
- Field data sheets
- Waterproof pen
- Gloves – latex, vinyl or nitrile (preferably)
- Appropriate health and safety equipment
- Sample bottles with preservatives
- Cooler with sufficient ice to cool samples to 4ºC
- Sample labels
- Strapping tape
- Disposable in-line 0.45-micron filters (see SOP No. 3.0, Field Filtration of Water Samples)
- Baggies (quart and gallon size)
- Bottle protectors
- 5 – Gallon buckets
- Clear tape
- Custody seals
- COC's
- Lab contact/ address
- Shipping forms
- Packing materials
- Trash Bags
- Bins for decontamination

4.2.2 Sampling Procedures

4.2.2.1 Pre-sampling Activities

1. Start at the well known or believed to have the least contaminated ground water and proceed systematically to the well with the most contaminated ground water. Check the well, the lock, and the locking cap for damage or evidence of tampering. Record observations.
2. Lay out sheet of polyethylene for placement of monitoring and sampling equipment
3. Remove well cap.
4. If the well casing does not have a reference point (usually a V- cut or indelible mark in the well casing), make one. Note that the reference point should be surveyed for correction of ground water elevations to the mean geodesic datum (MSL).
5. Measure and record the depth to water (to 0.01 ft) in all wells to be sampled prior to purging. Care should be taken to minimize disturbance in the water column and dislodging of any particulate matter attached to the sides or settled at the bottom of the well.

4.2.2.2 Sampling Procedures

1. Install pump: Slowly lower the pump, safety cable, tubing and electrical lines into the well to the depth specified for that well. The pump intake must be kept at least two (2) feet above the bottom of the well (where possible) to prevent disturbance and resuspension of any sediment present in the bottom of the well. Record the depth to which the pump is lowered.
2. Measure water level: Before starting the pump, measure the water level again with the pump in the well. Leave the water level measuring device in the well.
3. Purge Well: Start pumping the well at 200 to 500 milliliters per minute (ml/min) or 0.2 to 0.5 liters per minute (l/min). The water level should be monitored approximately every five minutes. Ideally, a steady flow rate should be maintained that results in a stabilized water level (drawdown of 0.3 ft or less from the static level). Pumping rates should, if needed, be reduced to the minimum capabilities of the pump to ensure stabilization of the water level. As noted above, care should be taken to maintain pump suction and to avoid entrainment of air in the tubing. Record each adjustment made to the pumping rate and the water level measured immediately after each adjustment.
4. Monitor Indicator Parameters: During purging of the well, monitor and record the field indicator parameters (temperature, specific conductance, pH, Eh and DO) approximately every five minutes. The well is considered stabilized and ready for sample collection when the indicator parameters have stabilized for three consecutive readings as follows:

   +/- 0.1 for pH
   +/- 3% for specific conductance (conductivity)
   +/-10 mv for redox potential
   +/- 10% for DO
   Dissolved oxygen and turbidity usually require the longest time to achieve stabilization.
5. Field measurement meters (pH/temperature, specific conductivity, dissolved oxygen, and oxidation-reduction potential) must be calibrated each day. Calibration and operation should follow the manufacturer's specific instructions and SOP 8.0, Field Parameter Measurements (including Instrument Calibration).

6. Collect Samples: Collect samples at a flow rate between 100 and 250 mL/min and such that drawdown of the water level within the well does not exceed the maximum allowable drawdown of 0.3 ft. VOC samples must be collected first and directly into sample containers. VOC samples should be collected at a flow rate of 0.1 L/min or less. All sample containers should be filled with minimal turbulence by allowing the groundwater to flow from the tubing gently down the inside of the container.
7. Collect QA/QC Samples.
8. Remove Pump and Tubing: After collection of the samples, the tubing, unless permanently installed, must be properly decontaminated or dedicated to the well.
9. Close and lock well.

4.2.3 Addressing Potential Problems

Problems that may be encountered using this technique include.

- Difficulty in sampling wells with insufficient yield.
- Failure of one or more key indicator parameters to stabilize.
- Cascading of water and/or formation of air bubbles in the tubing.
- Cross-contamination between wells.

Wells with insufficient yield (i.e., low recharge rate of the well) may dewater during purging. Care should be taken to avoid loss of pressure in the tubing line due to dewatering of the well below the level of the pump's intake. Purging should be interrupted before the water level in the well drops below the top of the pump, as this may induce cascading of the sand pack. Pumping the well dry should therefore be avoided to the extent possible in all cases. Sampling should commence as soon as the volume in the well has recovered sufficiently to allow collection of samples.

If one or more key indicator parameters fails to stabilize after 4 hours, one of four options should be considered:

- Continue purging in an attempt to achieve stabilization
- Discontinue purging, do not collect samples, and document attempts to reach stabilization in the field book.
- Secure the well, purge and collect samples the next day (preferred).

To prevent cascading and/or air bubble formation in the tubing, care should be taken to ensure that the flow rate is sufficient to maintain pump suction. Minimize the length and diameter of tubing (i.e., 1/4 or 3/8 inch ID) to insure that the tubing remains filled with groundwater during sampling.

To prevent cross contamination between wells it is strongly recommended that dedicated, in-place pumps be used. As an alternative, the potential for cross-contamination can be reduced by performing the more thorough decontamination procedures in accordance with SOP No. 6.0, Decontamination of Equipment.

4.3 FIELD QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES AND SAMPLES

QA/QC samples are designed to help identify potential sources of sample contamination to evaluate potential error introduced by sample collection and handling. All QA/QC samples are labeled and sent to the laboratory with other samples for analysis. The type and number of QA/QC samples are defined in SOP No. 9.0, Sample Management.

4.4 SAMPLE HANDLING

Sample containers, preservatives, and analyses are specified in SOP No. 9.0, Sample Management. Samples will also be labeled and handled as described in SOP No. 9.0.

5.0 DOCUMENTATION

Documentation of observations and data acquired in the field will provide information on the activities concluded and also provide a permanent record of field activities. The observations and data will be recorded with waterproof ink in a permanently bound weatherproof field logbook with consecutively numbered pages, and on field data sheets.

5.1 FIELD SAMPLING DATA SHEET

A field sampling data sheet for groundwater samples (Figure 1) will be completed at each sampling location. The data sheet will be completely filled in. If items on the sheet do not apply to a specific location, the item will be labeled as not applicable (NA). The information on the data sheet includes the following:

- Well number
- Field book reference number
- Sampling method
- Field personnel
- Date and time of sampling
- Sample identification number
- Person performing sampling
- Water level
- Depth to bottom of well
- Screened interval
- Pump depth
- Volume of water evacuated before sampling
- Purge rate
- Specific conductivity, temperature, dissolved oxygen, and pH during evacuation (note number of well volumes), including units of measurement.

- Type of container used
- Analysis requested
- Number of sample containers filled for each analyses
- Preservation of samples
- Decontamination time
- Record of any QA/QC samples from well
- Any irregularities or problems that may have a bearing on sampling quality
- Comments

5.2 FIELD NOTES

Field notes shall be kept in a bound field book. The following information will be recorded using water proof ink:

- Names of personnel
- Associated field form number for each location sampled.
- Weather conditions
- Date and time of sampling
- Location and well number
- Parameter stabilization info. (time, values, etc.).
- Condition of the well
- Decontamination information
- Calculations (e.g., calculation of evacuated volume)
- Calibration information
- Sampler's signature
- Other pertinent information (problems, special conditions, etc.)

Figure 1: Field Sampling Data Sheet For Groundwater Samples

Field Book Reference #: _____ Page __ of __

Well No.: _____ Date: _____

Field Personnel: _____ Arrival Time: _____

Sample Identification Number: _____

Sampling Method: ☐ Standard Volume Evacuated (prior to sample collection): ~ _____ Liters
☐ Low-Flow Volume Evacuated (see field parameter table below)

Water Level (ft BTOIC): _____ Depth to Bottom of Well (ft BTOIC): _____

TOIC Elevation: _____ Screened Interval (ft BTOIC): _____ Pump Depth (ft BTOIC):_____

Field Parameters

	Units	Initial purge	Vol/ Reading	Vol/ Reading	Vol/ Reading	Vol/ Reading	Vol/ Reading	Sample after purge
Time	Hr/min							
Volume Purged	L							
Purge Rate	L/min							
pH	SU							
Spec. Cond.	US/cm							
Temperature	°C							
Dissolved Oxygen	Mg/L							
Redox. Potential	mv							
Turbidity (optional)	NTU							
Water Level	ft btoic							

See Field COC form for sample bottles, analyses, and preservation

Equipment Decontamination Time: _____

QA/QC Samples Collected: ☐ Field Duplicate ☐ Rinsate Blank ☐ Field Blank
☐ Extra Volume (MS/MSD or MS/D)

Final water level after sample completion: _____(ft btoic)

Comments:
_____

Color: _____ Turbidity: ☐ Clear ☐ Slightly Cloudy ☐ Moderately Cloudy ☐ Very Cloudy

☐ Well Pumped Dry ☐ Insufficient water to sample (< 3 ft of water) ☐ Well is dry (no water) ☐ Other:_____

Recorded by: _____ Date: _____

Reviewed by: _____ Date: _____
(Supervisor or designee)

Freeport-McMoRan Sierrita Inc.

VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 3.0

FIELD FILTRATION OF WATER SAMPLES

1.0 PURPOSE AND SCOPE 3-1

2.0 RESPONSIBILITIES AND QUALIFICATIONS 3-1

3.0 RELATED STANDARD OPERATING PROCEDURES 3-1

4.0 EQUIPMENT LIST 3-1

5.0 FILTERING PROCEDURE (FOR DISSOLVED METALS) 3-1

5.1 PERISTALTIC PUMP 3-2
5.2 FISHER SCIENTIFIC ULTRACLEANING FILTER UNITS 3-2
5.3 GEOTECH DISPOS-A-FILTER FOR GROUNDWATER SAMPLING 3-3
5.4 SAMPLE HANDLING 3-3

6.0 DOCUMENTATION 3-3

1.0 PURPOSE AND SCOPE

The purpose of this document is to define the standard operating procedure (SOP) for filtering surface and groundwater samples for dissolved metals analysis. This procedure gives descriptions of equipment, field procedures, and quality assurance/quality control (QA/QC) procedures necessary to collect filtered samples in the field.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Design Contractor has the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate environmental staff to implement this SOP and for ensuring that the procedures are followed by all personnel.

All personnel performing these procedures are required to have the appropriate health and safety training. In addition, all personnel are required to have a complete understanding of the procedures described within this SOP and receive specific training regarding these procedures, if necessary.

All environmental staff and assay laboratory staff are responsible for reporting deviations from this SOP to the Design Contractor.

3.0 RELATED STANDARD OPERATING PROCEDURES

The procedures for field filtration of water samples set forth in this SOP are intended for use with the following SOPs:

SOP No. 1.0	Surface Water Sampling
SOP No. 2.0	Monitor Well Groundwater Sampling
SOP No. 6.0	Decontamination of Equipment
SOP No. 9.0	Sample Management

4.0 EQUIPMENT LIST

Sample bottles with preservatives added will be obtained from the analytical laboratory. Several extra sample bottles with no preservatives can be obtained, or a glass bowl with a lid can be used to temporarily contain water for filtering.

In addition to the sampling equipment listed in SOP No. 1.0, Surface Water Sampling, or SOP No. 2.0, Monitor Well Groundwater Sampling (as applicable), equipment that may be used during field filtering include:

- Sample bottles with and without preservatives
- Glass bowl with lid
- Sample transfer container

5.0 FILTERING PROCEDURE (FOR DISSOLVED METALS)

This section gives the step-by-step procedures for filtering water samples in the field using Fisher Scientific Ultracleaning filter units with disposal filters and B-D disposable syringes, geotech dispos-a-filter used for ground water sampling or a peristaltic pump with disposable filters for dissolved metals analysis. Water samples should be filtered within approximately two hours after sample collection.

5.1 PERISTALTIC PUMP

The following procedure is to be used for filtering when using a peristaltic pump with disposable 0.45-micron filters.

- Collect water sample as described in SOP No. 1.0, Surface Water Sampling, or SOP No. 2.0, Monitor Well Groundwater Sampling, as applicable.
- Temporarily contain water sample in a sample bottle with no preservatives or a glass bowl with a lid (previously decontaminated).
- Attach disposable filter (be sure arrow on filter is in direction of flow) to one end of surgical tubing and attach to peristaltic pump per manufacturer's instructions.
- Place the other end of tubing in sample, turn pump on, and allow sample to run through filter into an appropriate sample bottle with preservatives.
- Replace disposable filter and tubing between each sample location. The same sample filter and tubing can be used for field duplicates, if taken. If an equipment rinsate blank QA/QC sample is taken, the distilled or deionized water used to rinse sampling equipment should also be filtered through a new disposable filter and new tubing and placed in a sample bottle with preservatives.

5.2 FISHER SCIENTIFIC ULTRACLEANING FILTER UNITS

The following procedure is to be used for filtering when using a Fisher Scientific ultracleaning filter units with disposable 0.45-micron filters and B-D 60cc disposable syringes.

- Collect water samples as described in SOP No. 1.0, Surface Water Sampling, or SOP No. 2.0, Monitor Well Groundwater Sampling, as applicable.
- Temporarily contain water sample in a sample bottle with no preservatives or a glass bowl with a lid (previously decontaminated).
- Assemble Syringe: Fill the syringe with solution you want to filter and rinse the syringe with solution at least 2 times.
- Remove the cover from the package that contains the ultracleaning filter unit using aseptic technique.
- Attach the syringe to the ultracleaning filter unit and remove the assembly from the package.
- Hold the syringe with the filter pointed up and top it off by pushing a few drops through. (Do not contaminate the underside of the ultracleaning filter unit with your fingers.)

- Place the filter assembly over the appropriate sample bottle with preservatives and push the plunger to deliver the filtered solution into the container.
- Replace filter with new filter every 100mL of sample.
- Replace disposable filter between each sample location. The same sample filter can be used for field duplicates, if taken. If an equipment rinsate blank QA/QC sample is taken, the distilled or deionized water used to rinse sampling equipment should also be filtered through a new disposable filter and placed in a sample bottle with preservatives.

5.3 GEOTECH DISPOS-A-FILTER FOR GROUNDWATER SAMPLING

The geotech dispos-a-filter is disposable filter 0.45 micron pore size capsule designed to perform in-line water filtration in the field. It attaches to ¼ in to ½ in. sized sample tubing with specially designed sample tubing adapter.

- Attach filter to end of tubing from the ground water monitor well. Be sure the arrow on the filter points in the right direction of the flow.
- Make sure you have tight fit and avoid contamination by touching the outlet of the filter.
- Replace disposable filter between each sample location. The same sample filter can be used for field duplicates, if taken. If an equipment rinsate blank QA/QC sample is taken, the distilled or deionized water used to rinse sampling equipment should also be filtered through a new disposable filter and placed in a sample bottle with preservatives.

5.4 SAMPLE HANDLING

Sample containers, preservatives, and analyses are specified in SOP No. 9.0, Sample Management. Samples will also be labeled and handled as described in SOP No 9.0.

6.0 DOCUMENTATION

A field sampling data sheet for surface water and groundwater samples will be completed at each sampling location in accordance with the documentation procedures described in SOPs Nos. 1.0 and 2.0. Samples filtered in the field should be designated on the field data sheets and in the field logbook along with the method of filtering.

Freeport-McMoRan Sierrita Inc.

VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 4.0

NEAR SURFACE SOIL SAMPLING

1.0 PURPOSE AND SCOPE 4-1

2.0 RESPONSIBILITIES AND QUALIFICATIONS 4-1

3.0 RELATED STANDARD OPERATING PROCEDURES 4-1

4.0 EQUIPMENT LIST 4-1

5.0 PROCEDURES FOR NEAR SURFACE SOIL SAMPLING 4-2

- 5.1 SURFACE MATERIAL 4-2
- 5.2 SUBSURFACE MATERIAL 4-3
- 5.3 FIELD QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES AND SAMPLES 4-4
- 5.4 SAMPLE HANDLING 4-4

6.0 DOCUMENTATION 4-4

- 6.1 FIELD SAMPLING DATA SHEET 4-4
- 6.2 FIELD NOTES 4-5

Attachment A Field Sampling Data Sheet for Surface Material Samples 4-6

1.0 PURPOSE AND SCOPE

This Standard Operating Procedure (SOP) provides technical guidance and methods that will be used in collection of surface material and subsurface material samples for chemical analysis. This procedure gives descriptions of equipment, field sampling procedures, field data collection, personnel responsibilities, and quality assurance/quality control (QA/QC) procedures.

The SOP describes procedures for collection of surface material and subsurface material samples. For the purposes of this SOP, and unless governed by other project documents (for example, activity-specific SAPs), the term "surface material" refers to the top six inches (in) (15 centimeters [cm]) of soil following removal of surface vegetation, non-decomposed plant litter, and other debris from the sampling area and "subsurface material" refers to soil from 0 to 24 in (5 to 61 cm) below ground surface.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Design Contractor has the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate environmental staff to implement this SOP and for ensuring that the procedures are followed.

All personnel performing these procedures are required to have the appropriate health and safety training. In addition, all personnel are required to have a complete understanding of the procedures described within this SOP, and receive specific training regarding these procedures, if necessary.

All environmental staff and assay laboratory staff are responsible for reporting deviations from this SOP to the Design Contractor.

3.0 RELATED STANDARD OPERATING PROCEDURES

The procedures set forth in this SOP are intended for use with the following SOPs:

SOP No. 6.0	Decontamination of Equipment
SOP No. 9.0	Sample Management
SOP No. 20.0	Surveying (Conventional and GPS)
SOP No. 22.0	Utility Clearance
SOP No. 23.0	Investigation Derived Waste Management

4.0 EQUIPMENT LIST

The following materials and equipment may be necessary for surface material sampling:

- Sample containers
- Bound field logbook
- Sampling site location maps
- 300-foot and 100-foot tape measures or Survey Wheel and Brunton Compass

- Field Sampling Data Sheets for Surface Materials (Attachment A)
- Surveying stakes, lath, or flags for marking of grid nodes and/or sampling locations
- Monitoring equipment and personal protective equipment (PPE) as outlined in the Health and Safety Plan (HASP)
- Decontamination equipment and supplies (e.g., high pressure sprayer/washer, wash/rinse tubs, brushes, Alconox, plastic sheeting, paper towels, sponges, baby wipes, garden-type water sprayers, large plastic bags, potable water, 5-gallon buckets, distilled water and/or deionized water)
- Stainless steel hand augers, scoops or spoons, soil knife, pick, and mixing bowls
- Sample collection supplies (e.g., plastic recloseable plastic bags or equivalent, waterproof markers, sample labels, chain of custody [COC] forms, cooler for sample storage, ice or ice substitute, clear plastic and strapping tape, custody seals, trash bags)
- No. 10 mesh sieve
- GPS Unit
- Shovel
- Digital Camera
- Site Plans, Topographic Maps, or Aerial Photographs

Other site specific materials and equipment may be needed based on field conditions.

5.0 PROCEDURES FOR NEAR SURFACE SOIL SAMPLING

5.1 SURFACE MATERIAL

Surface material samples may be collected as grab or composite samples, as specified in the work plan. Such samples should be collected from the depth range of 0 to 6. in (0 to 15 cm). Prior to sampling, it is important to calculate the total volume of sample material to be collected at each increment sample location so that the volume required for each analysis is available for completely filling each sample container. The analysis-specific volumes are specified in the QAPP. Sampling locations specified in the work plan or FSP will be identified and marked using surveying stakes, lath, or flags, as practical.

For grab samples, surface material will be collected at each proposed sample location. Grab sample material will be homogenized in a stainless steel bowl before filling sample containers.

For composite samples, unless specified differently in the applicable work plan or FSP, composite surface material samples will be comprised of five increment sub-samples collected from each of the corners and center point of a 1-meter square. All or a portion of the increment samples are mixed together to create a composite sample representative of average constituent concentrations within the area to be characterized. For a given composite sample, the volume of each increment sample must be the same, and must equal 1/n of the required composite sample volume, where n equals the number of increment samples making up the composite sample (e.g., 5).

Surface material samples will be collected as follows:

1. At each sample location (for grab samples) or sub-sample location (for composite samples), clear an area approximately 12 in (30 cm) in diameter of surface vegetation, non-decomposed plant litter, and debris, as applicable.
2. Use a decontaminated stainless steel spoon or hand auger to collect material to a depth of 6 in (15 cm) from the surface or from within the excavator/loader bucket. A stainless steel pick may be used as needed to loosen the soil. To the extent possible, eliminate gravel-size or larger particles and debris based on visual observation.
3. Visually describe the material and record observations on the soil sample field data sheet.
4. Sieve the increment sample through a No. 10 mesh and place the passing fraction into a decontaminated stainless steel mixing bowl. Mix thoroughly.
5. For composite samples, repeat Steps 1 through 4 at each increment sample location for a given composite sample, adding each successive increment sample to the mixing bowl.
6. Thoroughly mix the sample material in the stainless steel bowl using a decontaminated stainless steel spoon. To homogenize, divide the sample into four quarters and mix each quarter, then combine the four quarters and mix the entire sample. Place mixture into appropriate laboratory-supplied sample containers.
7. Label and handle the containers as specified in SOP No. 9.0, Sample Management.

Sample increment locations will be surveyed using a GPS Unit.

5.2 SUBSURFACE MATERIAL

Sub-surface material samples should be collected from a depth range of 0 to 2 feet (0 to 0.5 meters). Prior to sampling, it is important to estimate the total volume of sample material to be collected at each increment sample location to ensure that the volume required for each analysis is available for completely filling each sample container. The analysis-specific volumes are specified in the QAPP. Sampling locations specified in the work plan or FSP will be identified and marked using surveying stakes, lath, or flags.

Sub-surface material samples will be collected as follows:

1. At each sample location, clear an area approximately 30 cm in diameter of surface vegetation (non-decomposed plant litter) and debris.
2. Use a decontaminated stainless steel spoon, shovel, hand auger, or excavator/loader bucket to collect subsurface material from the surface to a depth of 2 ft (0.5 m) below ground surface. A stainless steel pick may be used as needed to loosen the soil. To the extent possible, eliminate gravel-size or larger particles and debris based on visual observation. Place the material in a stainless steel mixing bowl. The material placed in the bowl should be representative of the entire depth horizon (i.e., 0 to 2 ft [0 to 0.5 m]).
3. Visually describe the material and record observations on the soil sample field data sheet.
4. If sieving is required per the SAP, sieve the increment sample through a No. 10 mesh and place the passing fraction into a decontaminated stainless steel mixing bowl. Mix thoroughly.

5. Thoroughly mix the sample material in the stainless steel bowl using a decontaminated stainless steel spoon. To homogenize, divide the sample into four quarters and mix each quarter, then combine the four quarters and mix the entire sample. Place mixture into appropriate laboratory-supplied sample containers.
6. Label and handle the containers as specified in SOP No. 9.0, Sample Management.

Sample increment locations will be surveyed using a GPS Unit.

5.3 FIELD QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES AND SAMPLES

QA/QC samples are designed to help identify potential sources of sample contamination to evaluate potential error introduced by sample collection and handling. All QA/QC samples are labeled and sent to the laboratory with other samples for analysis. The type and number of QA/QC samples are defined in SOP No. 9.0 Sample Management.

5.4 SAMPLE HANDLING

SOP No. 9.0, Sample Management specifies sample containers, preservatives, and analyses. SOP No. 9.0 also describes how samples will be labeled and handled.

6.0 DOCUMENTATION

Documentation of observations and data acquired in the field will provide information on the activities concluded and also provide a permanent record of field activities. The observations and data will be recorded with waterproof ink in a permanently bound weatherproof field logbook with consecutively numbered pages, and on field data sheets.

6.1 FIELD SAMPLING DATA SHEET

A field sampling data sheet (included as Attachment A) for surface material samples will be completed for each grab or composite sample. The data sheet will be completely filled in. If items on the sheet do not apply to a specific sample or location, the item will be labeled as not applicable (NA). The information on the sheet will include the following:

- Date and Time of sampling
- Personnel and Samplers Signature
- Sample identification number.
- Type of Sample
- Weather
- Type and size of container used
- Analysis requested
- Number of sample containers filled for each analyses
- Preservation of samples

- Record of any QA/QC samples
- Any irregularities or problems that may have a bearing on sampling quality

6.2 FIELD NOTES

Field notes will also be kept during sampling activities. The following information at a minimum will be recorded in a bound field logbook using waterproof ink:

- Names of personnel
- Weather conditions
- Date and time of sampling
- Location of sampling, including GPS coordinates
- Description of samples, and analyses to be performed
- Description of QA/QC samples
- Decontamination information
- Number of sample containers
- Sample handling and method of shipment

ATTACHMENT A

FIELD SAMPLING DATA SHEET FOR SURFACE MATERIAL SAMPLES

Sample Identification:		Date:
Samplers' Signature:		Time:
Type of Sample:	Surface:	Subsurface:
	Composite:	Grab:
Sample Location Coordinates:		
Type of Surface Cover:		
Depth Interval:		
Weather Conditions:		
Sample Description:		
Field Soil Description		
USCS Abbreviation		
Color		
Staining		
Odor		
Moisture		

Containers	Number	Preservatives

QA/QC Samples Collected:
Comments:

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VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 6.0

DECONTAMINATION OF EQUIPMENT

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2.0 RESPONSIBILITIES AND QUALIFICATIONS 6-1

3.0 RELATED STANDARD OPERATING PROCEDURES 6-1

4.0 EQUIPMENT LIST 6-2

5.0 PROCEDURE 6-2

5.1 DECONTAMINATION 6-2
5.1.1 Sampling Equipment 6-2
5.1.2 Large Equipment 6-3
5.1.3 Equipment Leaving the Site 6-3
5.1.4 Biota Sampling Equipment 6-3

6.0 DOCUMENTATION 6-3

1.0 PURPOSE AND SCOPE

This standard operating procedure (SOP) describes procedures that will be used for equipment decontamination. The collection of environmental samples requires that all equipment associated with collecting these samples be cleaned. This requirement reduces the possibility of contaminants being introduced into the sample from external sources. Additionally, equipment used for the removal and loading of contaminated media also requires decontamination to reduce site cross-contamination from the introduction of foreign material to the environment. This procedure establishes the cleaning and decontamination methods for achieving that goal.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Design Contractor has the overall responsibility for implementing this SOP. They will be responsible for assigning environmental staff to implement this SOP and for ensuring that the procedures are followed by all personnel.

All personnel performing these procedures are required to have the appropriate health and safety training. In addition, all personnel are required to have a complete understanding of the procedures described within this SOP and receive specific training regarding these procedures, if necessary.

All environmental and assay laboratory staff are responsible for reporting deviations from this SOP to the Design Contractor.

3.0 RELATED STANDARD OPERATING PROCEDURES

The procedures for decontamination of sampling equipment set forth in this SOP are intended for use with the following SOPs:

SOP No. 1.0	Surface Water Sampling
SOP No. 2.0	Monitor Well Groundwater Sampling
SOP No. 2.1	Water Elevation Measurements
SOP No. 3.0	Field Filtration of Water Samples
SOP No. 4.0	Near Surface Soil Sampling
SOP No. 5.0	Sediment Sampling
SOP No. 8.0	Field Parameters Measurement (including Instrument Calibration)
SOP No. 18.0	Subsurface Soil Sampling with a Hand Auger
SOP No. 19.0	Test Pit Excavation and Sampling
SOP No. 23.0	Investigation Derived Waste Management
SOP No. 25.0	Benthic Macroinvertebrate Sampling and Analysis
SOP No. 37.0	Sediment Bench Testing Procedures
SOP No. 38.0	Sediment Probing and Sampling Procedures

4.0 EQUIPMENT LIST

The following is a list of equipment that may be used to perform decontamination:

- Alconox detergent (or equivalent)
- Brushes
- Wash tubs (minimum of 3) or 5-gallon buckets (minimum of 3), as necessary
- Scrapers, as necessary
- Steam cleaner or high-pressure sprayer (portable), as necessary
- Sponges
- Chemical-free paper towels or Kimwipes
- Potable tap water
- Deionized or distilled water
- Garden type water sprayers
- 500 mL or lL spray bottles
- Plastic trash bags
- Plastic sheeting and clean plastic wrap/bags

5.0 PROCEDURE

5.1 DECONTAMINATION

5.1.1 Sampling Equipment

The following steps will be used to decontaminate small sampling equipment, such as bailers, stainless steel trowels, bowls, spoons, etc.:

- Personnel will dress in suitable safety equipment to reduce personal exposure.
- Set up a decontamination area with plastic sheeting, as necessary.
- Gross decontamination on equipment will be scraped off at the sampling site.
- Equipment that will not be damaged by water will be placed in a wash tub or bucket or sprayed with a solution containing Alconox or low-sudsing detergent along with potable water and scrubbed with a bristle brush or similar utensil. Equipment will be washed or sprayed with potable water, followed by a potable water rinse or spray. Equipment will then be double rinsed or sprayed with distilled or deionized water. Spray water may be collected by paper towels and disposed of appropriately.
- Equipment that may be damaged by water (such as a specific conductivity meter) will be carefully wiped clean when necessary using a sponge and detergent water and rinsed again with

a sponge dipped in distilled or deionized water. Care will be taken to prevent damage to equipment.

- Rinse and detergent waters will be replaced between sample locations.
- Used rinse and detergent water will be disposed of properly at a designated location at the site.

Following decontamination, equipment will be placed in a clean area or in clean plastic wrap/bags.

5.1.2 Large Equipment

Excavation equipment, loading equipment, and other large pieces of field equipment must be cleaned before and after use. Mop washing, steam cleaning, and/or high-pressure washing will be performed at an appropriate decontamination area specified by the Design Contractor. The decontamination area shall be capable of containing decontamination fluids and solids. The decontamination fluids shall be managed in accordance with SOP No. 23.0, Investigation Derived Waste Management.

The following steps for decontamination will be applied to large equipment:

- Physically remove as much of the visible material as possible from heavy equipment after use. If contaminated material is suspected based on observations, then collect and return the material to the area where it originated.
- Place heavy equipment on the decontamination pad in the decontamination area. If wash water is to be collected, verify that the collection mechanism functions properly and the pad has no leaks.
- Brush clean parts of heavy machinery that come into contact with the visible material (such as tires, excavator bucket, tracks, and bulldozer blades and tracks).
- Contain fluids, if appropriate. Dispose of solids with other contaminated materials.

5.1.3 Equipment Leaving the Site

All sampling equipment will be cleaned prior to leaving the site. Vehicles used during field activities shall be cleaned on an as-needed basis with soap and water on the outside and vacuuming the inside. Additionally, haul trucks will be inspected for excess soil and debris and cleaned, as necessary, before entering roadways.

5.1.4 Biota Sampling Equipment

Biota sampling equipment may be decontaminated by washing in Clorox bleach (10%) or Lysol for 20 minutes to kill potential pathogens, for example the terrestrial vertebrate traps such as Hanta virus. Equipment will then be rinsed three times with potable water.

6.0 DOCUMENTATION

Documentation of observations and data acquired in the field will provide information on the activities concluded and also provide a permanent record of field activities. The observations and data will be recorded with waterproof ink in a permanently bound weatherproof field logbook with consecutively numbered pages.

Sampling personnel will be responsible for documenting the decontamination of all sampling equipment. The information entered in the field book concerning decontamination should include the following:

- Decontamination personnel
- Date and start and end times
- Decontamination steps/observations
- Weather conditions

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VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 8.0

FIELD PARAMETER MEASUREMENTS (INCLUDING INSTRUMENT CALIBRATION)

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1.0 PURPOSE AND SCOPE

This standard operating procedure (SOP) describes procedures that will be used to obtain field parameter measurements for surface water and groundwater parameter samples. These parameters are pH, temperature, specific conductivity (SC), dissolved oxygen (DO), oxidation reduction potential (ORP), and turbidity. This SOP describes field measurement procedures, personnel responsibilities and qualifications, and quality assurance/quality control (QA/QC) procedures.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Design Contractor has the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate environmental staff to implement this SOP and for ensuring that the procedures are followed by all personnel.

All personnel performing these procedures are required to have the appropriate health and safety training. In addition, all personnel are required to have a complete understanding of the procedures described within this SOP and receive specific training regarding these procedures, if necessary.

All environmental staff and assay laboratory staff are responsible for reporting deviations from this SOP to the Design Contractor.

3.0 RELATED STANDARD OPERATING PROCEDURES

The procedures for field measurements set forth in this SOP are intended for use with the following SOPs:

SOP No. 1.0 Surface Water Sampling

SOP No. 2.0 Monitor Well Groundwater Sampling

SOP No. 6.0 Decontamination of Equipment

SOP No. 23.0 Investigation Derived Waste Management

4.0 EQUIPMENT LIST

In addition to the equipment cited in associated SOPs for the collection of surface and groundwater samples (SOP Nos. 1.0 and 2.0, respectively), the following meters are required for the implementation of this SOP.

- pH meter with a temperature scale
- Specific conductivity meter
- Dissolved oxygen meter
- Oxidation Reduction Potential meter
- Turbidity meter

5.0 FIELD PARAMETER MEASUREMENTS

Several of the parameters required to be measured are physically or chemically unstable and must be tested either in situ or immediately after sample collection using a field test kit or instrument. Examples of unstable parameters include pH, temperature, and dissolved oxygen. Although the specific conductivity of a substance is relatively stable, it is recommended that this characteristic be measured in the field. Most instruments measuring specific conductivity require temperature compensation; therefore, the temperature of the samples should be measured at the time the specific conductivity is measured.

Sampling personnel shall wear chemical-resistant gloves, which will be disposed of between locations when performing field measurements.

5.1 PROCEDURES FOR COLLECTING A SAMPLE FOR FIELD PARAMETER MEASUREMENTS

Collect water samples for chemical analysis as described in SOP Nos. 1.0 and 2.0. Additional sample (volume) will be collected and placed in a separate container (if not using an insitu probe) for measuring field parameters. Field parameter measurements may be taken immediately before or after sample collection depending on the type of sample collected. If determining parameter stabilization during well development, samples for field parameter measurements will be collected periodically. The sample container can be used to measure all field parameters of the sample. After the measurements have been recorded, the water should be discarded. Do not use this sample for chemical analysis.

5.2 METER USE AND CALIBRATION

Field instruments will be calibrated the day prior to commencement of field measurements and daily afterwards. Solutions used for standardizing and calibrating will be checked prior to field mobilization to determine if the expiration dates have been exceeded. Any expired solution will be discarded appropriately and replaced with a new solution.

5.2.1 pH Meter

Calibration and operation of the pH meter should follow the manufacturer's specific instructions. In general, calibration is done by adjusting the meter with standard buffers that bracket the expected pH of the aqueous samples. For specific instructions refer to the manufacturer’s instruction manual.

Field sampling personnel will measure pH as follows:

1. If the pH is measured in a container, rinse the sample container with deionized water and then rinse it three times with the water to be sampled prior to measurement. If using an in-flow multi-measurement system, measurements are continuously displayed.
2. Rinse the pH probe with deionized water. Be sure to protect the fragile glass bulb at the end of the probe from damage.
3. Immerse the electrode in the water, allow the pH to stabilize, and monitor the drift of the instrument.

4. When the pH reading stabilizes, record in the field logbook the temperature to the nearest $0.1^{o}C$ and the pH reading to the nearest 0.01 unit.

Quality control (QC) requirements for pH measurements are provided in Section 5.3.

5.2.2 Specific Conductivity Meter

Conductance is a measure of the ability of an aqueous solution to conduct electrical current and is expressed in reciprocal ohms (mhos). The International System of Units uses the siemen(s) to represent mhos. Calibration procedures are to be conducted according to the manufacturer's instructions. Record time, temperature, and instrument response in the field logbook.

The procedures for measuring conductivity are as follows:

1. Allow the reading to stabilize before recording measurements.
2. Record in the field logbook the conductivity and the units of measure.

QC requirements for conductivity measurements are provided in Section 5.3.

5.2.3 Dissolved Oxygen Meter

The concentrations of dissolved oxygen in groundwater samples provide an indication of the whether aerobic or anaerobic respiration is occurring in an aquifer system. Dissolved oxygen concentrations greater than 1 milligram per liter (mg/L) are favorable for aerobic respiration. Manufacturer's operating manuals, calibration, maintenance procedures will be followed and documented in the field logbook.

The procedures for using a DO meter are as follows:

1. Inspect the membrane before each field use for air bubbles, oily film, and/or holes. If the membrane is defective, it must be replaced and soaked before recalibration in accordance with manufacturer's instructions.
2. Read the DO meter to the nearest 0.1 mg/l. Record in the field logbook the DO concentration and the range setting of the DO meter.
3. Protect the DO probe when not in use to prevent the membrane from drying out or freezing.
4. Sampling tools, instruments, and equipment will be protected from sources of contamination before use and decontaminated after use as specified in SOP No. 6.0, Decontamination of Equipment.

QC requirements for DO measurements are provided in Section 5.3.

5.2.4 Oxidation Reduction Potential Meter

ORP is a measure of the tendency of a solution to donate or accept electrons. ORP is measured in units of milliVolts (mV). The ORP may be measured at the time of sample collection. Manufacturer's operating manuals, calibration, and maintenance procedures will be followed and documented in the field logbook.

ORP is measured as follows:

1. The electrode should stabilize within 2 to 5 minutes. When stable, take a reading and record it in the field logbook. Any instability will be noted and recorded.
2. Decontaminate the water quality meter probe and associated equipment in accordance with SOP No. 6.0, Decontamination of Equipment.

QC requirements for ORP measurements are provided in Section 5.3.

5.2.5 Turbidity

The turbidity may be measured at the time of sample collection. A portable turbidity meter will be used for field determination of turbidity in the parameter samples.

The turbidity meter is factory calibrated and requires no field calibration. The factory calibration shall be checked before the turbidity meter is sent to the field. Additionally, the calibration of the turbidity meter will be checked daily before collection of samples against a known formazin standard. The instrument will be recalibrated as necessary based on the daily check. Refer to the manufacturer's instruction manual for proper use.

The turbidity test measures an optical property of the water sample that results from the scattering and absorbing of light by the particulate matter present. The amount of turbidity registered is dependent on such variables as the size, shape, and refractive properties of the particles. This procedure is commonly calibrated using formazin turbidity standards, and the readings are in terms of nephelometric turbidity units (NTUs).

Turbidity is measured as follows:

1. If a portable turbidity unit is used, rinse the sample container with deionized water and then rinse it three times with the water to be sampled prior to measurement.
2. Fill up the sample container and put the cap on the container. Wipe off the outside of the sample container and place it into the portable turbidity unit. Take the turbidity reading and record it in the field logbook.
3. Decontaminate the turbidity meter sample container and associated equipment in accordance with SOP No. 6.0, Decontamination of Equipment.

QC requirements for turbidity measurements are provided in Section 5.3.

5.2.6 In-flow Multi-Parameter Monitoring System

The in-flow multi-parameter monitoring system or similar multi-parameter instruments, may be used for measuring pH, temperature, conductivity, DO, ORP, and turbidity. In-flow meters allow for the analysis of purge water, in-line, as it flows so that sampling can begin as soon as water stabilizes. The manufacturer's operation and maintenance manual shall be followed when operating or calibrating the instrument.

5.3 QUALITY ASSURANCE/QUALITY CONTROL

QA/QC activities will be conducted in accordance with the governing applicable documents as well as quality requirements presented in this SOP. As noted in Section 5.2, all meters will be calibrated daily prior to use. In addition, each meter will be inspected daily prior to calibration.

Furthermore, as described below a duplicate set of field parameter measurements will be collected for every 10 sampling stations.

5.3.1 QC Checks and Acceptance Criteria

One duplicate field parameter measurement shall be collected for every ten sampling locations (10% frequency). Field parameter measurements are considered satisfactory if the duplicate measurements fall within the acceptable range in the table below.

Field Parameter	Acceptable Range
pH	± 0.1 pH unit
Temperature	± 10%
Oxidation-Reduction Potential	± 5 mV
Conductivity	± 10%
Turbidity	± 10%
Dissolved Oxygen	± 0.1 mg/L

If duplicate acceptance criteria are not met, the instrument must be re-calibrated and new parameter measurements obtained at the sample location where the original duplicate sample did not meet acceptance criteria.

6.0 DOCUMENTATION

Documentation of observations and data acquired in the field will provide information on the activities conducted and also provide a permanent record of field activities. The observations and data will be recorded with waterproof ink in a permanently bound weatherproof field logbook with consecutively numbered pages, and/or on field data sheets as appropriate.

6.1 FIELD LOGBOOK

All information regarding calibration of field instruments will be recorded in the field logbook. The following information will be recorded in the field logbook:

- Type of meter calibrated and instrument manufacture (the instrument serial number should be recorded at the start of work and if instruments are changed)
- Date of calibration
- Person(s) performing the calibration
- Calibration solutions used
- Results of calibration measurements
- Any deviations from the SOPs

6.2 FIELD NOTES

All information regarding field parameter measurements taken at a sample location will be recorded on the appropriate field sample collection datasheet. At a minimum, this documentation will include:

- Sample location and sample identification number
- Date and time of measurement
- Weather conditions
- Measurement results, including units and scaling factors
- Person(s) conducting measurements
- Sample characteristics (color, odor, etc.)
- Results for any QC measurements (i.e., results for duplicate set of measurements)
- Any instrument maintenance or corrective actions necessary (including rinsing of probes between sampling locations)
- Any deviations from the SOPs

The field sample collection datasheet will cross-reference the logbook in which the applicable calibration information is recorded. If the sample collection datasheet does not include spaces to record the information noted above, this information will be recorded in the field logbook.

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VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 14.0

MONITORING WELL INSTALLATION

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1.0 PURPOSE AND SCOPE

The purpose of this document is to define the Standard Operating Procedure (SOP) for installing groundwater monitoring wells in unconsolidated geologic materials and bedrock at the Mine Site and in surrounding areas. It describes designs, procedures, and materials used to construct monitoring wells that will produce accurate groundwater level measurements and representative groundwater samples. Well construction and abandonment reports, if required, will be submitted to the State of Arizona Department of Water Resources (ADWR). The step-by-step procedures described herein are sufficiently detailed to allow field personnel to properly install monitoring wells.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The RI Project Manager or Field Manager have the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate environmental staff to implement this SOP and for ensuring that the procedures are followed by all personnel.

All personnel performing these procedures are required to have the appropriate health and safety training. In addition, all personnel are required to have a complete understanding of the procedures described within this SOP and receive specific training regarding these procedures, if necessary.

All project staff are responsible for reporting deviations from this SOP to the RI Project Manager or Field Manager.

3.0 RELATED STANDARD OPERATING PROCEDURES

The procedure for monitoring well installation set for in this SOP is intended for use with the following SOPs:

SOP No. 2.0	Groundwater Sampling
SOP No. 2.1	Water Level Measurement
SOP No. 6.0	Decontamination of Sampling Equipment
SOP No. 9.0	Sample Management
SOP No. 15.0	Well Development
SOP No. 17.0	Borehole Logging
SOP No. 20.0	Surveying (Land and GPS)
SOP No. 22.0	Utility Clearance
SOP No. 23.0	IDW Management

4.0 EQUIPMENT LIST

Equipment that will be used for installing groundwater monitoring wells includes (American Society for Testing and Materials [ASTM] 1996, U.S. Environmental Protection Agency [EPA] 1986, 1990):

- Well casing and well screen
- Bentonite pellets for the annular seal
- Filter pack sand
- Cement and powdered bentonite for grouting
- Stainless-steel centralizers
- Protective steel well casing with locking cap
- Steel guard posts
- Decontamination equipment and supplies (See SOP No. 6.0 Decontamination of Sampling Equipment)
- Well location map
- Drill rig capable of installing wells to the desired depth in the expected formation materials and conditions (i.e., capable of hanging well casing, tremie pumping sand and grout, and accurate measurement of material in the annulus). (See SOP No. 16.0 Drilling and Sampling of Subsurface Materials.)
- Weighted tape measure
- Water level probe
- Disposable latex gloves
- Appropriate health and safety equipment
- Waterproof pens
- Field logbook
- Calculator
- Well Completion Diagram (Figure 1).

5.0 GROUNDWATER MONITORING WELL INSTALLATION PROCEDURES

Well construction procedures will fulfill all applicable regulatory agency requirements for permit applications, material standards, and construction/completion protocols. Licensing and/or certification of the driller may be required. In order to maintain quality control and obtain accurate information, a field geologist or hydrogeologist will be on the site to supervise well construction and log details of the procedure. All activities will be conducted in conformance with the Project Health and Safety Plan.

5.1 MAINTENANCE OF DRILL RIG EQUIPMENT AND WELL MATERIALS

Decontamination procedures specified in SOP No. 6.0 Decontamination of Sampling Equipment, will be performed.

Drill rig injection and water pumps will be cleaned as necessary.

Any leaks from the drill rig occurring during well installation will be fixed or contained in such a way that they will not contaminate the borehole.

Care will be taken not to contaminate the well casing or the borehole with diesel fluid, hydraulic fluid, WD-40, oil, dirty tools, and so forth.

Drillers will use clean gloves when handling downhole equipment. Different gloves will be used for performing activities such as fueling, adding oil, and working on equipment.

Pipe lubricants that are used should not introduce contaminants into the borehole. Lubricants that are environmentally acceptable include Green Stuff®, King Stuff®, vegetable oil, Crisco™, and some Teflon™-based lubricants. Lubricants that are not acceptable include petroleum-based and most metal-based lubricants. The Site Manager will pre-approve lubricants that will be used, and the Material Safety Data Sheets (MSDS) for these lubricants will be provided for reference.

All well casing and screen will be free of foreign material. Casing and screen will be stored off the ground in the original manufacturer's shipping containers until they are installed in the borehole. Before installation, well casing, screen, and centralizers will be certified clean from the manufacturer or will be decontaminated according to SOP No. 6.0 Decontamination of Sampling Equipment. Acid rinse solutions should not be used for PVC decontamination. Clean latex or nitrile gloves will be worn when handling the well materials.

5.2 MONITORING WELL DESIGN AND COMPLETION

Procedures for installing three types of monitoring wells are presented in this section: water table wells in unconsolidated materials; water table wells in bedrock; and, deep bedrock wells below the water table. Installation of water table wells in unconsolidated material and bedrock is discussed in Section 5.2.2. Monitoring well installation in deeper bedrock borings is described in Section 5.2.3.

5.2.1 General Well Installation Procedures

Monitoring wells will be constructed in open boreholes or through the hollow stem augers or surface casing, depending on the stability of the borehole and materials encountered during drilling (ASTM 1996, EPA 1990).

For boreholes that may need to be backfilled to a certain depth before well installation, clean sand with a 3-foot bentonite seal will be added to fill the borehole to the desired depth for well installation. Wax coated pellets may be used if the saturated water column in the borehole is greater than 50 feet.

The annular space will be filled with a filter pack (adjacent to the well screen), a bentonite seal, and casing grout between the well string and the borehole wall. As the annular space is being

filled, the well string will be centered and suspended such that it does not rest on the bottom of the hole. At least two stainless steel centralizers will be used if the well is deeper than 50 feet—one at the bottom of the well screen and one at the top of the well screen. For deep bedrock wells, additional centralizers will be attached to the riser casing at 100 foot intervals and one near the top of the well string.

The field geologist will calculate and record the volume of the filter pack, bentonite seal, and grout required to fill the annular space based on the borehole size and casing size. The volume is calculated by subtracting the volume of the casing (based on the outer diameter) from the volume of the borehole using the equation:

$$V=\pi(r_b^2-r_c^2)h$$

where:

V =volume (in feet^3)

r_b = radius of borehole (in feet)

r_c = radius of casing (in feet)

h = height (in feet) between the top and bottom of the material (filter pack, bentonite, or grout).

$\pi = p^1$ (3.14)

Measurements made during filling of the annular space will be performed to the nearest 0.1 foot below ground surface (bgs) and will consist of the following:

- Total depth of borehole at the completion of drilling
- Total depth of the open borehole before the start of well construction
- Lengths of the end cap, screen sections, riser blank sections, and stickup of well above ground surface
- The depth to the top of the filter pack, top of the bentonite seal, and the top of each grout lift.

Following well completion, the horizontal location of the monitoring well will be surveyed in accordance with SOP No. 20.0 Surveying. The elevation of the ground surface and top of the PVC casing (i.e., water level measuring point) will also be determined. A notch will be cut on the north side of the PVC casing that will be used as a measuring point for water levels.

5.2.1.1 Casing and Screen Requirements

The casing requirements will be as follows (EPA 1990):

- All casing will be new, unused, and decontaminated according to the specifications of Section 5.1.
- All PVC will conform to the ASTM Standard F-480-88A or the National Sanitation Foundation Standard 14 (Plastic Pipe System).
- The casing will be straight and plumb.

Well screen requirements include:

- All requirements for casing, except for strength requirements, apply to well screens.
- Well screens will be 15 feet to 20 feet in length.
- Screens shall be machine-slotted.
- Screen slot openings shall be 0.010 inches or 0.040 inches depending on subsurface material sizes and groundwater flow rates.
- The bottom of the screen will be capped with a threaded cap.
- The top of the well screen will be placed above the static water level, if possible (except for the deep bedrock wells).

5.2.1.2 Well Filter Pack

The purpose of the well filter pack is to provide lateral support for the well screen, increase yield by improving the hydraulic conductivity in the immediate vicinity of the well, and retain the formation to prevent natural materials from entering the well. The filter pack material will be clean, inert, and well rounded, and will contain less than 2 percent flat particles. The filter pack material will be certified free of contaminants by the vendor or contractor. The filter pack will consist of 10/20 or 20/40 mix or equivalent of clean silica sand and will be placed from the bottom of the hole to at least 2 feet, but not more than 4 feet, above the top of the well screen (5 to 7 feet in the bedrock water table wells). The size of the filter pack material used will be selected as appropriate for the well screen slot size installed so that no more than 10% of the filter pack material is smaller than the slot size (ASTM 1996, EPA 1990). For auger boreholes, the filter pack will be placed in the hole by pouring the sand through the augers and slowly raising the augers out of the hole. For bedrock monitoring wells installed in open boreholes (by air rotary drilling), the screen and riser casing will be suspended at least one foot above the bottom of the borehole as the filter pack is poured directly into the borehole. The volume of the filter pack placed in the well will be recorded.

After the filter pack is placed, the well will be surged with a surge block or bailer for 10 minutes to ensure that the filter pack is settled so that the grout in the annular seal does not come into contact with the well screen. The top of the sand pack will be sounded using a weighted tape to verify its depth during placement. Additional filter pack material will be placed as required to return the level of the pack to at least 2 feet above the screen and the well will be surged for an additional 5 minutes. Again, additional filter pack material will be placed, as required, to bring the level to at least 2 feet above the screen.

5.2.1.3 Well Seal

The materials used to seal the annulus between the borehole wall and casing must prevent potential contaminant migration from ground surface or intermediate zones, isolate a discrete monitoring zone, preserve confining conditions, prevent intrusion of the overlying grout into the filter pack, and prevent cross-contamination between strata. The bentonite seal will consist of at least 3 feet, but not more than 5 feet, of bentonite pellets between the filter pack and the casing grout. A minimum of 20 feet of bentonite seal will be used in the deep bedrock wells. Wax-

coated sodium bentonite pellets (delayed hydration) may be used to allow the bentonite to fall through the water column and prevent bridging if the saturated water column is greater than 50 feet. If the bentonite seal is placed above the water table, then the bentonite will be hydrated using deionized or distilled water.

5.2.1.4 Annulus Backfill/Grout

The annular space above the filter pack and seal will be grouted with a bentonite/cement mixture. Grouting is used to minimize the vertical migration of water to the screened interval and to increase the stability and integrity of the well casing.

The cement/bentonite grout mixture shall consist of 95 to 97 percent Type V or Type II-V Portland Cement and 3 to 5 percent bentonite powder by weight (equivalent to one 94-pound bag of cement and between 2.8 and 4.7 pounds of bentonite). Approximately 8.5 gallons of water shall be used for each cement/bentonite batch. The grout mixture shall be prepared by thoroughly mixing the bentonite powder with water first and then mixing in the cement (USEPA 1990).

The casing grout requirements are as follows:

- The bentonite seal will be allowed to hydrate for a minimum of 1/2 hour before the grout is placed.
- The annular grout will extend from the top of the bentonite seal to approximately 3 feet below ground surface (bgs).
- Grout shall be placed in the well annulus using a side-discharge tremie pipe located within approximately 10 feet of the top of the bentonite seal and the tremie pipe will be pulled up as the annular space is filled. The tremie pipe will have a minimum inner diameter of 1.25 inches and be composed of steel or PVC.
- No single lift of grout will exceed 100 feet and each lift will be allowed to set before the next lift is placed.
- Pumping will continue until undiluted grout has been returned to the surface.
- After grouting, the well shall not be disturbed or be developed for a minimum of 24 hours. Additional grout will be added if settling occurs.

Alternatively, the annular space can be backfilled with a bentonite slurry if the potential exists for cross-contamination of adjacent wells. This may occur when wells are installed in pairs, and the grouted interval in a deep well coincides with the water bearing zone to be screened in a shallow well.

5.2.1.5 Surface Seal Installation

Groundwater monitoring wells will be constructed with above-ground completions. A concrete surface seal will be placed around the annulus of the well to a minimum depth of one foot or to the top of the bentonite/cement grout, whichever is deeper. Twenty-four hours should elapse between grout emplacement and installation of the surface seal to allow the grout to cure and shrink and prevent a cavity from forming between the two seals. The well casing will be extended 2 to 3 feet above land surface, and a reference point will be marked for future water

level measurements on the north side of the casing using a decontaminated metal file. A casing cap for each well will be provided, and the extended casing will be shielded with a protective steel casing that has a locking cap placed over the PVC well casing. The steel casings will be cemented in place and will extend a minimum of 3 feet below ground surface and 3 feet above ground surface. Center the protective steel casing around the monitoring well casing and insert the steel casing approximately 3 feet into the cemented annulus. The protective casings will be a minimum of 6 inches larger in diameter than the PVC monitoring wells. The protective steel casing will be seated in a 4-foot by 4-foot by 6-inch concrete surface pad. The pad will be sloped away from the protective casing. The concrete pad surface will extend approximately 1 inch above ground surface with about 5 inches below grade. At least one small hole will be drilled at the base of the protective casing to allow water to drain from the casing. The well number or identification code will be indelibly marked on the protective casing and on the well cap. A lockable cap or lid will be installed on the protective casing. In high traffic areas near roads or parking areas, the steel protective casing will be protected by four, 4-inch-diameter, Schedule 40, steel guard posts. The guard posts will be 6 feet in total length, with 3 feet bgs and 3 feet above ground surface. The guard posts will be set in concrete, but will not be installed in the concrete pad placed at the well base (ASTM 1996, EPA 1990).

All wells will be secured as soon as possible after drilling. Corrosion-resistant locks will be provided for the steel protective casing. The locks must either have identical keys or be keyed for opening with one master key.

5.2.2 Water Table Monitoring Wells

Water table wells will be installed in both unconsolidated materials and bedrock (consolidated) material. These two types of monitoring wells may require slightly different installations as discussed in the following subsections.

5.2.2.1 Unconsolidated Water Table Monitoring Well Materials

These monitoring wells will be installed in boreholes created by hollow-stem auger (HSA) or air rotary/casing advance drilling (SOP No. 16.0 Drilling and Sampling of Subsurface Materials). The well installation will be accomplished by placing the screen and riser pipe through the inside of the augers or casing. The filter pack will be added and the augers will be sequentially removed from the borehole, while carefully sounding the top of the filter pack to maintain the proper thickness of sand and to ensure that the filter sand does not bridge.

These shallow wells will be constructed of 4-inch diameter, Schedule 40 PVC. Well casing and screen will be flush threaded and the screen interval will be 15 feet in length. As discussed in Section 5.2.1.1, well screens will straddle the water table to allow for seasonal fluctuations (i.e., approximately 5 feet of the screen will be above the water table and 10 feet will be below the water table).

5.2.2.2 Bedrock Water Table Monitoring Well Materials

These monitoring wells will be installed in boreholes created by an air rotary/casing advance system (SOP No. 16.0 Drilling and Sampling of Subsurface Materials). The well installation is accomplished by placing the screen and riser pipe into the open borehole after the drilling equipment has been removed.

If the borehole/monitoring well will be located in a significant thickness of alluvial material, mining spoils, or weathered bedrock, a surface casing will be installed to the depth of competent bedrock.

All screen and casing requirements described for unconsolidated water table monitoring wells apply for bedrock water table wells, except that Schedule 80 PVC casing and screen will be installed. The screens will straddle the water table as previously discussed.

5.2.3 Deep Bedrock Monitoring Wells

Deep bedrock monitoring wells will be installed in consolidated bedrock material 100 to 200 feet below the water table.

5.2.3.1 Deep Bedrock Monitoring Well Materials

Deep bedrock monitoring wells will be installed in boreholes created by air rotary/casing advance technology. The screen and well casing will be suspended off the bottom of the borehole in order to protect the screen. Materials used for these deep wells will be the same specifications as described above with the exception of the use of Schedule 80 PVC. Screens will be 20 feet in length.

The filter pack will meet the same specifications as described in Section 5.2.1.2. The filter pack will be installed to a minimum of 7 feet above the top of the screen in order to protect the well screen.

Bentonite seal specifications are as described in Section 5.2.1.3. The seal in the deep wells will be a minimum of 20 feet thick to protect the well screen from grout infiltration.

6.0 DOCUMENTATION

Documentation of observations and data acquired in the field will provide information on the activities concluded and also provide a permanent record of field activities. The observations and data will be recorded with waterproof ink in a permanently bound weatherproof field logbook with consecutively numbered pages, and on field data sheets.

6.1 BORING LOG

A field geologist experienced in borehole drilling will be present at each operating drill rig. This geologist will be responsible for logging samples, monitoring drilling operations, recording water losses or gains and groundwater data, and preparing field boring logs. The procedures for lithologic logging of boreholes is contained in SOP No. 17.0, Borehole Logging. Boring log information will also be recorded in field logbooks.

6.2 MONITORING WELL COMPLETION DIAGRAMS

A completion diagram will be prepared for each groundwater monitoring well when installed (Figure 1). It will include the following information:

- Well identification (identical to the borehole identification)
- Drilling method

- Installation date(s)
- Total boring depth and total well depth
- Lengths and descriptions of the screen and casing
- Depths and descriptions of the filter pack, bentonite seal and casing grout
- Elevation of water surface before and immediately after well installation
- Summary of the material penetrated by the boring

6.3 FIELD LOGBOOK

Observations and data acquired in the field during installation of monitoring wells will be recorded to provide a permanent record (EPA 1986). These observations will be recorded with waterproof black ink in a bound, weatherproof field logbook with consecutively numbered pages. Corrections will consist of line-out deletions that are initialed and dated. If, during cold weather, the ink pen fails, a pencil may be used to record observations. The information in the field logbook will include the following, as appropriate:

- Project name and number
- Names and titles of all field personnel
- Drilling company name and personnel
- Type of drill rig
- Date well installation started and finished
- Boring number
- Well installation observations
- Daily progress
- Problems encountered and resolution
- Decontamination observations
- Weather conditions
- Grout, sand, and bentonite volume calculations prior to well installation
- The volume and composition of the grout, seals, and filter pack actually used during construction
- All measurements made to top of filter pack, seal, grout batches, screened interval, and other depths
- Screen slot size (in inches), slot configuration, nominal casing size, schedule, composition, and manufacturer
- Centralizer composition and locations
- Protective casing composition and nominal ID

- Surface completion information and date
- General groundwater observations
- Overnight water levels (before installation begins)
- Protective casing and surface completion details
- Other pertinent information

The field logbooks will be used daily by the field personnel and will be kept in the possession of field personnel or in a secure location during the project. All documentation regarding monitoring well installation will constitute a portion of the permanent project record.

7.0 REFERENCES

U.S. EPA. 1986. "RCRA Groundwater Monitoring Technical Enforcement Guidance Document (T.E.G.D.)." U.S. Environmental Protection Agency, Washington D.C., Document No. OSWER-9950.1

U.S. EPA. 1990. "Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells". U.S. Environmental Protection Agency, Washington D.C., Document No. EPA/600/4-89/034.

American Society for Testing and Materials (ASTM). 1996. "ASTM Standards on Groundwater and Vadose Zone Investigations: Drilling, Sampling, Well Installation and Abandonment Procedures."

Figure 1

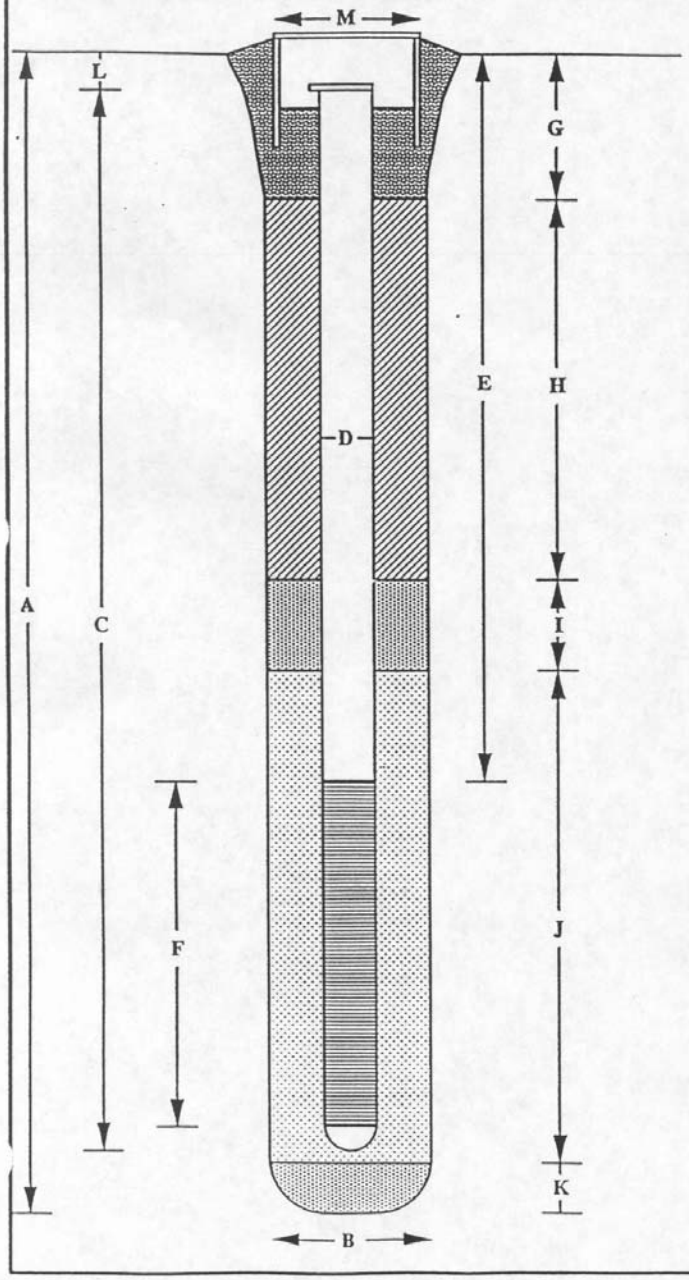
Monitoring Well Completion Diagram

WELL CONSTRUCTION RECORD

WELL NUMBER:_____ DATE INSTALLED:_____

DRILLING CONTRACTOR:_____ SUPERVISING GEOLOGIST:_____

PROJECT NUMBER:_____ LOCATION/SITE:_____



BORING

A. Total Depth (ft) _____

B. Boring Diameter (in.) _____

Drilling Method _____

WELL CONSTRUCTION

C. Casing Length (ft) _____

Type _____

D. Casing Diameter (ft) _____

E. Depth to Top of Slotted Interval (ft)_____

F. Perforated Casing Length (ft) _____

Perforated Interval From_____ to_____ ft

Perforation Type_____

Perforation Size _____

G. Surface Grout Interval (ft) _____

Grout Material _____

H. Backfilled Interval (ft) _____

Backfill Material_____

I. Sealed Interval (ft) _____

Seal Material_____

J. Filter Pack Interval (ft) _____

Pack Material _____

K. Bottom Seal Interval (ft) _____

Seal Material_____

L. Depth to Top of Casing (in) _____

M. Protective Casing Diameter (in) _____

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VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 15.0

WELL DEVELOPMENT

1.0 PURPOSE AND SCOPE 15-1

2.0 RESPONSIBILITIES AND QUALIFICATIONS 15-1

3.0 RELATED STANDARD OPERATING PROCEDURES 15-1

4.0 EQUIPMENT LIST 15-1

5.0 MONITORING WELL DEVELOPMENT PROCEDURES 15-2

6.0 DOCUMENTATION 15-3

6.1 Well Development Form 15-3
6.2 Field Notes 15-4

Attachment A Well Development Record

1.0 PURPOSE AND SCOPE

This Standard Operating Procedure (SOP) provides technical guidance and methods that will be used and procedures to be followed for developing groundwater monitoring wells. This SOP gives descriptions of equipment, field development procedures, field data collection, and personnel responsibilities.

The purpose of well development is to restore the hydraulic conductivity of the aquifer material surrounding the well to near pre-well installation conditions. This is accomplished by removing well drilling fluids, solids, or other particulates that may have been introduced or deposited on the borehole wall during drilling and well construction activities. Properly developed monitoring wells allow for the collection of representative groundwater samples.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The RI Project Manager or Field Manager have the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate environmental staff to implement this SOP and for ensuring that the procedures are followed.

All personnel performing these procedures are required to have the appropriate health and safety training. In addition, all personnel are required to have a complete understanding of the procedures described within this SOP, and receive specific training regarding these procedures, if necessary.

All environmental staff and assay laboratory staff are responsible for reporting deviations from this SOP to the RI Project Manager or Field Manager.

3.0 RELATED STANDARD OPERATING PROCEDURES

The procedures set forth in this SOP are intended for use with the following SOPs:

SOP No. 2.0	Groundwater Sampling
SOP No. 2.1	Monitoring Well Water-Level Measurement
SOP No. 6.0	Decontamination of Sampling Equipment
SOP No. 8.0	Field Parameter Measurements (including Instrument Calibration)
SOP No. 14.0	Monitoring Well Installation
SOP No. 23.0	Investigation Derived Waste Management

4.0 EQUIPMENT LIST

The following items will be required to develop groundwater monitoring wells:

- Well completion logs
- Well development records (see Attachment A)
- Well keys
- Stainless steel, adjustable rate, submersible pump, controller, and power source (generator or battery)

- Surge block
- Teflon® or Teflon-lined polyethylene tubing
- Stainless steel or Teflon® bailer
- Mechanical reel or truck-mounted wireline rig (for deep wells)
- Water quality meters for temperature, conductivity, pH and turbidity
- Plastic sheeting
- Decontamination equipment and supplies (see SOP No. 10 Decontamination)
- Personal protective equipment (PPE) as outlined in the Health and Safety Plan (HSP)
- Organic vapor detector (on wells scheduled for volatile organics analysis)
- Graduated 5-gallon bucket
- Drums or other large container for storing development water
- Water-level probe
- Weighted tape measure
- Calculator

5.0 MONITORING WELL DEVELOPMENT PROCEDURES

Before developing any well where samples will be collected for volatile organic compound (VOC) analysis, the head space in the well must be measured using an organic vapor detector as described in the Health and Safety Plan (HSP). The initial static water level will also be measured before development begins and well purge volume requirements will be calculated.

Monitoring well development will be accomplished using a surge block and/or a bailer and a submersible pump to flush the screen, sand pack material, and borehole wall of drilling fluids and fine sediment resulting from well drilling and installation activities. This procedure also allows for the removal of fine sediment, which may have accumulated within the inner well casing.

The surge block will initially be operated with short, gentle strokes above the well screen intake. Development will begin at the static water level and move progressively downward to prevent the surge block from becoming sand locked. The surge energy shall be gradually increased at each depth. Surging shall be alternated with removal of the fines with a pump or bailer. Note that surging of low-permeability formations can result in a collapsed well screen. Development of fine-grained materials will be accomplished by a gentle action to avoid reducing the natural hydraulic conductivity.

Well development will begin no sooner than 24 hours after the well as been grouted and will consist of removing approximately 3 to 10 well casing volumes from the well, plus a volume of water equal to any additional potable water added to the borehole during drilling or well installation. A well casing volume is determined by the following formula for 4-inch diameter wells:

(1) Well casing volume (gal) = Depth to bottom of well (ft) – Depth to water level (ft) x 0.65 (gal/ft)

(For a 2-inch diameter well, replace 0.65 with 0.16; and for a 6-inch diameter well, replace 0.65 with 1.5)

All depth measurements are taken from the top of the inner well casing at the designated measuring point. A weighted tape measure and electronic water-level indicator will be used to determine the depth to bottom of the well and depth to water level. These procedures are discussed in SOP No. 2.1 Water-Level Measurements.

Field parameters including pH, temperature, conductivity, and turbidity will be measured after each well casing volume has been evacuated. The calibration and operation of pH, conductivity and turbidity meters is discussed in SOP No. 8.0 Calibration of Field Instruments. The well will be developed until these field parameters have stabilized. Stabilized field parameters are defined as three consecutive readings where temperatures are within 1°C, pH readings are within 0.2 units, and conductivity and turbidity values are within 10%. If for any reason this cannot be accomplished, the well will be considered developed after being purged of 10 well casing volumes.

For slow producing wells (wells that do not fully recover within 8 hours), the wells shall be purged dry a minimum of three times. All purge water from the wells will be placed into an appropriate container and handled as IDW as discussed in the SAP.

All development equipment coming in contact with well water will be decontaminated in accordance with SOP No. 6.0 Decontamination, before each well is developed. Development equipment will be protected from the ground surface with clear plastic sheeting.

6.0 DOCUMENTATION

Documentation of observations and data acquired in the field will provide information on the activities concluded and also provide a permanent record of field activities. The observations and data will be recorded with waterproof ink in a permanently bound weatherproof field logbook with consecutively numbered pages, and on field data sheets.

6.1 WELL DEVELOPMENT RECORD

The following well development information will be recorded on the Well Development Form included as Attachment A.

- Well I.D. and location
- Date of well installation
- Date and time of well development
- Static water level from top of casing before and after development
- Total depth of well from top of casing
- Quantity of water used during drilling
- Volume of well casing volume
- Field measurements of pH, conductivity, turbidity, and temperature taken after each well casing volume has been evacuated
- Physical description of removed water throughout development
- Types of bailers/pumps etc. used to evacuate water

- Quantity of water removed and time of removal (incremental and total values)

6.2 FIELD NOTES

Field notes will also be kept during sampling activities. The following information at a minimum will be recorded in a bound field logbook using waterproof ink:

- Project name
- Names of personnel
- Weather conditions
- Well I.D. and location
- Date and times of well development

Attachment A

Well Development Record

URS CORPORATION
WELL DEVELOPMENT RECORD

SHEET _____ of _____

Project Name:_____ Project No.:_____

Well ID:_____ Date Installed:_____

Casing Diameter:_____

METHOD OF DEVELOPMENT

☐ Swabbing ☐ Bailing ☐ Pumping ☐ Describe_____

Equipment decontaminated prior to development ☐ Yes ☐ No

Describe

_____

_____

CASING VOLUME INFORMATION

Casing ID (inch)	1.0	1.5	2.0	2.2	3.0	4.0	4.3	5.0	6.0	7.0	8.0
Unit Casing Volume (A) (gal/ft)	0.04	0.09	0.16	0.2	0.37	0.65	0.75	1.0	1.5	2.0	2.6

PURGING INFORMATION

Measured Well Depth (B)_____ft.

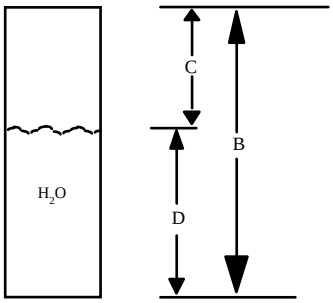
Measured Water Level Depth (C)_____ ft.

Length of Static Water Column (D)_____ - _____ = _____ft.
(B) (C)

Casing Water Volume _____ x _____ = _____gal
(A) (D)

Volume of Water Added to Well During Installation = _____gal

Total Purge Volume = _____ (gal)



Time	Pump Rate	Water Level Depth (ft)	Volume Removed (gal)	pH	Cond (mS/cm)	Temperature F or C	Turbidity (NTU)	Comments

Samplers Signature:_____ Date:_____

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VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 16.0

DRILLING AND SAMPLING OF SUBSURFACE MATERIALS

1.0 PURPOSE AND SCOPE 16-1

2.0 RESPONSIBILITIES AND QUALIFICATIONS 16-1

3.0 RELATED STANDARD OPERATING PROCEDURES 16-1

4.0 EQUIPMENT LIST 16-1

5.0 DRILLING PROCEDURES 16-2

- 5.1 Dual Wall Percussion Or Air-Rotary Drilling 16-2
- 5.2 Hollow-Stem Auger Drilling 16-3
- 5.3 Borehole Abandonment 16-4
- 5.4 Field Quality Assurance/Quality Control Procedures And Samples 16-4
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List of Figures

Figure 1 Soil Sample Field Data Sheet 16-8

1.0 PURPOSE AND SCOPE

The purpose of this document is to define the Standard Operating Procedure (SOP) for drilling of subsurface materials during the Sierrita Mine data gap assessment field program. This SOP will be used in conjunction with the other SOPs listed below, the Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP).

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The RI Project Manager or Field Manager have the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate environmental staff to implement this SOP and for ensuring that the procedures are followed.

All personnel performing these procedures are required to have the appropriate health and safety training. In addition, all personnel are required to have a complete understanding of the procedures described within this SOP, and receive specific training regarding these procedures, if necessary.

All environmental staff and assay laboratory staff are responsible for reporting deviations from this SOP to the RI Project Manager or Field Manager.

3.0 RELATED STANDARD OPERATING PROCEDURES

The procedures for drilling set forth in this SOP are intended for use with the following SOPs:

SOP No. 6.0	Decontamination of Sampling Equipment
SOP No. 9.0	Sample Management
SOP No. 14.0	Monitoring Well Installation
SOP No. 17.0	Borehole Logging
SOP No. 20.0	Surveying (Land and GPS)
SOP No. 22.0	Utility Clearance
SOP No. 23.0	Investigation Derived Waste Management

4.0 EQUIPMENT LIST

The following is a list of equipment that will be necessary to perform drilling and sampling of subsurface materials:

- Monitoring equipment and personal protective equipment (PPE) as outlined in the site-specific HSP
- Dual wall percussion or air rotary drill rig with appropriate sized drill rods and downhole bits/casing systems for drilling in bedrock and unconsolidated materials. Hollow-stem auger (HSA) drill rig with appropriately sized augers and drill rods for drilling in unconsolidated materials (optional)

- High pressure, hot water washer for decontamination
- Decontamination equipment and supplies (e.g., wash/rinse tubs, brushes, alconox, plastic sheeting, paper towels, sponges, baby wipes, garden-type sprayers, large plastic bags, potable water, distilled water and/or deionized water)
- Sampling equipment for HSA rig (e.g., stainless steel 2-inch outer diameter split spoon sampler)
- Reclosable plastic bags for archiving samples
- 55-gallon drums or other approved containers for containing soil cuttings

Other materials and equipment may be needed based on field conditions.

5.0 DRILLING PROCEDURES

Prior to drilling, borings will be numbered and the site cleared for utilities. Boring locations may be adjusted in the field due to the presence of underground utilities, overhead power lines, or other structures, or if access problems are encountered. Drilling locations will be approved by the Site Manager prior to initiating drilling activities.

Health and safety equipment specified in the site-specific HSP will be donned before proceeding with subsurface drilling activities. The HSP will specify action levels for various contaminants and the field monitoring required to measure ambient conditions.

All drill cuttings will be placed in labeled drums and moved to a central secured location for storage. Any water generated during drilling will be contained in labeled drums or tanks. Handling of investigation derived wastes (IDW) will be as specified in SOP 23.0 IDW Management.

Downhole equipment will be steam-cleaned prior to proceeding to the drill site and between subsequent boreholes using the procedures presented in SOP No. 6.0 Decontamination of Sampling Equipment. Split-spoon samplers will be decontaminated at the drill site between each sample interval.

All work areas around borings will be restored to a physical condition equivalent to that of pre-drilling, as near as practical. This will include drill cuttings removal and rut repair.

At the direction of the field geologist, only potable water may be introduced into boreholes. No bentonite, barite, polymers, or other additives or viscosifying agents will be introduced into the borehole or used during drilling. It is expected that it will not be necessary to introduce foaming agents into boreholes to lift cuttings during bedrock drilling. However, if the drilling subcontractor suggests that foaming agents are needed, the subcontractor must provide Material Safety Data Sheets (MSDS) for any product that they suggest. The MSDS will then be reviewed by URSGWC to determine if any unacceptable substances are present in the foaming agent before approving its use.

The rig shall be free of leaks that could contaminate the boreholes (i.e., hydraulic fluid, oil, fuel, etc.). Pipe lubricants that are used should not introduce contaminants into the borehole. Lubricants that are environmentally acceptable include Green Stuff®, King Stuff®, vegetable oil, Crisco™, and some Teflon™-based lubricants. Lubricants that are not acceptable include petroleum-based and most metal-based lubricants. The Site Manager will pre-approve lubricants that will be used.

5.1 DUAL WALL PERCUSSION OR AIR-ROTARY DRILLING

The procedures below address drilling of boreholes using a dual wall percussion or air-rotary drill rig. Dual wall percussion or air rotary drilling may be conducted to install alluvial/colluvial and bedrock monitoring wells. Samples of drill cuttings will be collected for visual logging purposes at five-foot intervals. At locations specified in the SAP, samples will also be collected and archived for possible future testing. Drilling and sampling procedures using a dual wall percussion or air-rotary drill rig are as follows:

- Remove stones, vegetation, etc., from the sampling location surface.
- Install 10-inch steel surface casing to an appropriate depth to stabilize the borehole.
- Convert to down-hole hammer or tricone bit and continue drilling through the surface casing to the desired depth. Use an appropriate drill bit to provide for a minimum 4-inch annulus around the groundwater monitoring well casing.
- Sampling of drill cuttings will be performed at five-foot intervals to the total depth of the borehole. Samples will be collected directly from the cyclone and placed in quart-sized baggies and labeled with the boring number and depth.
- Screen the sampled material using the instruments specified in the HSP.
- Log the sample in accordance with SOP No. 17.0 Borehole Logging.
- Follow sample handling procedures for collecting samples as described in SOP No. 9.0 Sample Management.
- Discard the unused samples and handle the waste as described in SOP 23.0 IDW Management.

5.2 HOLLOW-STEM AUGER DRILLING

The procedures below address drilling of boreholes and collection of subsurface soil samples using a HSA rig. HSA drilling may be conducted to install shallow monitoring wells in unconsolidated materials. Subsurface soil samples may be collected in some boreholes for laboratory chemical analysis at specific intervals as outlined in the project Work Plans. For boreholes where samples are not collected for chemical analysis, samples will be collected at five-foot intervals during drilling and placed in plastic bags. HAS drilling and samples procedures are as follows:

- Remove stones, vegetation, etc., from the sampling location surface.
- Use the appropriate sized augers to provide for a minimum 4-inch annulus around the groundwater monitoring well casing.
- Split-spoon sampling will be performed at five-foot intervals to the total depth of the borehole. The first sample interval will be from 0-2 feet, then 5-7 feet, and so on. The split-spoon sampler will always be advanced ahead of the lead auger to minimize potential cross-contamination.
- Collect a sample by driving the spilt-spoon sampler using a 140-pound hammer with a 30-inch drop. Record Standard Penetration Test blow counts for each 6-inch interval driven (for the first 18 inches) according to ASTM Method D 1586.

- Bring the sampler to the surface and open the split-spoon sampler.
- Screen the sampled material using the instruments specified in the HSP.
- Log the sample in accordance with SOP No. 17.0 Borehole Logging.
- If samples are collected, label and handle the sample containers in accordance with SOP No. 9 Sample Management. Place the sample container in a recloseable plastic bag and seal the bag and place the sample in a cooler with ice for shipment.
- Repeat the process until the total depth of the borehole is reached.

5.3 BOREHOLE ABANDONMENT

Borehole abandonment may be necessary in some cases. The following procedures will be used to abandon boreholes:

- All downhole equipment will be removed from the borehole. Cuttings scraped from the drill rods and bits will be drummed in accordance with the procedures for IDW management in SOP 23.0 IDW Management. Equipment will be decontaminated in accordance with SOP No. 6.0 Decontamination of Sampling Equipment.
- Boreholes will be grouted using cement-bentonite grout. The grout mix will be in the proportions of one sack of Portland cement (94 pounds), 2 to 5 pounds of powdered bentonite, and approximately 7 to 9 gallons of water. The bentonite will be well mixed with the water prior to adding the cement.
- Grouting will be performed by placing a tremie pipe to the bottom of the borehole and pumping grout through the tremie pipe until undiluted grout flows from the ground surface.
- Twenty-four hours after grouting, the borehole will be checked for settlement and topped off to the ground surface with grout.
- Details concerning the abandonment process will be recorded on the boring log and in the field logbook.

5.4 FIELD QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES AND SAMPLES

QA/QC samples are designed to help identify potential sources of sample contamination to evaluate potential error introduced by sample collection and handling. All QA/QC samples are labeled and sent to the laboratory with other samples for analysis. The type and number of QA/QC samples are defined in SOP No. 9.0 Sample Management.

5.5 SAMPLE HANDLING

Samples containers, preservatives, and analyses are specified in SOP No. 9.0, Sample Management. Samples will also be labeled and handled as described in SOP No. 9.0.

6.0 DOCUMENTATION

Documentation of observations and data acquired in the field will provide information on the activities concluded and also provide a permanent record of field activities. The observations and data will be recorded with waterproof ink in a permanently bound weatherproof field logbook with consecutively numbered pages, and on field data sheets.

Project staff are responsible for documenting drilling activities. Information will include borehole location, total depth of borehole, descriptions of drilling equipment used, and other applicable information.

6.1 BORING LOG

A field geologist experienced in borehole drilling will be present at each operating drill rig. This geologist will be responsible for logging samples, monitoring drilling operations, recording water losses or gains and groundwater data, and preparing field boring logs. The procedures for lithologic logging of boreholes is contained in SOP No. 17.0 Borehole Logging. Boring log information will also be recorded in field logbooks.

6.2 SOIL SAMPLE FIELD DATA SHEET

If samples are collected for chemical analysis, sampling activities and observations will be documented on a Soil Sample Field Data Sheet (Figure 1). The soil sample field sampling data sheet will be completed at each sample location. Information on the data sheet will include the following:

- Project name and number
- Field personnel
- Sample number, location, and type
- Sample collection date and time
- Sample depth interval
- Sample color, staining, or odor (describe)
- Monitoring equipment readings (screening and headspace)
- Type of sample containers, sample preservation
- Record of any QA/QC samples collected
- Any irregularities or other problems that may have an impact on sample quality
- Other applicable information

6.3 FIELD NOTES

Field notes will be kept during drilling and sampling activities. The following information will be recorded in a bound field log book using waterproof ink:

- Names of personnel at the drill site
- Weather conditions

- Drilling procedures
- Dates and times of drilling and sampling
- Location and borehole identification
- Times that procedures and measurements are completed
- Decontamination times and procedures
- Field instrument calibration information
- Records of visitors to the drill site
- Other applicable information

FIGURE 1
Soil Sample Field Data Sheet

Soil Sample Field Data Sheet

Sample Identification No. _____

Project Information

Project Name: _____

Contractor: _____ **Geologist/Sample Tech.:** _____

Subcontractor and Personnel: _____

Sample Location Information

Sample Location No. _____ Sampling Equip. _____

Sample Information

Date and Time of Sample Collection: _____

Sample Condition (circle): Saturated Unsaturated

Sample Type (circle): Discrete Vertical composite

Discrete: Sample Depth Interval _____

Vert. Comp.: VOC/SVOC Sample Depth _____ Non-VOC/SVOC Composite Interval _____

Total Volume of Non-VOC/SVOC Sample Required _____ No. of Increments _____

Required Volume of Each Increment _____

Volume Collected at Each Increment _____

Sample Collection Method _____

Sample Lithologic Description (from Sample Location Log):

_____

_____

PID/FID Measurements (record reading and depth interval) _____

_____

Sample Containers	Number	Preservatives	Analyses

Associated QA/QC Sample Nos.: _____

_____

Comments/Observations

_____

_____

Sampler's Name and Signature: _____

Freeport-McMoRan Sierrita Inc.

VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 17.0

LOGGING

1.0 PURPOSE AND SCOPE 17-1

2.0 RESPONSIBILITIES AND QUALIFICATIONS 17-1

3.0 RELATED STANDARD OPERATING PROCEDURES 17-1

4.0 EQUIPMENT LIST 17-1

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1.0 PURPOSE AND SCOPE

This Standard Operating Procedure (SOP) provides technical guidance and methods that will be used to describe subsurface soil and rock samples during data gap assessment action activities performed at the Freeport-McMoRan Sierrita Inc. (Sierrita) Mine Site.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Design Contractor has the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate environmental staff to implement this SOP and for ensuring that the procedures are followed by all personnel.

All personnel performing these procedures are required to have the appropriate health and safety training. In addition, all personnel are required to have a complete understanding of the procedures described within this SOP and receive specific training regarding these procedures, if necessary.

All project staff are responsible for reporting deviations from this SOP to the Design Contractor.

3.0 RELATED STANDARD OPERATING PROCEDURES

The procedure for logging set forth in this SOP is intended for use with the following SOPs:

SOP No. 6.0	Decontamination of Equipment
SOP No. 9.0	Sample Management
SOP No. 18.0	Subsurface Soil Sampling with a Hand Auger
SOP No. 23.0	Investigation Derived Waste Management

4.0 EQUIPMENT LIST

The following materials and equipment listed will be needed for logging:

- Log forms (Figure 1)
- Waterproof pens
- Hand lens (10X magnification or stronger)
- Metal or wooden tape measure
- Stainless steel knife, screwdriver, rock hammer
- Decontamination equipment and supplies (see SOP No. 6.0, Decontamination of Equipment)
- Reference tables listing ASTM and/or Unified Soil Classification System (USCS) codes and descriptions

Other materials and equipment may be needed based on field conditions.

5.0 PROCEDURES

This Design Contractor will be responsible for logging samples, recording water losses or gains, and preparing field logs. Procedures for completing logs are described below:

- Log information will be recorded on the log form.
- Logs will be prepared in the field by the Design Contractor as material is removed. The preparer will sign each log.
- All log entries will be legibly printed such that photo reproductions will be clear and legible.
- All relevant information in the log heading and log body will be completed. If surveyed horizontal control is not available, location sketches referenced by measuring distances or prominent surface features shall be shown on, or attached to, the log.
- An appropriate scale will be used on the log form (e.g., a scale of 1 inch on the log form equaling 1 foot of boring).
- Each and every material type encountered will be described on the log form. Material types will be logged directly from samples and indirectly interpolated using professional judgment between sampling intervals.
- Descriptions of intact unconsolidated soil samples will include parameters listed in Table 1. Material will be described in the following order:
    1. Material type (i.e., sand [sandstone], silt [siltstone], clay [claystone], etc.)
    2. Color
    3. Grain size, sorting, rounding, and make-up of the material (for sand or gravel)
    4. Types and amounts of secondary constituents
    5. Other pertinent characteristics (plasticity, hardness, bedding, etc.)
    6. Moisture content
    7. USCS code (for unconsolidated material)
- Unconsolidated materials will be classified in accordance with the USCS (equivalent to ASTM D 2488-93, “Description and Identification of Soil [Visual Manual Procedure]”; Attachment I and USEPA Manual 625/12-91/002 “Description and Sampling of Contaminated Soils”). Soil classifications will be made in the field at the time of sampling by the Design Contractor and are subject to change based on laboratory tests and subsequent review.
- In the field, visual estimates of the volume of secondary soil constituents will be reported by such terms as "trace" (1-3 percent), "slightly" (3-10 percent), "some" (10-25 percent), and "very" (25-50 percent) or by an estimated percentage.
- Consolidated material (e.g., igneous and metamorphic rocks) will be described by parameters listed in Table 2 and described in Tennisen (1983), ASTM D5434-97, “Standard Guide for Field Logging of Subsurface Explorations of Soil and Rock”, and ASTM C294-86(1991), “Standard Descriptive Nomenclature for Constituents of Natural Mineral Aggregates”. Material will be logged using drill cuttings and/or rock core. Material will be described in the following order:

1. Rock Type
2. Color
3. Grain size and shape
4. Texture (stratification. foliation)
5. Mineral composition
6. Weathering and alteration
7. Strength
8. Other relevant notes

- All special problems encountered and their resolution will be recorded on the log.
- The dates for the start and completion will be recorded on the log. Changes in shift, day, and Design Contractor will also be noted at the depth they occur.
- Logs will show sample location and depths.
- Logs will show depth of sampling.
- Logs will include other information relevant to a particular investigation, but not limited to:
  - Odors
  - Field screening or test results (e.g., organic vapors and/or radiological)
  - Any observed evidence of contamination in samples, cuttings or drilling fluid
- Special abbreviations used on a log will be defined either in the log where used, or in a general legend.

6.0 DOCUMENTATION

Documentation of observations and data acquired in the field will provide information on the activities concluded and also provide a permanent record of field activities. The observations and data will be recorded with waterproof ink in a permanently bound weatherproof field logbook with consecutively numbered pages, and on field data sheets.

6.1 LOG FORM

A field log form (Figure 1) will be completed summarizing field activities. The information on the log includes the following:

- Sampling locations
- Dates and time of sampling
- Person(s) performing sampling
- Log information

6.2 FIELD NOTES

Field notes will also be kept during logging activities. The following information will be recorded in a bound field log book:

- Names of personnel
- Weather conditions
- Date and time of sampling
- Location and sample station number
- Times that procedures and measurements are completed
- Decontamination times
- Other applicable information

7.0 REFERENCES

ASTM D2488-93 Standard Practice for Description and Identification of Soils (Visual Manual Procedure)

ASTM D5434-97 Standard Guide for Field Logging of Subsurface Explorations of Soil and Rock

ASTM C294-86(1991) Standard Descriptive Nomenclature for Constituents of Natural Mineral Aggregates

USEPA Manual 625/12-91/002 Description and Sampling of Contaminated Soils,

Tennisen, A.C., 1983, Nature of Earth Materials, 2nd Edition, pp.204-348.

Table 1
DESCRIPTION OF UNCONSOLIDATED SOIL

Parameter	Example
Depositional Environment and Formation, (if named and if known)	Alluvium, Twin Cities Formation
Unified Soil Classification System	Sandy Clay
Secondary Components and Estimated Quantities either by percentages or by descriptive percentage ranges (Note: terms used to indicate ranges should be described on the log or in a general legend)	sand: fine, with trace of med.
Color	gray
Consistency (cohesive soil). Use relative term	very soft, soft, medium, stiff, very stiff, hard
Density (non-cohesive soil). Use relative term	loose, medium, dense, very dense
Moisture Content. (Use relative term. Do not express as a percentage unless a value has been measured)	dry, damp, moist, wet, saturated
Texture/Fabric/Bedding	no apparent bedding, numerous vertical iron-stained tight fractures
Grain Angularity	rounded sand grains
Sorting (sands)	poorly sorted
Structure	slickensides
Grain or fragment size	coarse
Note "Fill", "Top of Natural Ground", and "Top of Bedrock" where appropriate	

Table 2
DESCRIPTION OF CONSOLIDATED ROCK

Parameter	Example
Formation Name (if known)	Togo Formation of the Belt Supergroup
Rock Type	Quartz monzonite, granite
Modifier denoting variety	Shaley, calcareous, siliceous, argillaceous, sandy, micaceous
Grain Size	Very coarse-grained, coarse-grained, medium-grained, fine-grained, very fine-grained
Grain Shape	Angular, subangular, subrounded, rounded, well-rounded
Color	Medium brown
Stratification/Foliation	Parting band, thinly bedded, thickly bedded, very thickly bedded, laminated, (Note: provide thickness range of each in legend)
Texture	Crystalline, porphyritic, glassy, poorly cemented, well cemented
Weathering/Alteration	Residual soil, completely weathered/altered, highly weathered/altered, moderately weathered/altered, slightly weathered/altered, fresh
Rock Strength	Extremely weak, very weak, weak, medium strong, strong, very strong, extremely strong
Structure and Orientation	Horizontal bedding, dipping beds at 30°, highly fractured, open near vertical joints, healed 30 degree fractures, slickensides at 45 degree, fissile
Core loss interval and reason for loss if known or "Unaccountable"	50-51', noncemented sandstone likely

Figure 1
LOG FORM

Borehole ID: _____
Sheet _____ of ____

			Location	
Project Name	Project Number	Project Manager	Field Manager	Site ID
Company		Ground Elevation	Depth	
Removal / Method		Date/Time Started	Date/Time Total Depth Reached	
Type of Sampling Device		Water Level (bgs) First / Final		
Sample Hammer Type / Driving Wt. / Drop		Hydrogeologist	Checked by/Date	
Location Description (include sketch in field logbook)				

Depth	Interval	Recovery	Blow Counts	Description (Include lithology, grain size, sorting, angularity, Munsell color name & notation, mineralogy, bedding, plasticity, density, consistency, etc., as applicable)	USCS Symb.	Lithology	Water Cont.	Remarks (Include all sample types & depth, odor, organic vapor measurements, etc.)

Freeport-McMoRan Sierrita Inc.

VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 18.0

SUBSURFACE SOIL SAMPLING WITH A HAND AUGER

1.0 PURPOSE AND SCOPE 18-1

2.0 RESPONSIBILITIES AND QUALIFICATIONS 18-1

3.0 RELATED STANDARD OPERATING PROCEDURES 18-1

4.0 EQUIPMENT LIST 18-1

5.0 SAMPLING PROCEDURES 18-2

5.1 SAMPLE COLLECTION 18-2

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5.2 FIELD QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES AND SAMPLES 18-3

5.3 SAMPLE HANDLING 18-3

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1.0 PURPOSE AND SCOPE

The purpose of this document is to define the Standard Operating Procedures (SOP) for subsurface soil sampling with hand augers. This procedure provides the technical guidance and methods that will be used for subsurface soil sampling using hand augers during data gap assessment activities performed at the Freeport-McMoRan Sierrita Inc. (Sierrita) Mine Site.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Design Contractor has the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate environmental staff to implement this SOP and for ensuring that the procedures are followed.

All personnel performing these procedures are required to have the appropriate health and safety training. In addition, all personnel are required to have a complete understanding of the procedures described within this SOP, and receive specific training regarding these procedures, if necessary.

All environmental staff and assay laboratory staff are responsible for reporting deviations from this SOP to the Design Contractor.

3.0 RELATED STANDARD OPERATING PROCEDURES

The procedures for sampling with a hand auger set forth in this SOP are intended for use with the following SOPs:

SOP No. 6.0	Decontamination of Equipment
SOP No. 9.0	Sample Management
SOP No. 17.0	Logging
SOP No. 22.0	Utility Clearance
SOP No. 23.0	Investigation Derived Waste Management

4.0 EQUIPMENT LIST

The following is a list of equipment that will be necessary to perform subsurface soil sampling using a hand auger:

- Stainless steel hand auger with handle extensions
- Stainless steel bowls
- Stainless steel spoon, scraper, or other tools for use in extracting soil samples from the auger barrel
- Waste containers as listed in SOP No. 23.0, Investigation Derived Waste Management
- Health and Safety equipment as outlined in the Site Health and Safety Plan
- Sample containers
- Bound field logbook

- Sample field data sheets
- Decontamination equipment (SOP No. 6.0, Decontamination of Equipment)

5.0 SAMPLING PROCEDURES

Prior to sampling, hand auger borings will be numbered and the site cleared for utilities as specified in SOP No. 22.0, Utility Clearance. Boring locations may be adjusted in the field due to the presence of underground utilities or other structures, or if access problems are encountered. Hand auger locations will be approved by the Design Contractor prior to initiating sampling activities. Sampling procedures are as follows:

- Health and safety equipment specified in the site-specific HSP will be donned before proceeding with subsurface sampling activities. The HSP will specify action levels for various contaminants and the field monitoring required to measure ambient conditions.
- All hand auger cuttings will be placed in labeled drums and moved to a central secured location for storage. Any water generated during drilling will be contained in labeled drums or tanks. Handling of investigation derived wastes (IDW) will be as specified in SOP No. 23.0, Investigation Derived Waste Management.
- Hand augers will be cleaned prior to proceeding to the sampling site and between subsequent boreholes using the procedures presented in SOP No. 6, Decontamination of Equipment.

5.1 SAMPLE COLLECTION

Soil samples will be collected at the locations and depths specified in the work plan or field sampling plan (FSP). The following procedure will be used for collecting soil samples with the hand auger or other appropriate sampler.

5.1.1 Hand Augering Procedures

- Decontaminate the hand auger and associated sampler in accordance with SOP No. 6.0, Decontamination of Equipment.
- Clear the borehole location of surface debris (e.g., gravel, vegetation). If the area is paved, remove pavement at the auger hole by coring or other methods prior to augering.
- Attach the auger bit to the drill rod extension, and attach the T-handle to the drill rod.
- Begin augering, periodically removing and depositing accumulated soils onto a plastic sheet spread near the hole. This prevents accidental brushing of loose material back down the borehole when removing the auger, and avoids possible contamination of the surrounding area. Following completion of hand augering and sampling at a location, this material will be transferred to a drum or other container in accordance with SOP No. 23.0, Investigation Derived Waste Management.
- After reaching the desired depth, slowly and carefully remove the auger from the boring. Remove any soil by hand that falls back into the borehole as the auger is removed.
- Once all the required sample material is collected, thoroughly mix the sample material in the stainless steel bowl using a decontaminated stainless steel spoon. To homogenize, divide the

sample into four quarters and mix each quarter, then combine the four quarters and mix the entire sample. Place mixture into appropriate laboratory supplied sample containers.

- Label and handle the sample containers in accordance with SOP No. 9.0, Sample Management.
- If VOC samples are required to be collected from hand auger borings, efforts will be made to limit the handling and exposure time of the soils. Sample containers will be compacted during filling to the top, with no headspace.

5.2 FIELD QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES AND SAMPLES

QA/QC samples are designed to help identify potential sources of sample contamination to evaluate potential error introduced by sample collection and handling. All QA/QC samples are labeled and sent to the laboratory with other samples for analysis. The type and number of QA/QC samples are defined in SOP No. 9.0, Sample Management.

5.3 SAMPLE HANDLING

Samples containers, preservatives, and analyses are specified in SOP No. 9.0, Sample Management. Samples will also be labeled and handled as described in SOP No. 9.0.

6.0 DOCUMENTATION

Documentation of observations and data acquired in the field will provide information on the activities concluded and also provide a permanent record of field activities. The observations and data will be recorded with waterproof ink in a permanently bound weatherproof field logbook with consecutively numbered pages, and on field data sheets.

Project staff are responsible for documenting sampling activities. Information will include borehole location, total depth of borehole, descriptions of hand auger equipment used, and other applicable information.

6.1 LOG

A Design Contractor experienced person in hand augering will be present at each site. This person will be responsible for logging samples, performing auger operations, and preparing field boring logs. The procedures for lithologic logging is contained in SOP No. 17, Logging. Logging information will be recorded in field logbooks.

6.2 SOIL SAMPLE FIELD DATA SHEET

If samples are collected for chemical analysis, sampling activities and observations will be documented on a Soil Sample Field Data Sheet (Figure 1). The soil sample field sampling data sheet will be completed at each sample location. Information on the data sheet will include the following:

- Project name and number
- Field personnel

- Sample number, location, and type
- Sample collection date and time
- Sample depth interval
- Sample color, staining, or odor (describe)
- Monitoring equipment readings (screening and headspace)
- Type of sample containers, sample preservation
- Record of any QA/QC samples collected
- Any irregularities or other problems that may have an impact on sample quality
- Other applicable information

6.3 FIELD NOTES

Field notes will be kept during use of the auger and sampling activities. The following information will be recorded in a bound field log book using waterproof ink:

- Names of personnel at the drill site
- Weather conditions
- Hand auger procedures
- Dates and times of sampling
- Location and borehole identification
- Times that procedures and measurements are completed
- Decontamination times and procedures
- Field instrument calibration information
- Records of visitors to the drill site
- Other applicable information

FIGURE 1

SOIL SAMPLE FIELD DATA SHEET

Sample Identification:		Date:
Samplers' Signature:		Time:
Type of Sample:	Surface:	Subsurface:
	Composite:	Grab:
Sample Location Coordinates:		
Type of Surface Cover:		
Depth Interval:		
Weather Conditions:		
Sample Description:		
Field Soil Description		
USCS Abbreviation		
Color		
Staining		
Odor		
Moisture		

Containers	**Number**	**Preservatives**

QA/QC Samples Collected:
Comments:

Freeport-McMoRan Sierrita Inc.

VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 20.0

SURVEYING (CONVENTIONAL AND GPS)

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2.0 RESPONSIBILITIES AND QUALIFICATIONS 20-1

3.0 RELATED STANDARD OPERATING PROCEDURES 20-1

4.0 REQUIRED ACCURACY 20-1

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7.0 DOCUMENTATION 20-4

1.0 PURPOSE AND SCOPE

This Standard Operating Procedure (SOP) provides technical guidance and procedures that will be employed to conduct conventional and Global Positioning System (GPS) surveying. It addresses equipment, field sampling procedures, field data collection, and personnel responsibilities.

Conventional and GPS survey techniques will be used to survey: monitoring well locations and elevations; soil sampling locations; utility clearance (as applicable); and other surface and subsurface features.

The SOP is a general discussion of methods and surveying criteria. It is anticipated that the surveying will be performed by an experienced contractor that is knowledgeable of specific conventional and GPS surveying techniques. Contractors conducting this work will be Arizona licensed surveyors. It is anticipated that the surveying method selection will be based on conditions encountered in the field and accuracy requirements.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Design Contractor has the overall responsibility for implementing this SOP. All personnel engaged in surveying will be knowledgeable and experienced in the surveying methods and equipment used. Surveying will be performed and/or directly overseen by a surveyor who is licensed and registered in the State of Arizona. Final surveys will be signed and certified by a licensed surveyor. The Design Contractor will be responsible for assigning appropriate environmental staff to implement this SOP and for ensuring that the procedures are followed.

All personnel performing these procedures are required to have the appropriate health and safety training.

3.0 RELATED STANDARD OPERATING PROCEDURES

The procedures set forth in this SOP are intended for use with the following SOPs:

SOP No. 1.0	Surface Water Sampling
SOP No. 4.0	Near-Surface Soil Sampling
SOP No. 5.0	Sediment Sampling
SOP No. 18.0	Subsurface Soil Sampling with a Hand Auger
SOP No. 19.0	Test Pit Excavation and Sampling
SOP No. 22.0	Utility Clearance
SOP No. 38.0	Sediment Probing and Sampling Procedure

4.0 REQUIRED ACCURACY

At a minimum, surveyed location coordinates will be determined to an accuracy of ± 0.1 foot. At a minimum, surveyed elevations will be determined to an accuracy of ± 0.01 foot for

conventional surveying. Vertical elevation measured by GPS are suspect due to limited system accuracy. Accuracy will be assessed using the Federal Geographic Data Committee (FGDC) Geospatial Positioning Accuracy Standards. Environmental Protection Agency's (EPA's) Latitude/Longitude Standard (final May/June 2000) may be used to code accuracy for on-site point features.

5.0 CONVENTIONAL SURVEY

5.1 EQUIPMENT LIST

All materials and equipment necessary for conventional surveying will be provided by the land surveying contractor.

5.2 CONVENTIONAL SURVEYING PROCEDURES

This section specifies surveying performance requirements for conventional surveying techniques. The surveying methods will be specified by the land surveying contractor, in conjunction with Freeport-McMoRan Sierrita Inc. (Sierrita) and the Design Contractor, and based on project requirements.

5.2.1 Survey Points

Prior to surveying, all features and/or locations to be surveyed may be marked in the field with labeled stakes, survey flags, paint, or other marking devices. A meeting will be held prior to commencement of survey activities to discuss the surveying requirements and locations prior to initiating surveying. The following guidelines will be used when surveying:

- Abandoned boreholes will be surveyed at the center of the grout plug.
- Monitoring wells and piezometers will be surveyed at the following locations:
  - The center of the top of the protective casing (either above-ground monument or flush-mounted below ground vault)
  - The top of the polyvinyl chloride (PVC) well/piezometer casing with cap off (north edge unless otherwise specified or marked)
  - The ground surface immediately adjacent to the north side of the cement surface seal or cement pad (unless otherwise specified).
- Other surface features (e.g., surface sampling locations, geophysical and sampling grid points, surface water features, buildings or other man-made features) will be surveyed at the point marked.

5.2.2 Benchmarks and Coordinate Systems

Land surveying control will be established from known National Geodetic Survey (NGS) benchmarks, using Arizona State Plane, Central Zone. Horizontal datum will be North American Datum (NAD) 83, or subsequent adjustments (e.g., High Accuracy Reference Network or High Precision Geodetic Network). The vertical datum will be North American Vertical Datum (NAVD) of 1988.

6.0 GPS SURVEYING

6.1 EQUIPMENT LIST

The following survey equipment may be needed for conducting GPS surveying for this project:

- Dual-frequency real-time kinematic (RTK) GPS system (including GPS receiver, antenna, data logger)
- GPS base station or post-processing of data collected in the field

6.2 SURVEYING PROCEDURES

This section provides a general summary of GPS surveying procedures and specific procedures for surveying monitoring well and surface water/sediment sampling locations. However, these procedures should be supplemented by the specific survey instrument manufacturer's recommendations and generally accepted surveying practices.

- Land surveying control will be established from known National Geodetic Survey (NGS) benchmarks, using Arizona State Plane, Central Zone. Horizontal datum will be NAD83, or subsequent adjustments (e.g., High Accuracy Reference Network or High Precision Geodetic Network). The vertical datum will be NAVD of 1988. (The mine's existing control is on NGVD 29.)
- Surveying equipment will be field-verified each day before beginning surveying by establishing the coordinates of a known location (e.g., benchmark) using the GPS unit. The benchmark identification (or description) and measured coordinates will be recorded in the survey logbook.
- A base station will be established within an appropriate distance from the furthest survey point, as determined by the instrument manufacturer's specifications. Alternatively, the data will be post-processed by the surveyor. The base station may be used in connection with the field unit measurements to provide differential corrections to the field data.
- At each survey location, the location identifier and coordinates will be measured and stored in the data logger. As a backup, the same information will be recorded in the survey logbook.
- Data stored in the data logger will be downloaded at the end of each day of surveying and checked to determine if the data is reliable and to verify that coordinates have been collected for each survey location.
- Known benchmarks will be used to establish control points.
- If the coordinates at a survey location cannot be determined due to the presence of tree cover or other obstacles which prohibit adequate signal reception, coordinates will be obtained at a minimum of two alternate locations (offsets) close to the original survey location. The distance and bearing from each of the alternate locations to the original survey location will then be determined using a measuring tape and compass.

The following procedure will be followed specifically for surveying monitoring well locations and top of casing elevations:

- Enter the monitoring well identification in the GPS data logger and also in the survey logbook for backup purposes.
- Measure the location in state plane coordinates (northing and easting) and elevation of the concrete pad adjacent to the monitoring well protective casing and store the coordinates and elevation in the data logger and record data in the survey logbook.
- Remove the monitoring well cap and measure the elevation of the top of the inner well casing (not the protective casing) on the north side of the well. Remove all visible debris from the tip of the survey rod before placing the rod on the top of the open well. Measure the top of casing elevation and store the elevation data in the data logger and in the survey logbook.

The following procedure will be followed specifically for surveying surface water and sediment sampling locations:

- Enter the survey location identification in the GPS data logger and also in the survey logbook.
- Place the survey rod at the stream bank adjacent to the sample location and measure the location (northing and easting) in state plane coordinates and the elevation. Store the information in the data logger and record it in the survey logbook.

7.0 DOCUMENTATION

Documentation of observations and data acquired in the field will provide information on the acquisition of samples and also provide a permanent record of field activities and shall conform to the Standards for Surveying as stipulated by the Arizona State Board of Licensure for Professional Engineers and Professional Surveyors. The observations and data will be recorded with waterproof ink in a permanently bound weatherproof field logbook with consecutively numbered pages, and on field data sheets as applicable.

The survey location identifier (i.e., sample location designation or monitoring well designation) and corresponding coordinates and elevation will be recorded in the data logger. As a backup, this information will also be recorded in the survey logbook. The documentation must be of sufficient adequacy to relocate survey points if station markers are lost or destroyed. Surveying activities and field observations will also be recorded in the survey logbook. Information that will be documented in the logbook include:

- Project name and number
- Surveying personnel
- Weather conditions
- Equipment used
- Daily field verification information (i.e., benchmark identification and coordinates)
- Survey location identification
- Survey location coordinates (northing and easting) and elevation
- Descriptions and coordinates of alternate survey locations (offsets)
- Measured distances from alternate survey locations to original survey locations

- GPS data and measurements documentation must include:
  - the make and type of the system used
  - the type of corrections made
  - the basis for the corrections
  - the accuracy calculated based on the corrections
  - a table which includes readings, location descriptor, northing and easting according to the State Plane or UTM coordinate system, any estimated elevation (if determined), and a map or sketch which indicates the GPS locations obtained
- A description of any conditions that may affect data integrity

Freeport-McMoRan Sierrita Inc.

VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 22.0

UTILITY CLEARANCE

1.0 PURPOSE AND SCOPE 22-1

2.0 RESPONSIBILITIES AND QUALIFICATIONS 22-1

3.0 RELATED STANDARD OPERATING PROCEDURES 22-1

4.0 EQUIPMENT LIST 22-1

5.0 PROCEDURES 22-2

6.0 DOCUMENTATION 22-2

1.0 PURPOSE AND SCOPE

This Standard Operating Procedure (SOP) provides technical guidance and procedures for utility clearance and location. It addresses field procedures, field data collection, and personnel responsibilities.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Design Contractor has the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate environmental staff to implement this SOP and for ensuring that the procedures are followed.

All personnel performing these procedures are required to have the appropriate health and safety training. In addition, all personnel are required to have a complete understanding of the procedures described within this SOP, and receive specific training regarding these procedures, if necessary.

All environmental staff and assay laboratory staff are responsible for reporting deviations from this SOP to the Design Contractor.

All utility clearances will comply with applicable portions of the Site Health and Safety Plan (HASP).

3.0 RELATED STANDARD OPERATING PROCEDURES

The procedures set forth in this SOP are intended for use with the following SOPs:

SOP No. 4.0	Near Surface Soil Sampling
SOP No. 9.0	Sample Management (for documentation procedures)
SOP No. 18.0	Subsurface Soil Sampling with a Hand Auger
SOP No. 19.0	Test Pit Excavation and Sampling
SOP No. 20.0	Surveying (Conventional and GPS)

4.0 EQUIPMENT LIST

The following list of equipment and materials may be needed for Utility Clearance:

- Maps and Plans of Utility Locations
- Tape Measure
- Wood stakes or lath
- Survey flags and spray paint
- GPS Unit (or survey equipment, as applicable)
- Field logbook

5.0 PROCEDURES

Locations selected for intrusive field activities (e.g., trenching) will be cleared of utilities before field activities begin. Utility clearance may also be required prior to employing geophysical techniques. Each location will be cleared for the following utilities, as applicable; natural gas, telecommunications, water and sewer, electrical, fiber optics and cable. At some locations there may be additional utilities and features that may require clearance, for example, buried tanks, petroleum service lines, irrigation lines, and building foundations, etc.

Notification will be made to all applicable utility companies with respect to the planned activities. Applicable Freeport-McMoRan Sierrita Inc. (Sierrita) departments and personnel that may have knowledge or management responsibilities of utilities (for example engineering or Health and Safety) will also be notified. On-site meetings will be scheduled with all applicable utility contacts to conduct utility locating and clearance. A utility locating and clearance meeting(s) will include utility representatives and representatives from all contractors involved in the projected activities.

Some public utility companies guarantee that they will be present at the scheduled meet time. Other utility companies may call to reschedule at a different time, or day, or reschedule the day of the scheduled utility meet. If possible, the utility clearance should be done a minimum of 2 days prior to intrusive work to allow enough time for utilities companies to clear their lines and to avoid delays in the field program. When scheduling a utility locate, it is recommended that you request that the contacted utility companies call if they are not going to attend the utility meeting.

Utility locates conducted by mine personnel on work areas on mine property are good for 5 calendar days. Off-site utility locates conducted by outside utility companies are good for 10 calendar days.

The utility companies will identify their utilities with spray paint on the ground, or other means of identification. They also may leave a map at the location with their lines identified.

6.0 DOCUMENTATION

Documentation of observations and data acquired in the field will provide a permanent record and information on the utility clearance. The observations and data will be recorded with waterproof ink in a permanently bound weatherproof field logbook with consecutively numbered pages.

Field notes will also be kept during sampling activities. The following information at a minimum will be recorded in a bound field logbook using waterproof ink:

- Project name
- Names of personnel present during utility clearance
- Weather conditions
- Date and time of utility meeting
- Description of utility clearance activities, any utility clearance sign-off (as applicable)
- Sketch maps or any current or historical maps used in locating utilities (or references to locations of maps for future reference).

- Location (GPS or land survey, as applicable)
- As applicable, a photographic record of utility locations

Freeport-McMoRan Sierrita Inc.

VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 23.0

INVESTIGATION DERIVED WASTE MANAGEMENT

1.0 PURPOSE AND SCOPE 23-1

2.0 RESPONSIBILITIES AND QUALIFICATIONS 23-1

3.0 RELATED STANDARD OPERATING PROCEDURES 23-1

4.0 EQUIPMENT LIST 23-1

5.0 PROCEDURES 23-2

5.1 SOIL IDW 23-2
5.2 LIQUID IDW 23-2
5.3 PPE AND DISPOSABLE INVESTIGATION EQUIPMENT 23-3
5.4 OFF-SITE DISPOSAL AND DISPOSAL OF HAZARDOUS MATERIALS 23-3

6.0 DOCUMENTATION 23-4

1.0 PURPOSE AND SCOPE

This Standard Operating Procedure (SOP) provides technical guidance and methods that will be used for the handling, management, and disposal of investigation derived waste (IDW) encountered or generated during environmental activities. This SOP gives descriptions of equipment, field development procedures, field data collection, and personnel responsibilities.

2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Design Contractor has the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate environmental staff to implement this SOP and for ensuring that the procedures are followed.

All personnel performing these procedures are required to have the appropriate health and safety training. Personnel overseeing the handling and disposal of IDW will have IDW management knowledge and experience, or will work under the direct field supervision of knowledgeable and experienced personnel. Personnel will perform this work in accordance with the site health and safety plan (HASP).

All environmental staff and assay laboratory staff are responsible for reporting deviations from this SOP to the Design Contractor.

3.0 RELATED STANDARD OPERATING PROCEDURES

The procedures set forth in this SOP are intended for use with the following SOPs:

SOP No. 1.0	Surface Water Sampling
SOP No. 2.0	Monitor Well Groundwater Sampling
SOP No. 4.0	Near Surface Soil Sampling
SOP No. 18.0	Subsurface Soil Sampling with a Hand Auger
SOP No. 19.0	Test Pit Excavation and Sampling

4.0 EQUIPMENT LIST

The following materials and equipment may be needed for IDW management:

- Personal protective equipment (PPE) as outlined in the HASP
- Decontamination equipment and supplies (e.g., wash/rinse tubs, brushes, alconox, plastic sheeting, paper towels, sponges, baby wipes, garden-type water sprayers, large plastic bags (minimum 0.85 mil), potable water, distilled water and/or deionized water)
- Department of Transportation (DOT)-rated 55-gallon drums or other approved containers for containing soil cuttings, decontamination water, and formation water
- Drum/bung wrench and drum funnel
- Heavy equipment forklift or vehicle with drum grappler (as necessary)

- Laboratory-supplied sample containers
- Photoionization detector (PID) or flame ionization detector (FID)
- Wood pallets (as necessary)
- Non-porous (e.g., stainless steel) shovels
- Polyethylene tanks (as necessary)
- Field notebook and waterproof and permanent marking pens

5.0 PROCEDURES

It is anticipated that both non-liquid and liquid IDW will be generated or encountered during field activities. IDW generated during the data gap assessment actions is expected to include:

- Soil cuttings and other soil wastes generated during sampling
- Well development and purged water
- Wash and rinse waste from decontamination activities
- Used PPE and other non-soil solid wastes

Sections 5.1 and 5.2 describe procedures for disposal of IDW. Section 5.4 addresses management and disposal requirements for off-site disposal and potentially hazardous materials.

5.1 SOIL IDW

- Soil cuttings generated during soil sampling will be placed into DOT-rated 55-gallon drums, or appropriately sized containers at the point of generation.
- Mixing of the cuttings from several sampling locations is permissible in order to fill the drums.
- When drums or containers are full, or daily activities are completed, the drum lids and rings will be fastened. Full drums or containers will be transported to the designated IDW accumulation area on a regular basis to avoid accumulation of drums or containers at investigation sites for extended periods of time. Appropriate analyses will be evaluated prior to disposal.
- The waste soil drums or containers will be disposed offsite, as appropriate, based on analytical results.

5.2 LIQUID IDW

- Well development, purge, abandonment, and decontamination water will be contained in DOT-rated drums, or appropriately sized watertight containers, at the point of generation.
- When drums or tanks are full, or daily activities are completed, the containers will be sealed; for example, drum lids and rings will be fastened.
- Waste water IDW that is generated and containerized at project sites will be disposed offsite, as appropriate, based on analytical results.

5.3 PPE AND DISPOSABLE INVESTIGATION EQUIPMENT

- The plan for managing used PPE and other non-soil solid waste generated during field activities (e.g., sample handling) is to collect it in plastic trash bags and for the material to be disposed of as a solid waste.
- Potentially contaminated PPE or disposable investigation equipment will be decontaminated prior to placement in the plastic bags or containers, if warranted.
- Decontamination procedures consist of brushing off, or using small amounts of water to scrub off, gross potential contamination.

5.4 OFF-SITE DISPOSAL AND DISPOSAL OF HAZARDOUS MATERIALS

If it is necessary for IDW to be disposed of off-site, only Company-approved facilities will be used.

Disposal off-site of waste materials will be in accordance with the Administrative Order on Consent, Clause 29.

29a. Prior to any off-Site shipment of waste material generated by the work performed under this Agreement to an out-of-state waste management facility Respondent shall provide written notification of the shipment to the appropriate state environmental official in the receiving facility's state and to the U.S. Environmental Protection Agency (EPA). This notification requirement shall not apply to any off-site shipments when the total volume of all such shipments will not exceed 10 cubic yards.

29b. Respondent shall include the following information in the notification: (1) the name and location of the facility to which the waste material is to be shipped, (2) the type and quantity of the waste material to be shipped, (3) the expected schedule for the shipment of the waste material and (4) the method of transportation. Respondent shall notify the state in which the receiving facility is located of major changes in the shipment plan, such as a decision to ship the waste material to another facility within the same state or to a facility in another state.

29c. The identity of the receiving facility and state will be determined by Respondent following the award of the contract for the removal actions. Respondent shall provide the information required by Paragraph 29.b as soon as practicable after the award of the contract and before the waste material is shipped.

29d. Before shipping any waste material generated by the work performed under this Agreement to an off-Site location, Respondent shall obtain EPA's certification that the proposed receiving facility is operating in compliance with the requirements of Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) Subsection (§) 121(d)(3), 42 *United States Code* (U.S.C.) § 9621(d)(3), and 40 Code of Federal Regulations (C.F.R.) § 300.440. Respondent shall only ship waste material generated by the work performed under this Agreement to an off-Site facility that complies with the requirements of the statutory provision and regulation cited in the preceding sentence.

6.0 DOCUMENTATION

Documentation of field observations and data will provide information on the activities concluded and also provide a permanent record of field activities. The observations and data will be recorded with waterproof ink in a permanently bound weatherproof field notebook with consecutively numbered pages.

Project staff are responsible for thoroughly documenting IDW handling and disposal activities and are responsible for documenting the collection, transportation, labeling (if applicable), and staging or disposition of IDW. The information entered concerning IDW should include the following:

- Project Name
- Names of personnel
- Site location
- Type of activities
- Date waste generated
- Boring, well, or site number(s)
- Matrix
- Type of container(s)
- Estimated volume
- Disposition of contents
- Comments (field evidence of contamination [e.g., PID reading, odors])
- Any variance to procedures described in this SOP

Freeport-McMoRan Sierrita Inc.

VOLUNTARY REMEDIATION PROGRAM

STANDARD OPERATING PROCEDURE NO. 31.0

PUMPING TESTS

1.0 PURPOSE AND SCOPE 31-1

2.0 PUMPING TEST IMPLEMENTATION 31-1

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Attachment 1 Aquifer Test Data Forms

1.0 PURPOSE AND SCOPE

Hydraulic testing may be conducted to:

- Provide downgradient characterization of COIs in both the alluvium and bedrock formations;
- Assess the hydraulic characteristics and parameters of both the alluvium and bedrock formations, including vertical hydraulic gradient; and
- Assess the hydraulic connection between the alluvium and bedrock formations and response to precipitation events.

Hydraulic testing will potentially include step, constant rate, recovery testing and/or slug testing, with the exact testing depending on the saturated thickness and well yields. Hydraulic testing of well pairs would consist of a 4-hour step-discharge test to estimate the optimum pumping rate for the pumping well, a minimum 4-hour to maximum 72-hour constant-rate test (conducted at the rate selected from the step-discharge test), and a minimum 2-hour recovery test.

Following testing, water level data will be analyzed using standard aquifer test analysis methods. The methods used will be carefully selected to best fit aquifer conditions and meet the method assumptions. The following outlines procedures for conducting the pumping tests, collecting data and data analysis.

2.0 PUMPING TEST IMPLEMENTATION

2.1 Pumping Test Set-Up

The pumping well and selected observation wells will be equipped with pressure transducers, which will connect to a Hermit® 3000 data logger (or equivalent datalogger). The discharge line will be fitted with an in-line flow meter capable of both instantaneous and totalized flow measurement. Withdrawn groundwater will be routed to an agreed discharge point, natural depression or excavated sump. A variable speed electrical submersible pump, powered by a generator capable of producing the required power for the pump, will be used and sized to handle the maximum anticipated flow rate at the maximum anticipated pumping water level. All drop pipe and discharge lines will also be sized to accommodate the maximum anticipated flow rate. A ball or butterfly valve may also be used to control the pump discharge rate.

During test setup, the field crew will verify that all the necessary equipment is available or will be available by the anticipated start of the step-discharge test. The following is a list of equipment and materials anticipated for use during the pumping tests:

- Pressure transducers rated to the anticipated pressures (i.e., water level submergence) for the pumping well and selected monitoring/observation wells, and a Hermit 3000 data logger
- Electronic water level meters of sufficient length
- Synchronized watches for observers

- Semilog three-cycle graph paper, rulers, pencils, and forms for recording water level measurements
- Aquifer Test Data Form (Appendix 1)
- Laptop computer with spreadsheet and pumping test analysis software
- Appropriately sized submersible pump, polyethylene discharge pipe, ball/gate valves, flow meter, and generator
- Tool box, duct tape, etc.
- Health and safety equipment as specified in the Health and Safety Plan (HSP)

2.2 Instrument Calibration

The flow meter, transducers, and electronic water level meters will be calibrated or checked to make sure they are working properly before commencement of each pumping test. Copies of instrument calibration documents will be filed with the records of the test data. Calibration records should contain the laboratory measurements. The following checks and calibrations will be performed for pumping test equipment:

- The in-line flow meter will be checked on site using a manometer and calibrated orifice.
- The unique input parameters for each pressure transducer will be input to the data logger. The accuracy of the transducers will be checked by moving the transducer up and down in the well a known vertical distance and reading the pressure (or feet of water) values recorded at the data logger. The known amount that the transducer is moved up or down should match the value displayed on the data logger. Also, the sign of the value on the data logger will be checked to verify the direction of transducer movement.
- The water level meters will be checked to make sure that there are no lengths of cable cut off, and that the footages are accurate (compare with steel tape). The probes will be submerged into water to verify that the tone and/or indicator light are functional.
- Calibrate all water quality meters, if used during testing, as specified in SOP No. 8.

2.3 Pumping Test Procedures

The following sections describe the three main components of the pumping tests.

Step-Discharge Test – An approximately 2-8-hour step-discharge test will be conducted at pre-selected rates based on results from well development or previous pumping tests (if any). The purpose of the step-discharge test is to estimate the optimum sustainable pumping rate for the constant-rate test, and to assess how specific capacity varies with increasing pumping rates.

The step-discharge test will involve pumping the well at five successively increasing discharge rates. Each pumping rate (step) will continue for at least 1 hour, or until water levels generally stabilize. Water level data from the pumping well and observation wells located within 400 feet of the pumping well will be collected using a Hermit 3000 data logger on a linear time schedule at 1-minute intervals.

After completion of the step-discharge test, the water level data will be analyzed to estimate the optimum pumping rate for the constant-rate test. A qualified person familiar with aquifer test data analysis will perform these analyses.

Constant-Rate Test – A minimum 4-hour to maximum 72-hour, constant-rate test will be conducted after the aquifer has recovered to within 95 percent of pre-step test static conditions. Water levels will be measured at least three times to verify that static conditions have been re-established.

The constant-rate test will involve pumping the well at a constant discharge rate for up to 72 hours, or until water levels generally stabilize in both the pumping well and observation wells. The pumping rate at which the constant-rate test is conducted will be calculated from results of the step-discharge test.

During the test, water-level data will be collected continuously in the pumping well and observation wells on a logarithmic time schedule as described below.

- Water level data from the pumping well and surrounding observation wells (located within a radial distance of 400 feet from the pumping well) will be collected continuously using pressure transducers and a Hermit 3000 data logger. Water levels will be measured according to the following time schedule:
  - 0 to 10 minutes: 0.5- to 1-second intervals
  - 10 to 15 minutes: 12-second intervals
  - 15 to 100 minutes: 2-minute intervals
  - 100 to 1,000 minutes: 30-minute intervals
  - 1,000 to 10,000 minutes: 200-minute intervals

  Observation wells located greater than 400 feet from the pumping well should be monitored manually at the following time schedule, if possible:
  - 0 to 1,000 minutes: 120-minute intervals
  - 1,000 to 10,000 minutes: 480-minute intervals

  In addition, manual water level measurements should be collected from the pumping well and all observation wells equipped with pressure transducers at the following time schedule, if possible:
  - 0 to 240 minutes: 15-minute intervals
  - 240 minutes to 10,000 minutes: 120-minute intervals

  All manual water level measurements will be recorded on Aquifer Test Data Forms (Appendix 1).

A detailed list of activities to be performed during the constant-rate test follows.

- Prior to initiating the constant-rate test, static water level will be measured in all observation wells and in the pumping well (to nearest 0.01-foot). Measurements will be made from a surveyed reference point on the well or from top of casing.

- The start time of the data logger will be synchronized with that of the pump. This can be accomplished with hand signals or with the delayed start feature on the Hermit 3000. Ensure that the pump does not start before the data logger so that the initial water level is recorded.
- At the start of the pumping test, record the date and time.
- Monitor the pumping well discharge rate and maintain a constant flow. Monitor the pumping rate every 15 minutes during the first four hours and at 30-minute intervals throughout the remainder of the test. Measurements will be recorded on the Aquifer Test Data Form (Appendix 1) and in the field notebook.
- If water quality parameters for withdrawn groundwater are required, it is suggested that withdrawn groundwater samples be collected every 2 hours and water quality parameters measured.
- Maintain fuel in the generator to ensure the generator does not fail during testing. All refuel times will be noted in field notebook.
- During pumping, plot the data (time versus drawdown) on semilog graph paper or with computer software to assess the progress of the test and to determine when sufficient data have been collected and the test can be terminated.

The objective of real-time data analysis is to assess the progress of the test and to determine when the pumping test can be terminated. There is generally no need to continue a test if water levels have sufficiently stabilized. When the time versus drawdown data for the most distant observation well begins to plot as a straight line (constant slope) on the semilog graph paper, the test can be terminated unless delayed yield and/or boundary conditions are anticipated. However, the test should run for a minimum of 24 hours before being terminated.

Recovery Test – When the constant-rate test is terminated, the data logger cycle will be terminated and started again to record recovery data. The data logger will be programmed to collect recovery data in a logarithmic mode at the same intervals as those used for the constant-rate test. The start of data recording will be timed precisely to the shut down of the generator and pump. The pump will be equipped with a check valve to prevent water in the discharge pipe from reentering the well once pumping ceases.

The recovery test will be terminated when water levels in the observation wells have recovered to within 90 percent of pre-test static levels. Recorded data will be downloaded from the data logger to a computer disk with file names that reflect the well name and test type (step-discharge, constant-rate, or recovery). Backup disks will also be created for contingency purposes.

2.4 Investigation-Derived Waste (Withdrawn Groundwater)

Withdrawn groundwater will be collected and transferred to a designated area, either depression in topography or excavated sump.

3.0 DATA ANALYSIS

Data analyses and interpretations from the pumping tests will be included in the RI/FS report.

Drawdown and recovery data will be compiled and analyzed to estimate:

- Hydraulic conductivity, transmissivity, and specific yield or storativity;
- Estimate the radius of influence;
- Assess whether any hydrogeologic boundaries were encountered (i.e., faults or recharge boundaries); and
- Assess whether any hydraulic communication between aquifer units exists.

All analyses will be performed using AQTESOLV® for Windows software (Duffield, 1996) and/or Microsoft Excel®. The pump test data will be analyzed using appropriate methods as presented in Table 1 (use references for equations). The method of analysis will be selected by matching known aquifer conditions with the required assumptions outlined in Table 1. If the hydrogeologic conditions and pumping test data satisfy more than one method of analysis, then results will be presented for each method used.

4.0 REPORTING

Pumping test data analyses and interpretations will be presented in the RI/FS Report. At a minimum, this portion of the RI/FS Report will include:

- A description of the procedures implemented during testing;
- Interpretations of pumping test data;
- Tables containing well completion information (e.g., well elevations and screened intervals) and water level data (e.g., initial and final pumping water levels);
- Tables summarizing estimated aquifer property values and water quality parameters collected during the pumping tests; and
- AQTESOLV® reports and graphs, as well as any manually produced graphs and calculations.

5.0 REFERENCES

Duffield, Glenn M., 1996. AQTESOLV for WindowsTM, User's Guide. HydroSOLVE, Inc.

TABLE 1

ATTACHMENT 1

SHEET ___ OF ___

AQUIFER TEST DATA FORM
Project: _____
Location: _____

Project #:	**Start Date:**	**Start Time:**	**Field Supervisor:**
Client:	**End Date:**	**End Time:**	**Project Manager:**

Date	**Time (min)**	**Cumulative Discharge (gallons)**	**Pumping Well Water Level (ft-btoc)**	**OBSERVATION WELLWATER LEVEL DATA**					
				_____ (ft-btoc)	**_____ (ft-btoc)**	**_____ (ft-btoc)**	**_____ (ft-btoc)**	**_____ (ft-btoc)**	**_____ (ft-btoc)**
Date	**Time (min)**	**Cumulative Discharge (gallons)**	**Pumping Well Water Level (ft-btoc)**	**OBSERVATION WELLWATER LEVEL DATA**					

				______ (ft-btoc)	______ (ft-btoc)	______ (ft-btoc)	______ (ft-btoc)	______ (ft-btoc)	______ (ft-btoc)

Submitted By: ______________________________ Reviewed By: ______________________________

Date: ______________________________ Date: ______________________________

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VOLUNTARY REMEDIATION PROGRAM

Standard Operating Procedure No. 40

Slug Test Procedure

Rev. #: 1

Rev Date: September 2012

Scope and Application

The objective of this Standard Operating Procedure (SOP) is to establish uniform procedures for slug testing to estimate the hydraulic conductivity of the groundwater zone near a well. A slug test is completed by "instantaneously" inducing an artificial change in hydraulic head and measuring the rate of the groundwater return to equilibrium (static) conditions. This SOP provides detailed information on test methodology, planning, and application. Detailed equipment lists and procedure sheets for testing using solid slugs, inflow (water slug), baildown, and pneumatic testing methods are provided.

The data analysis portion of slug testing is not covered in this SOP. It is strongly recommended that the appropriate staff are consulted and involved in the design and analysis phases.

Application

Slug tests are used as an economic, simple, and rapid way to obtain data needed to estimate near-well hydraulic conductivity (Bulter, 1998). However, slug tests should not be viewed as a replacement for larger scale estimates of hydraulic conductivity provided from pumping tests (Kruseman and de Ridder, 1994). The shorter time frame and limited stress on the groundwater zone provides a hydraulic conductivity estimate on a smaller scale (near-well) than pumping tests, and the results are more representative of the lower bound of the groundwater zone hydraulic conductivity. Due to the localized scale of slug testing, the affect of the well filter pack, well development, and well skin are more significant than during pumping tests. The stress on the well (i.e. initial change in head) needs to be large enough to have a measurable response and to ensure the response is a function of the groundwater zone hydraulics and not due to well filter pack interactions.

Slug Test Design

Project objectives should be considered to determine if slug testing will provide adequate characterization of groundwater zone hydraulic conductivity. For example, slug testing may useful in mapping hydraulic conductivity heterogeneities, or used to calibrate high resolution hydraulic testing results provided by direct push tools. However, slug testing would not be appropriate to obtain groundwater zone storage estimates. In addition, slug testing may not be appropriate for bedrock where there may be incomplete understanding of the fracture network. A pumping test or open borehole testing may be more appropriate in bedrock.

The design phase includes several elements which include the following (please note, there may be exceptions – specific designs need to be made in consideration of the project conceptual site model and objectives).

1. Review of the conceptual site model, including boring logs, cross sections, plume information, hydrostratigraphic zones, previous estimates of hydraulic conductivity, and regional estimates from published sources. Special attention should be given to a particular well screen interval in order to test the target groundwater zone. If a well is screened across multiple hydrostratigraphic zones, uncertainty associated with estimated hydraulic conductivity values for a given zone is introduced. However, there are exceptions if the permeability of the zones that are crossed by the well screen differ significantly.

2. Review of regulatory program rules or guidance to ensure proper compliance with procedures. In most cases, slug testing using pneumatic or solid slug methods will not require permitting; however, use of in-flow procedures may require permitted acceptance (Underground Injection Control).

3. Compile detailed information for each test well:

    i. Well construction information – well casing/screen diameters and lengths.

    ii. Screen type/slot size.

    iii. Total depth – reviewing the measurement of the total depth of test well aids in development assessment. If the total depth has decreased substantially since installation, sediment buildup may be occurring and redevelopment should be completed before testing.

    iv. Filter pack construction (diameter and material).

    v. Historic and current groundwater levels – this will aid in the determination of the appropriate slug test type.

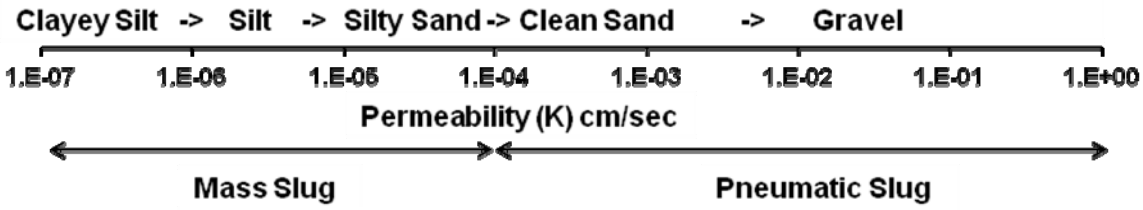
    vi. Well development record – testing improperly developed wells will result in anomalous results.

    vii. Recent well sampling logs – historic sampling data will provide information on the potential yield of the well and groundwater quality (turbidity).

4. Planning testing methods: In light of the information researched in items 1 through 3, slug test methods should be designed based on the groundwater zone information and data needs for proper analysis.

    - Solid Slug – used for rising and falling head tests in wells of adequate water column length with fully or partially submerged screens. If screen is partially submerged (crosses the groundwater table), then a rising head test is the only applicable method.
    - Inflow – used for falling head tests where the water column is too small to accommodate typical slug test equipment.
    - Baildown – used for rising head tests.
    - Pneumatic – used for falling head tests (pressurizing) with fully submerged well screens.

    a. Aquifer information: The initial hypotheses of the groundwater zone characteristics and permeability based on either previous testing, qualitative information (boring logs), or other studies in the area is an important consideration when determining the methodology for testing. For instance, if boring logs suggest a sand and gravel formation and sampling logs indicate good well yield, then a hypothesis may be made that the formation is a relative high permeability. Therefore, if the well screens are fully submerged, pneumatic slug testing would be a good method to use. The below chart is a depiction on the type of test in relation to permeability. In addition, if the permeability is expected to be low, then limiting the initial change in head to the least (i.e. 1 foot) will help with time efficiency.



    b. Additional data needs: Additional data needs may be required for validity of the slug test method (Butler, 1998) or external factors. This

includes duplicate testing, rising and/or falling head tests, multiple tests with varying initial displacements, and background data to assess background water level trends. Generally, three tests per well is satisfactory with two duplicate tests at the same displacement and one with double the original displacement. Background data would be obtained near areas with either tidal or pumping influences. If applicable and possible, arrange to have nearby active pumping wells shut down for at least 48 hours prior to testing or have them pump at a constant rate during testing. Testing should not be completed during periods of significant precipitation.

5. Data acquisition: change in head measurements should be collected at a frequency of 0.5 seconds or less for high permeability groundwater zones (gravels and sands). A lower frequency can be selected for lower permeability groundwater zones (silts and clays). Pressure transducers with dataloggers should be used to collect water level data. Manual water level measurements should be collected to verify the electronic data collected using pressure transducers. For low permeable formations with full submerged well screens, manual data acquisition only maybe reasonable.

Personnel Qualifications

Field personnel will have sufficient "hands-on" experience necessary to successfully complete the slug test field work. Training requirements for conducting slug tests include reviewing this SOP and other applicable SOPs and/or guidance documents and instrument calibration.

Field personnel will have completed current health and safety training e.g., 40-hour Hazardous Waste Operations training, site-specific training (UP Contractor Orientation Training), e-RAILSAFE^{SM} certification, and first aid and cardiopulmonary resuscitation (CPR) training, as appropriate.

Cautions

Field personnel must ensure that they are familiar with the electronic data logging equipment, they have all proper materials, and all instruments and tapes are calibrated.

Small-diameter pressure transducers (typically 0.5 to 0.75 in) are available that cover a range of pressures. Install the pressure transducer at a reasonable distance below the targeted drawdown estimated for the well to prevent noise. Do not install the transducer closer than six inches off the base of the well. To prevent pressure transducer malfunction or damage, do not submerge pressure transducers in excess of the operating range.

Test pressure transducers/data logger readings using a bucket or barrel filled with water. Submerge each pressure transducer, accurately measure the water head above the pressure transducer, and compare the measurement to the reading. This check will only work with vented transducers. Non-vented transducers will record the barometric pressure exerted onto the water column along with the water column. Check pressure transducer response to changing heads by raising the pressure transducer a certain distance, observing the change in head, and then measuring the distance manually. Water level meters should be in good working condition and calibrated, ensuring there are no breaks or splices in the cable.

Pressure transducers should be allowed to thermally equilibrate with groundwater and stretching of pressure transducer cable for approximately 10 minutes prior to test initiation.

Solid slugs should be calibrated to determine volume for theoretical displacement. In most cases, rental slugs offer economic and data quality benefits over build slugs. Purge volumes should be measured when completing baildown testing.

The general rule of thumb for the initial displacement is between 1 to 3 feet. Water levels should be recorded to within 80% to 90% recovery. In addition, duplicate tests should be completed only after the first test has recovered by 95% or greater.

Containerize all purged water. Discharge water must be disposed according to all applicable laws, regulations and project guidelines. Contact the governing agencies to determine which restrictions apply. ARCADIS should not be responsible for signing manifests and should not "take possession" of discharged water.

Keep sensitive electronic equipment away from devices that generate significant magnetic fields. For example, do not place pressure transducers near electric power generators or electric pump motors. Likewise, radio signals may cause pressure

transducers or computers to malfunction. Secure the pressure transducer cables at the wellhead to prevent movement that would affect measurements. Mark a reference point on pressure transducer cables and check regularly to detect slippage.

Make sure all equipment that enters the test well (slug, water-level meter, pressure transducer) is decontaminated before use. If testing multiple wells, start with the least contaminated and progress to the most contaminated.

Slug tests should not be conducted in wells where Non Aqueous Phase Liquids are present.

Remember, data backup is always necessary. A job loss would occur if data would be accidently lost. Always back up data on a laptop computer and a flash drive and keep at different spots (i.e. back pack and glove compartment) to reduce the risk of data loss (i.e. computer failure).

Health and Safety Considerations

The site-specific HASP will be used to guide the tests in a safe manner without incident which should include a Job Safety Analysis (JSA). The following specific health and safety issues must be considered when conducting slug tests:

- Appropriate PPE must be worn to avoid contact with site chemicals of concern during slug test.
- Well covers must be carefully removed to avoid potential contact with insects or animals Well caps should be tethered to avoid potential eye injury in case of gas buildup in the well.
- Pressurization or vacuum hazards associated with pneumatic slug testing.

Waste Management

Rinse water, PPE and other waste materials generated during equipment decontamination will be placed in appropriate containers and labeled. Containerized waste will be disposed of consistent with appropriate waste management procedures for investigation-derived waste.

Data Recording and Management

Field personnel will complete the Slug Test Log. Data will be copied to a flash drive and transmitted to the project team as soon as possible to ensure no data loss. Field equipment calibration, decontamination activities, and waste management activities will be recorded in the field logbook.

Quality Assurance

Review data collected during the slug test in the field to determine that the data are reasonable given site-specific conditions. Compare the theoretical head displacement calculated from the slug volume or pressure to the observed displacement. If the data are questionable, the field equipment must be checked to confirm it is working properly and the test will be repeated, if possible. Consult with the project hydrogeologist to work through issues encountered in the field and to help determine the validity of the test.

Any issues that may affect the data must be recorded in the field log book for consideration by the evaluator.

References

Butler, J.J., Jr., 1998. *The Design, Performance, and Analysis of Slug Tests*, Lewis Publishers, New York, 252p.

Kruseman, G.P. and N.A. de Ridder, 1994. *Analysis and Evaluation of Pumping Test Data (2nd ed.)*, Publication 47, Intern. Inst. for Land Reclamation and Improvement, Wageningen, The Netherlands, 370p.

ASTM D4044, *Standard Test Method (Field Procedure) for Instantaneous Change in Head (Slug Tests) for Determining Hydraulic Properties of Aquifers.*

Method Procedure Sheets

I. SOLID SLUG - Scope and Application

The use of a solid slug allows for both falling- and rising-head slug tests to be completed. Solid slug(s) of a known volume are inserted and removed from the water column in a well in a near-instantaneous manner. The water level response is observed using a pressure transducer.

II. Equipment List

The following materials will be available, as required, during slug testing using a solid slug:

- Personal protective equipment, as required by the site Health and Safety Plan
- Solid slug(s) of known volume
- Pressure transducer and barologger
- Pressure transducer software
- Laptop computer
- Rope
- Water level meter
- Measuring tape
- Spring-loaded clamps
- Decontamination equipment
- Slug test field form
- Field notebook
- Waterproof marker

III. Procedure

1. Decontaminate all down-well equipment: pressure transducer and cable, slug(s), rope or cable, water level meter.

2. Measure depth to water and well total depth. Determine the water column length.

3. Review the well construction log to determine screened interval and depth to bottom.

4. Program the pressure transducer to record water levels at the following suggested frequencies. Note that the lithologic descriptions and datalogger memory should be used to select the highest measurement frequency possible.

    a. In hydrologic settings where high hydraulic conductivity is expected, water levels should be measured at 0.5 second intervals, or the highest frequency available. This measurement frequency should be selected for gravels and sands.

    b. In hydrologic settings where low hydraulic conductivity is expected, water levels should be measured at 1 to 2 second intervals. This measurement frequency should be selected for silts and clays.

5. Program the barologger to record barometric pressure at the same interval as the pressure transducers measuring water levels. The barologger should be placed in the headspace of an adjacent well.

6. Install the pressure transducer deep enough within the water column to not interfere with the testing equipment. Do not install closer than 6 inches above the well bottom. Remember to use measurements and not the well bottom as silt can clog the pressure transducer. Clamp the pressure transducer cable to the well casing or other static object.

7. View the measured water level in real time on the laptop computer. Wait for the water levels to stabilize. Note that temperature fluctuations on the pressure transducer will affect measured water levels (i.e. temperature differences between the above surface and groundwater environments).

8. Measure the slug and rope assembly length and mark the rope at a length as follows:

    Rope Mark #1 = Depth to Potentiometric Surface from TOC

    Rope Mark #2 = Depth to Potentiometric Surface from TOC + Length of Slug + Safety Factor (Safety Factor = 10% of the Length of Slug)

    When deployed, this mark will be at the well top of casing. This will place the slug to be totally submerged. If insufficient water column is available to cover the slug assembly top, note the theoretical length of the slug to be inserted into the water column. Upon removal, measure the wet slug length.

9. Slowly insert the slug assembly into the well and stop just above the potentiometric surface rope mark #1.

10. With slack in the rope and the slug being suspended above the water column, place the rope mark #2 at the top of casing. Clamp the non-slug end of the rope to a static object.

11. Quickly drop the slug into the water column.

12. Observe the water level response on the laptop computer and/or measure depth to water, being careful not to interfere with the pressure transducer cable. Several manual depth to water measurements should be made throughout the test.

13. Allow sufficient time for water level to recover to static level. If completing one test (just a falling head test or just a rising head test), then 80% recovery is sufficient. Duplicate tests are highly recommended and the next test should be completed after the first test has recovered to greater than 95%. A third test at a displacement of twice the initial is recommended.

14. Quickly remove the slug assembly from the water column. If needed, the slug assembly can be left in the well above the static water level in order to limit pressure cable disturbance.

15. Repeat steps 12 and 13.

16. Repeat both the falling- and rising-head slug tests for data reproducibility. If possible, complete a third test with a slug or combination of slugs that equates to twice the volume as the original.

17. Save all data files to the laptop, backup on flash drive and finalize any field notes.

18. Review the data collected to determine the reasonableness of the preliminary results. The observation of apparently anomalous results will be discussed with senior project staff prior to additional testing or leaving the field site. The water level record for each test should show static conditions, the insertion or removal of the slug(s), and the water level response. Make notes on the field form and notebook concerning any irregularities.

19. Decontaminate all down-well equipment.

I. WATER SLUG (INFLOW) - Scope and Application

A known volume of potable water (slug) may be used to complete falling-head slug tests. Water of a known volume is poured into a well in a near-instantaneous manner. The water level response is observed using a pressure transducer. Slug tests using a water slug are most appropriate for fully submerged well screen (i.e. water table above the well screen top), and where a relatively slow response is anticipated. These constraints limit the probability of slug water entering the filter pack and vadose zone, and for slug insertion to be near instaneous relative to the observed response.

Consult with local regulatory requirements concerning underground injections. The injection volume and injectate are typically innocuous enough that a permit-by-rule authorization is granted in lieu of an underground injection control permit.

II. Equipment List

The following materials will be available, as required, during slug testing using a water slug:

- Personal protective equipment, as required by the site Health and Safety Plan
- Potable water (do not use distilled water as it is not conductive and will not work with electronic water level meters)
- Pressure transducer and barologger
- Pressure transducer software
- Laptop computer
- Graduated cylinder or similar measuring device
- Funnel with large neck and opening (wide mouth)
- Water level meter
- Spring-loaded clamp
- Decontamination equipment
- Slug test field form
- Field notebook

III. Procedure

1. Decontaminate all down-well equipment: pressure transducer, pressure transducer cable, and water level meter.

2. Measure depth to water and well total depth. Determine the water column length.

3. Review the well construction log to determine screened interval and depth to bottom.

4. Program the pressure transducer to record water levels at the following suggested frequencies. Note that the lithologic descriptions and datalogger memory should be used to select the highest measurement frequency possible.

    a. In hydrologic settings where high hydraulic conductivity is expected, water levels should be measured at 0.5 second intervals, or the highest frequency available. This measurement frequency should be selected for gravels and sands.

    b. In hydrologic settings where low hydraulic conductivity is expected, water levels should be measured at 1 to 2 second intervals. This measurement frequency should be selected for silts and clays.

5. Program the barologger to record barometric pressure at the same interval as the pressure transducers measuring water levels. The barologger should be placed in the headspace of an adjacent well.

6. Program the barologger to record barometric pressure at the same interval as the pressure transducers measuring water levels. The barologger should be placed in the headspace of an adjacent well.

7. Install the pressure transducer deep enough within the water column to not interfere with the testing equipment. Do not install closer than 6 inches above the well bottom. Remember to use measurements and not the well bottom as silt can clog the pressure transducer. Clamp the pressure transducer cable to the well casing or other static object.

8. View the measured water level in real time on the laptop computer or use water level meter. Wait for the water levels to stabilize. Note that temperature fluctuations on the pressure transducer will affect measured water levels (i.e. temperature differences between the above surface and groundwater environments).

9. Determine the volume of the water slug. A general guideline is that initial displacements are generally between 1 and 3 feet, but should depend on the anticipated response (i.e. larger initial displacements should be chosen for formations with high hydraulic conductivity, smaller initial displacements can be used for formations with low hydraulic conductivity).

Slug Volume (gal)	Slug Volume (ml)	Casing Diameter (in)	Theoretical Initial Displacement (ft)
0.25	946	2	1.56
0.5	1893	2	3.13
1	3785	2	6.25
0.5	1893	4	0.77
1	3785	4	1.54
2	7570	4	3.08
1	3785	6	0.68
2	7570	6	1.36
3	11355	6	2.04

Notes:
gal = gallons, U.S. liquid
ml = milliliters
in = inches
ft = feet

10. Measure the slug volume and place in a container that is easy to quickly pour from. Note the measured volume.

11. Insert the wide mouth funnel into the well casing.

12. Quickly pour the slug through the funnel and into the well. Note the approximate time required to insert the slug.

13. Observe the water level response on the laptop computer or use water level meter.

14. Measure depth to water, being careful not to interfere with the pressure transducer cable. Several manual depth to water measurements should be made throughout the test.

15. Allow sufficient time for water level to recover to static level. If completing one test, then 80% recovery is sufficient. Duplicate tests are highly recommended and the next test

should be completed after the first test has recovered to greater than 95%. A third test at a displacement of twice the initial is recommended.

16. Repeat steps 9 through 14.

17. Save all data files to the laptop, backup to flash drive and finalize any field notes.

18. Review the data collected to determine the reasonableness of the preliminary results. The observation of apparently anomalous results will be discussed with senior project staff prior to additional testing or leaving the field site. The water level record for each test should show static conditions, the insertion or removal of the slug(s), and the water level response. Make notes on the field form and notebook concerning any irregularities.

19. Decontaminate all down-well equipment.

I. Baildown - Scope and Application

The use of a bailer to remove a volume of water (slug) is used to complete rising-head tests. A bailer removes water from a well in a near-instantaneous manner. The water level response is observed using a pressure transducer.

II. Equipment List

The following materials will be available, as required, during slug testing using a solid slug:

- Personal protective equipment, as required by the site Health and Safety Plan
- Bailers of known size/capacity
- Pressure transducer and barologger
- Pressure transducer software
- Laptop computer
- Rope
- Water level meter
- Measuring tape
- Spring-loaded clamps
- Decontamination equipment
- Slug test field form
- Field notebook
- Waterproof marker

III. Procedure

1. Select a bailer according to a target initial displacement using the table below. A general guideline is that initial displacements are between 1 and 3 feet, but should depend on the anticipated response (i.e. larger initial displacements should be chosen for formations with high hydraulic conductivity, smaller initial displacements can be used for formations with low hydraulic conductivity).

Bailer Volume (gal)	Bailer Volume (ml)	Casing Diameter (in)	Theoretical Initial Displacement (ft)
0.25	946	2	1.56
0.5	1893	2	3.13
1	3785	2	6.25
0.5	1893	4	0.77
1	3785	4	1.54
2	7570	4	3.08
1	3785	6	0.68
2	7570	6	1.36
3	11355	6	2.04

Notes:
gal = gallons, U.S. liquid
ml = milliliters
in = inches
ft = feet

2. Decontaminate all down-well equipment: pressure transducer and cable, rope or cable, water level meter.

3. Measure depth to water and well total depth. Determine the water column length.

4. Review the well construction log to determine screened interval and depth to bottom.

5. Program the pressure transducer to record water levels at the following suggested frequencies. Note that the lithologic descriptions and datalogger memory should be used to select the highest measurement frequency possible.

    a. In hydrologic settings where high hydraulic conductivity is expected, water levels should be measured at 0.5 second intervals, or the highest frequency available. This measurement frequency should be selected for gravels and sands.

b. In hydrologic settings where low hydraulic conductivity is expected, water levels should be measured at 1 to 2 second intervals. This measurement frequency should be selected for silts and clays.

6. Program the barologger to record barometric pressure at the same interval as the pressure transducers measuring water levels. The barologger should be placed in the headspace of an adjacent well.

7. Install the pressure transducer deep enough within the water column to not interfere with the testing equipment. Do not install closer than 6 inches above the well bottom. Remember to use measurements and not the well bottom as silt can clog the pressure transducer. Clamp the pressure transducer cable to the well casing or other static object.

8. View the measured water level in real time on the laptop computer or use water level meter. Wait for the water levels to stabilize. Note that temperature fluctuations on the pressure transducer will affect measured water levels (i.e. temperature differences between the above surface and groundwater environments).

9. Measure the bailer and rope assembly length and mark the rope at a length as follows:

Rope Mark #1 = Depth to Potentiometric Surface from TOC

Rope Mark #2 = Depth to Potentiometric Surface from TOC + Length of Slug + Safety Factor (Safety Factor = 10% of the Length of Slug)

When deployed, this will ensure that the bailer is fully submerged. If a sufficient water column is not available to obtain a full bailer, measure the volume removed upon removal.

10. Slowly insert the bailer into the well and stop just above the potentiometric surface rope mark #1.

11. With slack in the rope and the bailer being suspended above the water column, lower the bailer and place the rope mark #2 at the top of casing. Clamp the non-bailer end of the rope to a static object to keep in place.

12. Wait for water level to equilibrate using response from the laptop computer or from water level meter.

13. Quickly remove the bailer from the water column and carefully pull it to surface. Pour the removed water into an empty bucket.

14. Observe the water level response on the laptop computer and/or measure depth to water, being careful not to interfere with the pressure transducer cable. Several manual depth to water measurements should be made throughout the test.

15. Allow sufficient time for water level to recover to static level. If completing one test, then 80% recovery is sufficient. Duplicate tests are highly recommended and the next test should be completed after the first test has recovered to greater than 95%. A third test at a displacement of twice the initial is recommended.

16. Measure the volume of water removed by the bailer that was poured into the empty bucket using a graduated cylinder.

17. Repeat steps 10 and 15.

18. Repeat rising-head slug tests for data reproducibility. If possible, complete a third test with a bailer or multiple bailers connected in series that equates to twice the volume as the original.

19. Save all data files to the laptop, backup on flash drive and finalize any field notes.

20. Review the data collected to determine the reasonableness of the preliminary results. The observation of apparently anomalous results will be discussed with senior project staff prior to additional testing or leaving the field site. The water level record for each test should show static conditions, the insertion or removal of the slug(s), and the water level response. Make notes on the field form and notebook concerning any irregularities.

21. Decontaminate all down-well equipment.

I. PNEUMATIC SLUG - Scope and Application

Pneumatic slug tests are conducted by sealing the well head and applying air pressure to depress the water level. As air pressure is increased in the well, the water level falls until the water pressure and the air pressure return to equilibrium. After the water level is stable, air is released from the sealed well head by opening an air release valve. The water level recovery is a rising head slug test and produces very high quality data with little interference. A pressure transducer is used to monitor and record the change of the water level in the well during the pneumatic slug test.

II. Equipment List

- Personal protective equipment, as required by the site Health and Safety Plan
- Pneumatic slug test manifold
- Pressure transducer and cable
- Pressure transducer software
- Air pressurization source (compressed or pump) and appropriate hoses
- Leak prevention supplies (Teflon pipe sealant, plumbers putty or similar product)
- Laptop computer
- Water level meter
- Measuring tape
- Decontamination equipment
- Slug test field form
- Field notebook
- Waterproof marker

III. Procedure

1. Decontaminate all down-well equipment: pressure transducer and cable, water level meter.

2. Measure depth to water and well total depth. Determine the water column length.

3. Review the well construction log to determine screened interval and depth to bottom.

4. Attach the pneumatic slug test manifold onto the top of the well casing. Tighten the rubber connector to ensure an airtight seal.

5. Place the pressure transducer at the proper depth (deep enough to accommodate initial change in head but no deeper than six inches abovethe well bottom) by measuring the location where the transducer cable will be secured to the compression connector. Tighten the cable seal by hand to seal the connection to the transducer cable.

6. Program the pressure transducer to record water levels at the following suggested frequencies. Note that the lithologic descriptions and datalogger memory should be used to select the highest measurement frequency possible.

    a. In hydrologic settings where high hydraulic conductivity is expected, water levels should be measured at 0.5 second intervals, or the highest frequency available. This measurement frequency should be selected for gravels and sands.

    b. In hydrologic settings where low hydraulic conductivity is expected, water levels should be measured at 1 to 2 second intervals. This measurement frequency should be selected for silts and clays..

7. View the measured water level in real time on the laptop computer. Wait for the water levels to stabilize. Note that temperature fluctuations on the pressure transducer will affect measured water levels (i.e. temperature differences between the above surface and groundwater environments).

8. Close the air release valve.

9. Close the inlet air valve with the pressure regulator closed.

10. Verify incoming pressure is less than safe operating pressure of manifold pressure regulator (<40 psi is necessary) before attaching air hose (not applicable for hand pump).

11. Attach air hose and open regulator to verify incoming pressure (not applicable for hand pump).

12. Close regulator and open the inlet air valve

13. Slowly open the pressure regulator to pressurize well head and depress water level a sufficient distance without lowering the head below the top of the well screen (2.31 feet of water is equal to 1 psi). Keep the rule of thumb of 1 to 3 feet displacement. Larger displacements may be appropriate for highconductivity formations. Begin with a low pressure and gradually increase the pressure in order to obtain the desired displacement and do not over pressurize the well (do not exceed ~2 psi). If using a hand pump, pressurize well head with pump with regulator open.

14. Close the regulator and leak check the system with leak detection fluid and fix any leaks. If the leak is very slow, or down the well, the regulator may be used to maintain a constant pressure head.

15. Check the pressure transducer response and air pressure to verify system is stable. If it is stable proceed to the next step, if not check the seals.

16. Record a baseline pressure for a minimum three minutes. Record data on the field form.

17. Close inlet valve and quickly open the release valve to initiate the test.

18. Allow sufficient time for water level to recover to static level. If completing one test, then 80% recovery is sufficient. Duplicate tests are highly recommended and the next test should be completed after the first test has recovered to greater than 95%. A third test at a displacement of twice the initial is recommended.

19. Save all data files to the laptop and backup flash drive.

20. Finalize any field notes.

21. Review the data collected to determine the reasonableness of the preliminary results. The observation of apparently anomalous results will be discussed with senior project staff prior to proceeding. The water level record for each test should show static conditions, pressurization of the well column, and the recovery response. Make notes on the field form and notebook concerning any irregularities.

22. Decontaminate all down-well equipment.

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VOLUNTARY REMEDIATION PROGRAM

Standard Operating Procedure No. 41

Specific Capacity Test Procedure

Rev. #: 1

Rev Date: December 2012

Introduction

Specific capacity testing is a field method used to estimate the transmissivity of a saturated geologic medium surrounding the screened or open interval of a well. A specific capacity test involves pumping groundwater from a well at a constant rate and quantifying the pumping rate and the magnitude of drawdown inside of the tested well after a known duration of pumping. Specific capacity tests are also referred to as single well pumping tests or constant rate tests.

The transmissivity is calculated based on the observed test pumping rates, the drawdown measured immediately before the end of pumping, the pumping duration that preceded the drawdown measurement, the effective radius of the well, and the estimated storativity of the formation. If the thickness of the effective water bearing zone transmitting groundwater to the well intake is assumed to be approximately equal to the length of the intake, the hydraulic conductivity can be estimated by dividing the transmissivity by the length of the intake.

Materials

The equipment to be used for specific capacity testing is listed below:

- Peristaltic or submersible pump capable of withdrawing groundwater at a controlled rate between a fraction of one gallon per minute and several gallons per minute;
- Dedicated silicone tubing (for inside the peristaltic pump) and polyethylene tubing (for the intake of the peristaltic pump and discharge of either pump);
- Power source for the pump;
- Calibrated in-line totalizing flow meter or two calibrated buckets;
- Stopwatch; and
- Electronic water-level indicator.

Pre-Test Setup

Prior to installing the submersible pump or peristaltic pump tubing into the well to be tested, the static water level inside the well is measured to the nearest 0.01 feet relative to a specified datum at the top of the well using the electronic water-level indicator. The water level and the time of the measurement are recorded in the field notebook. The water level is measured again several minutes after the initial measurement. This measurement and time are recorded. This

procedure is repeated until two consecutive measurements are identical, indicating approximately static conditions. The static depth to water is recorded.

The submersible pump or peristaltic pump tubing is installed into the well to at least 10 feet below the static water level, or within approximately 1 foot of the bottom of the well if the initial water column in the well is less than 11 feet. The depth of the submersible pump or peristaltic pump tubing below the static water level (indicating the length of the pre-test water column above the pump) is recorded. After the submersible pump or peristaltic pump tubing is installed, but prior to pumping, the water level in the well is monitored until it has returned to within 0.01 feet of the static water level.

Test Procedures

The specific capacity test is performed as follows:

1. Hold the water level probe in the well just above the static water level. If an in-line totalizing flow meter is used, record the pre-test volume measurement in the field notebook. If no in-line flow meter is available, place the end on the discharge line in one of the two calibrated buckets. Record the total volumetric capacity of each bucket.
2. Simultaneously start the pump and the stopwatch. Record the start time.
3. Immediately begin monitoring the water level in the well. If the water level inside the test well declines rapidly, quickly reduce the pumping rate to a slower, constant rate. To avoid pumping the well “dry” during the test, the drawdown after one minute of pumping should be less than or equal to 20% of the height of the pre-pumping water column above the submersible pump or peristaltic pump tubing. All pumping rate adjustments should be completed within one or two minutes of the start of pumping, after which no adjustment should be made other than minor adjustments that may be necessary to maintain a steady pumping rate.
4. Continue to pump for at least 20 minutes, recording the water level in the well approximately every 5 to 10 minutes throughout the test. If an in-line flow meter is used, record the volume measurement on the totalizer gauge approximately every 2 minutes during the test. If calibrated buckets are used to measure the pumping rate, record the time at which the volumetric capacity of the bucket is reached, and record the bucket capacity. Transfer the discharge line to the other (empty) calibrated bucket and record the time when it becomes full. Repeat this procedure for the duration of the test.
5. The specific capacity test is complete after at least 20 minutes of pumping have elapsed. A longer pumping period is not necessary to estimate transmissivity from the test. However, increasing the length of the test may further increase the reliability of the resulting transmissivity estimate. Immediately before the termination of pumping, record the final water level measurement plus the time of the measurement.
6. Calculate and record the total volume of groundwater removed from the well during the test, and the total duration of the test. Divide the total volume (in gallons) by the total pumping

duration (in minutes) to calculate and record the average test pumping rate (in gallons per minute).

Specific Capacity Test Data Reduction

Data from a specific capacity test are reduced to a transmissivity estimate for water-bearing formation surrounding the intake of the tested well by solving for the value of transmissivity in the equation (Walton 1962):

$$Q/s = T / [264 \log(Tt/2693r_w^2S) - 65.5],$$

where Q/s is the specific capacity of the well in gallons per minute per foot, Q is the average test pumping rate in gallons per minute, s is the drawdown measured inside of the tested well after a known duration of pumping (t), T is the transmissivity of the water-bearing zone surrounding the intake of the tested well, S is the estimated storativity of the aquifer, r_w is the effective radius of the well, and t is the time in minutes between the start of pumping and the time when the drawdown was measured. If the well screen is surrounded by a sand pack that may be assumed to be substantially more permeable than the formation, the effective radius of the well is taken to be that of the borehole.

The value of S may be estimated without introducing serious error into the results. For confined aquifers, S should be estimated as 0.0001. For unconfined aquifers, the short-term storativity may be comparable to that of a confined aquifer. Only after a protracted pumping duration (several hours or more) does the storativity begin to approach the aquifer specific yield of approximately 0.2 to 0.3 (Nwankwor et al., 1984). For unconfined aquifers, a storativity value of 0.01 or greater can be used to calculate transmissivity if the specific capacity test is run for greater than one hour.

To obtain an estimate of the hydraulic conductivity of the water-bearing zone that transmits groundwater to the well, the calculated transmissivity value may be divided by the estimated thickness of the water-bearing zone. In a stratified formation in which the horizontal hydraulic conductivity may be expected to greatly exceed the vertical hydraulic conductivity, the thickness of the water-bearing zone may be estimated as the length of the well intake to obtain an estimate of the hydraulic conductivity immediately surrounding the well intake.

It should be noted that the Walton (1962) specific-capacity data analysis method is based on the modified non-equilibrium equation. According to Kruseman and deRidder (1990), these methods are useful provided that:

$$u < 0.15,$$

where $u = r^2S/4Tt$, r= effective well radius, S = storativity, T = transmissivity of the test zone (formation interval adjacent to saturated sandpack), and t is the pumping duration. Following

data analysis, the value of u should be calculated to confirm that the above condition is satisfied. If u > 0.15, then a different hydraulic conductivity test method should be employed.

In addition, in circumstances when the pumping rate is low (e.g., less than 1 gallon per minute) and the drawdown is high or occurs within the sandpack, the water removed from well and sandpack storage should be calculated and subtracted from the pumped volume to estimate the volume of water produced by the formation. The volume of water produced by the formation should be divided by the pumping duration to obtain an effective average test pumping rate for use in calculating T and K.

References

Kruseman, G.P., and N.A. de Ridder. Analysis and Evaluation of Pumping Test Data. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands. Second Edition, Publication 47, 377 p. 1990.

Nwankwor, G.I., Cherry, J.A., and R.W. Gillham, 1985, A comparative study of specific yield determinations for a shallow sand aquifer, Ground Water, Vol. 22, No. 6, pp. 764-772.

Walton, W.C., 1962, Selected Analytical Methods for Well and Aquifer Evaluation, Illinois State Water Survey Bulletin 19.

Attachment B

Field Forms

ARCADIS

Daily Log

Well(s) _____ Project No. AZ001033.0014 Page _____ of _____

Site Location Sierrita Mine, Green Valley, Arizona

Prepared by _____

Date/Time	Description of Activities

ARCADIS

Page_____ of _____

PHOTOGRAPH LOG

Project Number _____ Date _____

Site Description _____

_____

_____

Photo No. Brief Description of Each Photograph

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ARCADIS

Logged By:	Dates Drilled:	Drilling Contractor	Project Name:	Method/Equipment:	Boring Number:

See Unified Soil Classification System for sampling method, classifications and laboratory testing methods.	Boring Diam.(in.):	Surface Elev.(ft.):	Groundwater Depth (ft): First Water ▽ Static Water ▼	Total Depth (ft.):	Drive wt.(lbs.):	Drop Dist.(in.):

Feet (bgs)	Boring or Well Completion	Depth, (ft.)	Sample Recovery	Blows/6"	Classification Letter	Description (classification, color w/code using ASTM standard, grain shape, consistency, moisture, other, odor)	PID/FID (ppm)	Sample Name		Feet (bgs)
1										1
2										2
3										3
4										4
5										5
6										6
7										7
8										8
9										9
10										10
11										11
12										12
13										13
14										14
15										15
16										16
17										17
18										18
19										19
20										20
21										21
22										22
23										23
24										24
25										25

Project No. _____ Date _____ Page **1** of _____

ARCADIS

ARCADIS US
410 North 44th Street, Suite 1000
Phoenix, Arizona 85008

Phone: (602) 438-0883
FAX: (602) 438-0102

Well Development Form

Project Name: Voluntary Remediation Program Groundwater Data Gaps Assessment

Project Numbe AZ001033.0014

Project Locatic Sierrita Mine, Green Valley, Arizona

Project/No. _____ Well ID _____ Date _____

Screened Interval _____ Measuring Point Description _____ Well Materials: ___ PVC ___ St. Steel

Static Water Level _____ Casing Diameter (in) _____ Pump On _____

Pump Off _____

Total depth _____ Boring Diameter (in) _____ Pump Intake _____

Water Column _____ Development Method: Volume Purged (g) _____

Gallons Per Foot _____ Centrifugal _____ Development Criteria: ___ Boring Vol. ___ Casing Vol. ___ Parameters

Submersible _____

Surge Block _____

Gallons in Casing/Boring _____ Bailed _____ Developed By: _____

Other _____

Time	Minutes Relapsed	Rate (gpm) or (ML)	DTW (ft)	Gallons Purged	pH	Cond. (umhos) (ms/cm)	Turb (NTUs)	Redox (mV)	Diss. O2 (mg/L)	TEMP. (C) or (F)	Remarks

Boring/Casing Volumes
2" = 0.16 3" = 0.37 4" = 0.65 6" = 1.47 8" = 2.61 10 " = 4.08 12" = 5.88

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Phone: (602) 438-0883
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Step-Drawdown Pump Test Measurement Form

Project Name:	Voluntary Remediation Program Groundwater Data Gaps Assessment
Project Number:	AZ001033.0014
Project Location:	Sierrita Mine, Green Valley, Arizona

Test Date/Time START:		**Transducer Type:**	
Test Date/Time END:		**Transducer Serial:**	
Well Identification:		**Acquisition Rate:**	HR:MN:SC
Total Depth, TOC:	Feet	**Transducer File:**	
Static Water, TOC:	Feet	**Transducer Depth:**	
Casing Diameter:	Inches	**Pump Depth:**	Feet
Borehole Diameter:	Inches	**Pump Type:**	
Screen Length/Depth	Feet	**Pump Serial:**	

Time (HR:MN:SEC)	Water Level (FT BTOC)	Flow Rate (gpm)	Totalizer (gallons)	Total Discharged (gallons)	Comments
0:00					

Form Recorded By: _____ **Date/Time:** _____

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Step-Drawdown Pump Test Measurement Form

Project Name:	Voluntary Remediation Program Groundwater Data Gaps Assessment
Project Number:	AZ001033.0014
Project Location:	Sierrita Mine, Green Valley, Arizona

Test Date/Time START: _____
Test Date/Time END: _____
Well Identification: _____
Total Depth, TOC: _____ Feet
Static Water, TOC: _____ Feet
Casing Diameter: 4 Inches
Borehole Diameter: 8 Inches
Screen Length/Depth _____ Feet

Transducer Type: _____
Transducer Serial: _____
Acquisition Rate: _____ HR:MN:SC
Transducer File: _____
Transducer Depth: _____
Pump Depth: _____ Feet
Pump Type: _____
Pump Serial: _____

Time (HR:MN:SEC)	Test Well Water Level (FT BTOC)	Flow Rate (gpm)	Totalizer (gallons)	Total Discharged (gallons)	Obs Well: Water Level (FT BTOC)	Obs Well: Water Level (FT BTOC)	Comments
0:00							

Form Recorded By: _____ **Date/Time:** _____

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Constant Rate Test Measurement Form

Project Name:	Voluntary Remediation Program Groundwater Data Gaps Assessment
Project Number:	AZ001033.0014
Project Location:	Sierrita Mine, Green Valley, Arizona

Test Date/Time START:			**Transducer Type:**		
Test Date/Time END:			**Transducer Serial:**		
Well Identification:			**Acquisition Rate:**		HR:MN:SC
Total Depth, TOC:		Feet	**Transducer File:**		
Static Water, TOC:		Feet	**Transducer Depth:**		
Casing Diameter:	4	Inches	**Pump Depth:**		Feet
Borehole Diameter:	8	Inches	**Pump Type:**		
Screen length/Depth		Feet	**Pump Serial:**		

Time (HR:MN:SEC)	Water Level (FT BTOC)	Flow Rate (gpm)	Totalizer (gallons)	Total Discharged (gallons)	Comments
0:00					

Form Recorded By: _____ **Date/Time:** _____

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FAX: (602) 438-0102

Constant Rate Test Measurement Form

Project Name:	Voluntary Remediation Program Groundwater Data Gaps Assessment
Project Number:	AZ001033.0014
Project Location:	Sierrita Mine, Green Valley, Arizona

Test Date/Time START:		**Transducer Type:**	
Test Date/Time END:		**Transducer Serial:**	
Well Identification:		**Acquisition Rate:**	HR:MN:SC
Total Depth, TOC:	Feet	**Transducer File:**	
Static Water, TOC:	Feet	**Transducer Depth:**	
Casing Diameter:	4 Inches	**Pump Depth:**	Feet
Borehole Diameter:	8 Inches	**Pump Type:**	
Screen Length/Depth	Feet	**Pump Serial:**	

Time (HR:MN:SEC)	Test Well Water Level (FT BTOC)	Flow Rate (gpm)	Totalizer (gallons)	Total Discharged (gallons)	Obs Well: Water Level (FT BTOC)	Obs Well: Water Level (FT BTOC)	Comments
0:00							

Form Recorded By: **Date/Time:**

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Phoenix, Arizona 85008

Phone: (602) 438-0883
FAX: (602) 438-0102

Slug Testing Measurement Form

Project Name: Voluntary Remediation Program Groundwater Data Gaps Assessment
Project Number: AZ001033.0014
Project Location: Sierrita Mine, Green Valley, Arizona

Test Date/Time START: ______________
Test Date/Time END: ______________
Well Identification: ______________
Total Depth, TOC: ______________ Feet
Static Water, TOC: ______________ Feet
Casing Diameter: ______________ Inches
Borehole Diameter: ______________ Inches
Screen Length/Depth ______________ Feet

Transducer Type: ______________
Transducer Serial: ______________
Acquisition Rate: ______________ HR:MN:SC
Transducer File: ______________
Slug Type: ______________
Initiation Method: ______________
Rising/Falling Head: ______________

Time (HR:MN:SEC)	Water Level (FT BTOC)	Comments
0:00		

Time (HR:MN:SEC)	Water Level (FT BTOC)	Comments
0:00		

Form Recorded By: ______________ **Date/Time:** ______________

Page /

ARCADIS

ARCADIS US
410 North 44th Street, Suite 1000
Phoenix, Arizona 85008

Phone: (602) 438-0883
FAX: (602) 438-0102

Ground And Surface Water Sample Field Data Sheet

Project Name: Voluntary Remediation Program Groundwater Data Gaps Assessment
Project Number: AZ001033.0014
Project Location: Sierrita Mine, Green Valley, Arizona

General Information

Instrument Type: ______ Weather: ______
Instrument Number: ______
Sampler's Name: ______
Date(s): ______

Well/Boring Information

Location/Boring Number: ______ Date: ______
Well/Boring Diameter (in): ______ Time: ______
Sample Identification: ______
Sampler's Signature: ______
Depth to Water Level (ft-btoc): ______
Total Depth of Well (ft-btoc): ______
Well Casing Volume (gallons): ______
Volume to be Purged (gallons): ______

Field Water Quality Parameter Measurements

	Initial	1st Vol	2nd Vol	3rd Vol	4th Vol	5th Vol	Sample
Time:							
Volume (gallons):							
pH (SI units)							
Temperature (^{o}C):							
Conductivity (umhos/cm):							
Salinity (%):							
Dissolved Oxygen (mg/L):							
Turbidity (Ntus):							
Color:							
Odor:							

Sample Collection Information

Containers	Number	Preservatives	Analyses

QA/QC Samples Collected: ______

Comments:

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Appendix B

Quality Assurance Project Plan
Addendum

ARCADIS
Infrastructure · Water · Environment · Buildings

Imagine the result

Freeport-McMoRan Sierrita Inc.

Quality Assurance Project Plan Addendum

Voluntary Remediation Program
Sierrita Mine

Green Valley, Arizona

November 2014

ARCADIS

Penny Hunter
Principal Scientist/CPM

Dennis Capria
ARCADIS Quality Assurance Coordinator

Voluntary Remediation Program

Quality Assurance Project Plan Addendum

Sierrita Mine
Green Valley, Arizona

Prepared for:

Freeport-McMoRan Sierrita Inc.

Prepared by:
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Tel 303-231-9115
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Our Ref.:
AZ001233.0014.0001

Date:
November 2014

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2 c Parameters, Methods, and Target Reporting Limits for Metals – Soil

3 Sample Containers, Preservation, and Holding Times

4 Analytical Quality Control Limits

Attachments

Attachment A Laboratory Standard Documentation (On Disk)

Attachment B EQuIS Standard Operating Procedure

ARCADIS

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ARCADIS

Acronyms

ADEQ	Arizona Department of Environmental Quality
ADHS	Arizona Department of Health Services
AWQS	Arizona Aquifer Water Quality Standards
CLP	Contract Laboratory Program
DQO	Data Quality Objectives
EDD	Electronic Data Deliverable
GPL	Groundwater Protection Limit
NFG	National Functional Guideline
QAC	Quality Assurance Coordinator
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
RPD	Relative Percent Difference
SAP	Sample Analysis Plan
Sierrita	Freeport-McMoRan Sierrita Inc.
Site	The Sierrita VRP Site
SOP	Standard Operating Procedure
SPLP	Synthetic Precipitation Leaching Procedure
SRL	Soil Remediation Level
TDS	Total Dissolved Solids
URS	URS Corporation
USEPA	United States Environmental Protection Agency
VRP	Voluntary Remediation Program

1. Introduction

This Quality Assurance Project Plan (QAPP) is an Addendum to the QAPP (URS Corporation [URS] 2008) prepared for groundwater and soil investigation activities and data collection/data management for the Arizona Department of Environmental Quality's (ADEQ) Arizona Voluntary Remediation Program (VRP). This QAPP Addendum provides guidance for data collection and analysis associated with the Freeport-McMoRan Sierrita Inc. (Sierrita) VRP Site (Site), located 6200 West Duval Mine Road, Green Valley, Pima County, Arizona.

This QAPP was prepared by ARCADIS to address updates to laboratory analysis methods and standard operating procedures (SOPs) for data collection described in ARCADIS Data Gaps Work Plan (Work Plan) and associated Sampling and Analysis Plan (SAP). The QAPP is directed towards the VRP as it addresses groundwater and soil sampling and analysis.

This QAPP Addendum, along with the QAPP (URS 2008) are intended to guide all sampling, measurement, and other field and laboratory measurement activities conducted as part of the work performed by ARCADIS. To the extent that previous and future work plans are written and approved relevant to this QAPP Addendum, those activities will be incorporated by reference to the scope of the QAPP Addendum herein. This QAPP Addendum was prepared in a manner consistent with the following documents, where applicable:

- ADEQ Quality Management Plan. EQR 10-04 August 2010. https://azdeq.gov/function/programs/download/qmp.pdf

- United States Environmental Protection Agency (USEPA) guidance document entitled *EPA Requirements for Quality Assurance Project Plans*, EPA-QA/R-5 (USEPA 2001, Reissued May 2006) http://epa.gov/quality/qs-docs/r5-final.pdf

- USEPA *Guidance for Quality Assurance Project Plans,* EPA-QA/G-5 (USEPA 2002); http://epa.gov/quality/qs-docs/g5-final.pdf

Information contained in this QAPP Addendum has been organized into the following sections:

Section	Content
Project Management	
1	Project Description
2	Project Organization
Measurement/Data Acquisition	
3	Quality Objectives and Criteria for Measurement Data
4	Analytical Laboratory Procedures
5	Data Verification and Validation

Details on each of the subjects listed above are provided in the subsequent sections.

1.1 Project Description

The data collection is to be performed under the ADEQ's Arizona VRP. For a project description, please see the Work Plan for details.

1.2 Project Schedule

An estimated schedule for the planning and data gap characterization activities will be developed for the project. The field activities, starting with pre-mobilization, are estimated to begin following review and approval of the Work Plan and QAPP.

2. Project Organization

The activities to be completed under the Work Plan will require integration of personnel from the organizations identified below, collectively referred to as the "project team." The responsibilities of each member of the project team are detailed below.

2.1 Overall Project Management

ARCADIS personnel will perform project-related sampling activities and will evaluate data and prepare associated deliverables as specified in the Work Plan. Project direction will be provided by the ADEQ VRP. A list of key project management personnel is provided below.

Company/Organization	Title	Name	Phone Number
Freeport-McMoRan Sierrita Inc.	Project Manager	Deborah Chismar	520.393.2347
VRP	Project Manager	John Patricki	602.771.4397
	Project Manager	Danielle Taber	602.771.4414
ARCADIS	Project Manager	Penny Hunter	303.231.9115x154
ALS Laboratories	Project Manager	Debbie Fazio	970.224.2559
	QA Manager	Robert P.DiRienzo	970.224.2559
SLV Laboratories	Project Manager	Christine Meyer	208.784.1258
	QA Manager	John. L Kern	208.784.1258

2.2 Task Managers

The staff performing the site activities will be directed by representatives of the project team. The personnel responsible for each of the site activities are listed below.

Company/Organization	Title	Name	Phone Number
ARCADIS	Field Coordinator/Field Operations Manager	Shawn Roberts	913.492.0900
	Health and Safety Officer	TBD	TBD
	QA Officer	Dennis Capria	315.671.9299
	Data Validator	Mary Ann Doyle	518.250.7386

3. Quality Objectives

This section addresses the data quality objective (DQO) process applied in development of the Sierrita VRP QAPP. The DQO process is a systematic planning tool based on the Scientific Method for establishing criteria for data quality and for developing data collection designs. Establishing formal DQOs during the QAPP stage of a project allows clear and unambiguous definition of project objectives, decisions, and decision criteria so that data of sufficient type, quality, and quantity are generated to meet project objectives. The formal implementation of a DQO process brings structure to the planning process, thereby resulting in defensible decision-making.

3.1 Specifying Quality Objectives

The DQO process is a series of planning steps designed to ensure that the type, quantity, and quality of environmental data used in decision-making are appropriate for the intended purpose. USEPA has issued guidelines to help data users develop project-specific DQOs (USEPA 2006). These guidelines were followed for the development of the DQOs for data gaps, and are identified in the Work Plan.

Site characterization activities for the VRP were performed in 2008 and 2009. Table 2 of the Work Plan summarizes these sampling activities, including the objectives, a results, preliminary conclusions, and recommendations for each groundwater sampling location. Data gaps were identified following these activities, and the responses or action items identified is presented in Table 3 of the Work Plan. These data gaps identify supplemental site characterization activities.

4. Analytical Laboratory Procedures

Field activities are described in the Work Plan and supplemental SAP, and include descriptions of sample collection and preparation procedures, field decontamination procedures, and field screening methods. The field activities will involve collecting environmental samples and associated quality control (QC) samples. The anticipated number of samples to be collected, the number of QC samples, and the constituents to be analyzed are presented in Table 1.

4.1 Laboratory Selection

The analytical analysis will be performed by Arizona Department of Health Services-(ADHS-) approved laboratories: ALS located in Fort Collins, Colorado and SVL Laboratory located in Kellogg, Idaho. All associated laboratory documentation including Quality Assurance Manual, Laboratory SOPs, and Certifications, are provided in Attachment A.

The tables listed below summarize the general analytical requirements:

Table	Title
1	Sample Quantities and Quality Control Frequencies
2a, 2b	Parameters, Methods, and Target Reporting Limits – Groundwater
2c	Parameters, Methods, and Target Reporting Limits – Soil
3	Sample Containers, Preservation, and Holding Times
4	Analytical Quality Control Limits

The primary sources to describe the analytical methods to be used during the investigation sampling are provided in USEPA SW-846 Test Methods for Evaluating Solid Waste, Third Edition, Update 4.

Groundwater, soil, and concrete samples will be analyzed following the methods listed in Tables 2a through 2c and QC frequencies listed in Table 1. Results for all matrices will be reported in units presented in Table 2a through 2c.

4.1 Analytical Method Requirements

Table 4 presents advisory precision and accuracy QC limits for chemical constituents used during data review to assess analytical performance. Tables 2a through 2c indicate that the method reporting limits for each metal and radionuclide are lower than their respective relevant action levels (URS 2008), which include Aquifer Water Quality Standard (AWQS), Soil Remediation Level (SRL), and Groundwater Protection Limit (GPL). Data representativeness is addressed by the sample quantities and locations identified in the Work Plan and in Table 1 of this QAPP Addendum. All applicable method requirements and action levels are documented and cited in the appropriate tables (Tables 1 through 4, respectively).

Data comparability will be achieved by using standard USEPA-approved methods. Data completeness will be assessed at the conclusion of the analytical activities.

4.2 Analytical Methods

Samples collected during the investigation will be measured for concentrations of specific analytes, as shown in Tables 2a through 2c. In summary, groundwater samples will be analyzed for the following:

- Dissolved Metals by USEPA 200.7 or 200.8 or 245.1
- U-234 by ASTM D3972(U-02)
- U-235 by ASTM D3972(U-02)
- U-238 by ASTM D3972(U-02)
- Ra-226 by USEPA 903.1
- Ra-228 by USEPA 904.0
- Gross alpha by USEPA 900.0
- Gross beta by USEPA 900.0
- Bicarbonate as $CaCO_3$ by SM2320B

- Carbonate as $CaCO_3$ by SM2320B
- Total Alkalinity by SM2320B
- Chloride by USEPA 300.0
- Conductivity by USEPA120.1
- Fluoride by SM 4500
- Hardness as $CaCO_3$ by USEPA 200.7 as calculation
- Nitrate/Nitrite as Nitrogen by USEPA 353.2
- pH by USEPA 9040B
- Total Dissolved Solid (TDS) by SM2540C
- Sulfate by SM 4500

Soil samples will be analyzed for the following:

- Synthetic Precipitate Leaching Procedure (SPLP) Antimony by SPLP 1312; USEPA 6010
- Total Antimony by USEPA 6010

Current USEPA-approved and SW-846 methods will be used for all applicable parameters and sample media. The primary sources to describe the analytical methods to be used during the investigation sampling are provided in USEPA Test Methods for Evaluating Solid Waste, Third Edition, Update IV Washington, D.C. 1996.

4.3 Data Categories

Three data categories have been defined in the QAPP (URS 2008) to address various analytical data uses and the associated quality assurance/quality control (QA/QC) effort and methods required to achieve the desired levels of quality. A conformance

summary document will be performed by the laboratory on the analytical results to confirm that the data meet the method's QA/QC requirements. These categories are:

Screening Data: Screening data affords a rapid preliminary assessment of site characteristics or conditions. These data collection activities involve rapid, non-rigorous methods of analysis and quality assurance. Screening DQOs are generally applied to physical and/or chemical properties of samples, preliminary ecological and/or human health and safety indicators, and visual or other qualitative observations used to make rapid assessment decisions for deployment or additional assessment.

Screening Data with Definitive Confirmation: Screening data provide rapid identification and quantitation; however, because screening generally involves the use of less precise methods of analysis with less rigorous sample preparation, the quantitation may be relatively imprecise. Generally, at least 10 percent of the data are confirmed using analytical methods and QA/QC procedures and criteria associated with definitive data. This objective can also be used to verify less rigorous laboratory-based methods. This objective of data quality is available for data collection activities that require qualitative and/or quantitative verification of a select portion of sample findings.

Definitive Data: Definitive data are generated using rigorous analytical methods, such as approved USEPA reference methods. Data are analyte-specific, with confirmation of analyte identity and concentration. Methods produce tangible raw data (e.g., chromatograms, spectra, digital values). Data may be generated at the Site or at an off-site location, as long as the QA/QC requirements are satisfied. For data to be definitive, either analytical or total measurement error must be determined. Definitive data are used for formal site characterization, environmental monitoring, confirmation of field data, to support decision-making, and for risk assessments.

It is anticipated that both screening and definitive data will be collected during the assessment. Groundwater and soil samples may be collected for laboratory analysis or for observational review to refine and optimize the sampling and assessment approach. For the purposes of the assessment, three levels of data reporting have been defined. They are as follows:

Level 1 – Minimal Reporting. Minimal or "results only" reporting is used for analyses that, due either to their nature (e.g., field monitoring) or the intended data use (e.g., preliminary screening), do not generate or require extensive supporting documentation.

Level 2 – Modified Reporting. Modified reporting is used for analyses that are performed following standard USEPA-approved methods and QA/QC protocols. Based on the intended data use, modified reporting may require some supporting documentation, but not full Contract Laboratory Program- (CLP-) type reporting.

The following are Level 2 laboratory data report required elements:

- Chain of custody
- Case narrative
- Final parameter concentration for all samples
- Preparation or extraction and analysis dates/times
- Method blanks
- Matrix spike and matrix spike duplicate recoveries and relative percent difference (RPD)
- Laboratory duplicate RPD
- Laboratory control sample recoveries.

Level 4 - Full Reporting: Full "CLP-type" reporting is used for those analyses that, based on the intended data use, require full documentation. The Level 4 laboratory data report includes the elements for Level 2 listed above and the following:

- Calibrations (initial and continuing)
- Instrument blanks
- Internal standard areas
- Serial dilution %D
- Raw data output for all field samples and associated QA/QC samples.

It is anticipated that both screening and definitive data will be generated during the investigation.

4.4 Laboratory Quality Control

The purpose of the laboratory QA/QC program is to produce data of known quality that satisfy the project objectives and that meet or exceed the requirements of the standard methods of analysis.

According to each laboratory Quality Assurance Manual submitted in Attachment A, all internal laboratory QC checks will be used to monitor data integrity. These checks will include method blanks, laboratory control samples, matrix spike/matrix spike duplicates, laboratory duplicates, internal standards, surrogate samples, and calibration standards. Project laboratory QC limits are identified in Table 4. Laboratory control charts will be used to determine long-term instrument trends and control limits.

The QA managers at each laboratory will be responsible for conducting and reporting corrective actions if problems arise during the course of laboratory analytical procedures. Deficiencies discovered as a result of the data review, as well as the corrective actions implemented in response, will be documented and submitted in the form of a written report addressing the following topics, as applicable to each method:

- Assessment of the data package
- Description of any protocol deviations
- Failures to reconcile reported and/or raw data
- Assessment of any compromised data
- Qualify data as appropriate
- Overall appraisal of the analytical data
- Table of site name, sample quantities, matrix, and fractions analyzed.

It should be noted that qualified results do not necessarily invalidate data. The goal to produce the best possible data does not necessarily mean that data must be produced without QC qualifiers. Qualified data can provide useful information.

During the review process, laboratory qualified and unqualified data are verified against the supporting documentation. Based on this evaluation, qualifier codes may be added, deleted, or modified by the data reviewer.

Resolution of any issues regarding laboratory performance or deliverables will be handled between the laboratory and the data validator. Suggestions for reanalysis, if necessary, may be made by the Quality Assurance Controller (QAC) at this point.

4.1 Data Qualifiers

When appropriate the laboratories will qualify the analytical data using the State of Arizona Data Qualifiers, Revision 3.0, 2007.

4.2 Laboratory reporting

Analytical results will be reported by the laboratory in pdf format and EDD format outlined in EQUIS Lab SOP FSMP Rev. 9 (Attachment B) and of the Form Is (results sheets) in a PDF or electronic spreadsheet format, within 15 working days from date of receipt.

5. Data Verification and Validation

Data verification and validation will be conducted as outlined in USEPA Guidance on Environmental Data Verification and Data Validation EPA QA/G-8 (USEPA 2002), USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, October 2004, and the Inorganic Data Standard Operating Procedures, USEPA Region IX, available at the time of project initiation, where appropriate. These procedures and criteria may be modified, as necessary, to address project-specific and method-specific criteria, control limits, and procedures. Data validation will be conducted in accordance with the USEPA National Functional Guidelines (NFGs).

The ARCADIS Project Chemistry group meets the requirements of third-party data validation as described in USEPA document G-8, referenced above. The personnel performing validation are not associated with the field staff involved in the collection of samples or end users (project team) preparing data reports for the client.

5.1 Data Verification

The data verification process evaluates completeness, correctness, and general compliance of specific data against the method, procedure, and any contractual requirements. Data verification ensures that the records associated with a specific data set actually reflect all of the processes and procedures used to generate the data.

One hundred percent of the samples in the overall data set will be data verified. The data validator will verify that reduction of laboratory measurements and laboratory reporting of analytical parameters is in accordance with the procedures specified for each analytical method and/or as specified in this QAPP Addendum. Any deviations from the analytical method or any special reporting requirements apart from those specified in this QAPP Addendum will be detailed on chain-of-custody forms.

5.2 Data Validation

Data validation is a standardized review process for judging the analytical quality and usefulness of a discrete set of chemical data and is necessary to ensure that data of known and documented quality are used in making environmental decisions that meet the DQOs for the Site. Data validation is a systematic process that compares a body of data to the requirements in a set of documented acceptance criteria to ascertain its

completeness, correctness, and consistency. The data validator uses all data verification records, including the verified data, to perform the steps of data validation.

One hundred percent of the samples will be Level 2 data validated. Ten percent of the overall data set will be validated as a Level 4 review. The Level 2 validation will include a review of the chain of custody and sample receipt, holding times, method blanks, field blanks, equipment blanks, matrix spike/matrix spike duplicate recoveries, and RPD, laboratory duplicate RPD, laboratory control sample/laboratory control sample duplicate recoveries and RPD for all methods where applicable, and package completeness.

In addition to the Level 2 elements, a Level 3 includes a detailed review of initial calibration, continuing calibration, tuning, transcription errors, and laboratory raw data to check for errors in calculation and compound identification. All data provided by the laboratory will be validated for all QA/QC parameters including accuracy, precision, completeness, and comparability in accordance with USEPA guidance. All validation and verification reports will be prepared in accordance with ADEQ-approved checklists, if applicable.

Data validation reports and all EDDs will be kept in electronic format (PDF) at the environmental consultant's office.

6. References

American Public Health Association (APHA). 1998. 20th edition Standard Methods for the Examination of Water and Wastewater.

ARCADIS. 2014a. Data Gap Work Plan, Freeport Sierrita Mine Green Valley, Arizona. August 2014.

ARCADIS. 2014b. Sampling and Analysis Plan, Freeport Sierrita Mine Green Valley, Arizona. August 2014.

Arizona Administrative Code (A.A.C.), Title 18. Environmental Quality, Department of Environmental Quality Remedial Action, R18-7-205ADEQ, January 2007.

URS Corporation (URS). 2008. Addendum to Sampling & Analyses Plan (SAP) & Quality Assurance Project Plan (QAPP), Voluntary Remediation Program (VRP), Freeport-McMoRan Sierrita Green Valley, Arizona. Prepared for Freeport-McMoRan Sierrita Inc. September.

U.S. Environmental Protection Agency (USEPA). 1993. Methods for the Determination of Inorganic Substances in Environmental Samples, EPA/600/R−930100.

USEPA. 1996. Test Methods for Evaluating Solid Waste. Washington, D.C., SW-846 Third Edition, Update 4: Office of Solid Waste and Emergency Response. December 1996.

USEPA. 2002. Guidance for Quality Assurance Project Plans. EPA-QA/G-5. Office of Environmental Information, December 2002.USEPA 2002. Guidance on Environmental Data Verification and Data Validation EPA QA/G-8, Office of Environmental Information, November 2002.

USEPA. 2004. Contract Laboratory Program National Functional Guidelines for Inorganic Data Review. EPA-540/R-04-004. October 2004.

Tables

Table 1
Sample Quantities and Quality Control Frequencies
QAPP Addendum
Freeport-McMoRan Sierrita Inc.

Parameter	Estimated Environmental Sample Quantity	Field QC Analyses				Laboratory QC Sample						Total
		Trip Blank		Field Duplicate		Matrix Spike		Matrix Spike Duplicate		Lab Duplicate		
		Freq.	No.	Freq.	No.	Freq.	No.	Freq.	No.	Freq.	No.	
Groundwater												
Dissolved Metals (200.7/200.8) [1]	TBD	--	--	1/20	1	1/20	1	1/20	1	1/20	1	TBD
Dissolved Mercury (245.1) [1]	TBD	--	--	1/20	1	1/20	1	1/20	1	1/20	1	TBD
Bicarbonate as CaCO3 (SM2320B)	TBD	--	--	1/20	1	NA	--	NA	--	1/20	1	TBD
Carbonate as CaCO3 (SM2320B)	TBD	--	--	1/20	1	NA	--	NA	--	1/20	1	TBD
Chloride (EPA 300.0)	TBD	--	--	1/20	1	1/20	1	1/20	1	1/20	1	TBD
Conductivity (EPA120.1)	TBD	--	--	1/20	1	NA	--	NA	--	1/20	1	TBD
Fluoride (EPA 300.0)	TBD	--	--	1/20	1	1/20	1	1/20	1	1/20	1	TBD
Hardness as CaCO3 (SM 2340B)	TBD	--	--	1/20	1	1/20	1	1/20	1	1/20	1	TBD
Nitrate/Nitrite as N (EPA 353.2)	TBD	--	--	1/20	1	1/20	1	1/20	1	1/20	1	TBD
pH (SM4500)	TBD	--	--	1/20	1	NA	--	NA	--	1/20	1	TBD
Total Dissolved Solid (TDS) (SM 2540C)	TBD	--	--	1/20	1	NA	--	NA	--	1/20	1	TBD
Sulfate (EPA 300.0)	TBD	--	--	1/20	1	1/20	1	1/20	1	1/20	1	TBD
Total Alkalinity (SM 2320)	TBD	--	--	1/20	1	NA	--	NA	--	1/20	1	TBD
Gross alpha (EPA 900.0)	TBD	--	--	1/20	1	1/20	1	1/20	1	1/20	1	TBD
Gross beta (EPA 900.0)	TBD	--	--	1/20	1	1/20	1	1/20	1	1/20	1	TBD
Ra-226 (EPA 903.1)	TBD	--	--	1/20	1	1/20	1	1/20	1	1/20	1	TBD
Ra-226 + Ra-228 (Calculation) [2]	--	--	--	--	--	--	--	--	--	--	--	--
Ra-228 (EPA 904.0)	TBD	--	--	1/20	1	1/20	1	1/20	1	1/20	1	TBD
U-234 (ASTM D3972)(U-02)	TBD	--	--	1/20	1	1/20	1	1/20	1	1/20	1	TBD
U-235 (ASTM D3972)(U-02)	TBD	--	--	1/20	1	1/20	1	1/20	1	1/20	1	TBD
U-238 (ASTM D3972)(U-02)	TBD	--	--	1/20	1	1/20	1	1/20	1	1/20	1	TBD
Soil												
Antimony (SPLP 1312 EPA 6010)	6	--	--	1/20	1	1/20	1	1/20	1	1/20	1	10
Antimony (EPA 6010)	6	--	--	1/20	1	1/20	1	1/20	1	1/20	1	10

Notes:

[1] Dissolved Metals suite includes: Aluminum, Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Mercury, Molybdenum, Nickel, Potassium, Sodium, Selenium, Thallium, Uranium, Zinc.

[2] Ra-226 + Ra-228 is a calculated parameter and although it is reported, it is not included in sample environmental and quality control sample analyses.

Freq- Frequency

TBD-To be determined

-- Not applicable

No.- Number

QC- Quality Control

Table 2a
Parameters, Methods, and Target Reporting Limits for Radionuclides – Groundwater
QAPP Addendum
Freeport-McMoRan Sierrita Inc.

Analyte	CAS Number	Groundwater AWQS (mg/L)	MDC (pCi/L)
Groundwater Radiochemical Analysis			
U-234 (ASTM D3972)(U-02)	13966-29-5	NE	0.2
U-235 (ASTM D3972)(U-02)	15117-96-1	NE	0.2
U-238 (ASTM D3972)(U-02)	7440-61-1	NE	0.2
Ra-226 (EPA 903.1)	13982-63-3	NE	1
Ra-226 + Ra-228 (Calculation)[1]	--	5	--
Ra-228 (EPA 904.0)	15262-20-1	NE	1
Gross alpha (EPA 900.0)	12587-46-1	15	3
Gross beta (EPA 900.0)	12587-47-2	4 millirem/year[2]	4

Notes:

USEPA. United States Environmental Protection Agency. Office of Solid Waste and Emergency Response. *Test Methods for Evaluating Solid Waste SW-846 3rd ed. Update IV Washington, D.C 1996*

ASTM Method D3972 (U-02) American Society for Testing and Materials; ALS Standard Operating Procedure, Actinides-Uranium, Plutonium and Americum/Currium (Partial)

Sequential Separation By Ion Exchange Referenced Method: ASTM 3972, DOE U-02, SOP ID: 778, Revision R14, Effective Date: April 22, 2013.

[1] Ra-226 + Ra-228 is a required calculated parameter

[2] AWQS is 4 millirem/year or approximately 50 pCi/L

Acronyms and Abbreviations:

AWQS = Aquifer Water Quality Standards

MDC Minimum Detectable Concentration (No Reporting Limit or Minimum Detection Limit for this method)

NE No Standard Established

pCi/L = picocuries per liter

Table 2b
Parameters, Methods, and Target Reporting Limits for Metals – Groundwater
QAPP Addendum
Freeport-McMoRan Sierrita Inc.

Analyte	CAS Number	Groundwater AWQS (mg/L)	MDL (mg/L)	RL (mg/L)
Groundwater				
Dissolved Metals				
Aluminum EPA 200.7	7429-90-5	NE	0.036	0.080
Antimony EPA 200.8	7440-36-0	0.006	0.000026	0.003000
Arsenic EPA 200.8	7440-38-2	0.01	0.00031	0.003000
Barium EPA 200.7	7440-39-3	2.0	0.0006	0.002
Beryllium EPA 200.8	7440-41-7	0.004	0.00005	0.0002
Cadmium EPA 200.8	7440-43-9	0.005	0.000031	0.000200
Calcium EPA 200.7	7440-70-2	NE	0.029	0.040
Chromium EPA 200.7	7440-47-3	0.1	0.0018	0.006
Cobalt EPA 200.7	7440-48-4	NE	0.00072	0.006
Copper EPA 200.7	7440-50-8	NE	0.003	0.010
Iron EPA 200.7	7439-89-6	NE	0.023	0.060
Lead EPA 200.8	7439-92-1	0.05	0.000035	0.003
Magnesium EPA 200.7	7439-95-4	NE	0.090	0.200
Manganese EPA 200.7	7439-96-5	NE	0.0013	0.004
Mercury EPA 245.1	7439-97-6	0.002	0.000045	0.0002
Molybdenum EPA 200.7	7439-98-7	NE	0.0027	0.008
Nickel EPA 200.7	7440-02-0	0.1	0.002	0.010
Potassium EPA 200.7	7440-09-7	NE	0.170	0.500
Sodium EPA 200.7	7440-23-5	NE	0.07	0.500
Selenium EPA 200.8	7782-49-2	0.05	0.00052	0.003000
Thallium EPA 200.7	7440-28-0	NE	0.0058	0.015
Uranium EAP 200.8	7440-61-1	NE	0.000028	0.001000
Zinc EPA 200.7	7440-66-6	NE	0.003	0.010
General Chemistry Parameters				
Bicarbonate as CaCO3 (SM2320B)	471-34-1 (HCO3)	NE	--	1.0
Carbonate as CaCO3 (SM2320B)	471-34-1 (CO3)	NE	--	1.0
Total Alkalinity (SM2320B)	471-34-1 (ALK)	NE	--	1.0
Chloride (EPA 300.0)	16887-00-6	NE	0.047	0.20
Conductivity (EPA120.1)	NA	NE	--	5.0 umhos/cm
Fluoride (EPA 300.0)	16984-48-8	NE	0.027	0.10
Hardness as CaCO3 (SM 2340B)[1]	NA	NE	--	--
Nitrate/Nitrite as Nitrogen (EPA 353.2)	NA	NE	0.033	0.05
pH (SM4500)	NA	NE	--	1.0 s.u.
Total Dissolved Solid (TDS) (SM2540C)	NA	NE	--	10
Sulfate (EPA 300.0)	14808-79-8	NE	0.055	0.30

Notes:

USEPA. United States Environmental Protection Agency. Office of Solid Waste and Emergency Response. *Test Methods for Evaluating Solid Waste SW-846 3rd ed. Update IV Washington, D.C 1996*

[1] Total Hardness is reported as a calculation.

Acronyms and Abbreviations:

AWQS = Arizona Aquifer Water Quality Standards
NE No Standard Established
MDL Minimum Detection Limit
RL Reporting Limit
s.u. Standard Unit scale 1 - 14
umhos/cm Micromhos per centimeter or Nephelometric Turbidity Units

Table 2c
Parameters, Methods, and Target Reporting Limits for Metals – Soil
QAPP Addendum
Freeport-McMoRan Sierrita Inc.

Analyte	CAS Number	Soil Residential SRL[1]				Reporting limits	
		mg/kg				MDL mg/L or mg/kg	RL mg/L or mg/Kg
		Carcinogen 10^{-6} Risk	Carcinogen 10^{-5} Risk	Non-Carcinogen	Non-residential SRL		
Soil							
Metals							
Antimony, SPLP (EPA 6010 SPLP 1312)	7440-36-0	NE	NE	NE	NE	0.000026 mg/L	0.003 mg/L
Antimony, Total (EPA 6010)	7440-36-0	NE	NE	31	410	0.78 mg/Kg	2 mg/Kg

Notes:

[1] Arizona Administrative Code. Title 18, Chapter 7. Title 18. Environmental Quality, Chapter 7. Arizona Department of Environmental Quality Remedial Action. Appendix A. Soil Remediation Levels (SRLs). http://www.azsos.gov/public_services/title_18/18-07.htm

Acronyms and Abbreviations:

NE No Standard Established
MDL Minimum Detection Limit
RL Reporting Limit

Table 3
Sample Containers, Preservation, and Holding Times
QAPP Addendum
Freeport-McMoRan Sierrita Inc.

Parameter	Methods[1,2,3]	Bottle Type[4]	Preservation	Holding Time[2]
Groundwater				
Metals Dissolved	EPA 200.7/200.8/245.1	1-500 mL HDPE Bottle	HNO3 to pH<2; Cool to <6°C	6 months
Hardness as CaCO3	SM 2340B	Analyze from sample in Metals Dissolved bottle	HNO3 to pH<2; Cool to <6°C	6 months
Total Alkalinity	SM2320B	1-500 mL HDPE Bottle	None	14 days
Bicarbonate as CaCO3				
Carbonate as CaCO3				
Chloride	EPA 300.0	Analyze from sample in the Total Alkalinity bottle	None	28 days
Fluoride				
Total Dissolved Solid (TDS)	SM 2540C	Analyze from sample in the Total Alkalinity bottle	None	7 days
Sulfate	EPA 300.0		None	28 days
Conductivity	EPA120.1	Analyze from sample in the Total Alkalinity bottle	None	28 days
pH	SM4500		None	Analyze immediately
Nitrate and Nitrite as N	EPA 353.2	1-500 mL HDPE Bottle	H2SO4 to pH<2; Cool to <6°C	28 days
U-234	(ASTM D3972)(U-02)	1-1000 mL Polyethylene Bottle	HNO3 to pH<2; Cool to <6°C	NA
U-235				
U-238				
Ra-226	EPA 903.1	Analyze from sample in Ra-228 bottle	HNO3 to pH<2; Cool to <6°C	NA
Ra-226 + Ra-228 (Calculation)	NA	NA	NA	NA
Ra-228	EPA 904.0	1-2000 mL Polyethylene Bottle	HNO3 to pH<2; Cool to <6°C	NA
Gross alpha	EPA 900.0	1-500 mL Polyethylene Bottle	HNO3 to pH<2; Cool to <6°C	NA
Gross beta	EPA 900.0	Analyze from sample in Gross alpha bottle	HNO3 to pH<2; Cool to <6°C	NA
Soil				
SPLP Antimony	SPLP 1312 EPA 6010	8 oz soil jar	Collection to extraction asap; extraction preserved HNO3 to pH<2; Cool to <6°C	180 days
Total Antimony	EPA 6010	8 oz soil jar	Cool to <6°C	180 days

Notes:

[1] USEPA. Office of Solid Waste and Emergency Response. *Test Methods for Evaluating Solid Waste. SW-846 3rd ed. Update IV Washington, D.C. 1996.*

[2] All holding times are measured from date of collection.

[3] ASTM Method D3972 (U-02) American Society for Testing and Materials; ALS Standard Operating Procedure, Actinides-Uranium, Plutonium and Americum/ Currium (Partial) Sequential Separation By Ion Exchange Referenced Method: ASTM 3972, DOE U-02, SOP ID: 778, Revision R14, Effective Date: April 22, 2013.

[4] HDPE High Density Polyethylene

Acronyms and Abbreviations:

NA Not Applicable
HNO3 Nitric Acid
mL milliliter

Table 4
Analytical Quality Control Limits
QAPP Addendum
Freeport-McMoRan Sierrita Inc.

Parameter	Accuracy - % Recovery			Precision - RPD/DER		
	Surrogate	MS/MSD	LCS	MS/MSD /RPD	Lab Duplicate	Field Duplicate
Groundwater- Inorganic						
Metals, Dissolved (200.7/200.8)	--	70-130	85-115	20	20	30
Mercury, Dissolved (EPA 245.1)	--	70-130	85-115	20	20	30
Total Alkalinity (SM 2320)	--	--	85-115	--	20	30
Bicarbonate as CaCO3 (SM2320B)	--	--	85-115	--	20	30
Carbonate as CaCO3 (SM2320B)	--	--	85-115	--	20	30
Chloride (EPA 300.0)	--	90-110	90-110	20	20	30
Conductivity (EPA120.1)	--	--	--	--	20	30
Fluoride (EPA 300.0)	--	90-110	90-110	20	20	30
Hardness as CaCO3 (SM 2340B)	--	70-130	85-115	20	20	30
Nitrate/Nitrite as N (EPA 353.2)	--	90-110	90-110	20	20	30
pH (SM 4500)	--	--	--	--	20	30
Total Dissolved Solid (TDS) (SM 2540C)	--	--	--	--	10	30
Sulfate (EPA 300.0)	--	90-110	90-110	20	20	30
Parameter	**Surrogate**	**MS/MSD**	**LCS**	**MS/MSD /RPD**	**DER**	**Field Duplicate**
Groundwater- Radiological						
Gross alpha (EPA 900.0)	--	70-130	70-130	--	2.13	30
Gross beta (EPA 900.0)	--	70-130	70-130	--	2.13	30
Ra-226 (EPA 903.1)	--	67-126	67-126	--	2.13	30
Ra-226 + Ra-228 (Calculation)	--	--	--	--	--	--
Ra-228 (EPA 904.0)	--	70-130	70-130	--	2.13	30
U-234 (ASTM D3972)(U-02)	--	82-122	82-122	--	2.13	30
U-235 (ASTM D3972)(U-02)	--	NS	NS	--	2.13	30
U-238 (ASTM D3972)(U-02)	--	78-126	78-126	--	2.13	30
Parameter	**Surrogate**	**MS/MSD**	**LCS**	**MS/MSD /RPD**	**Lab Duplicate**	**Field Duplicate**
Soil						
Antimony SPLP 1312 EPA 6010	--	70-130	85-115	20	20	50
Antimony EPA 6010	--	70-130	85-115	20	20	50

Notes:

[1] The listed QC limits are based on SW-846 guidance and are advisory. The actual limits are determined based on laboratory performance. Frequent failure to meet the QC limits; however, warrants investigation of the laboratory.

Ra-226 + Ra-228 is a calculated parameter with no assciated QC limits. Refer to separate analytes.

NS U-235 not spiked due to low activity of compound per ASTM Method D3972 (U-02) American Society for Testing Materials; ALS Standard Operating Procedure, Actinides-Uranium, Plutonium and Americum/Currium (Partial) Sequential Separation By Ion Exchange Referenced Method: ASTM 3972, DOE U-02, SOP ID: 778, Revision R14, Effective Date: April 22, 2013.

Acronyms and Abbreviations:

-- Not applicable

MS/MSD Matrix spike/matrix spike duplicate

LCS Laboratory control sample

RPD Relative Percent Difference

DER Duplicate Error Ratio, Calculated between field sample and its duplicate.

ARCADIS

Attachment A

Laboratory Standard Documentation
(on Disk)

ARCADIS

Laboratory Certifications

Arizona Department of Health Services
Office of Laboratory Licensure, Certification & Training
250 North 17th Avenue, Phoenix, AZ 85007

Wednesday, July 16 2014

AZ License: **AZ0742**

Lab Director: **Mr. Roy French**

Lab Name: ALS Environmental - Fort Collins
Phone: 970 490-1511
Fax: 970 490-1522

Program **HW**

Parameter	EPA Method	Billing Code	Cert Date
Alpha-Emitting Radium Isotopes	EPA 9315	RADIO	01/15/09
Gross Alpha And Beta	EPA 9310	RADIO	01/15/09
Radium 228	EPA 9320	RADIO	01/15/09

Total Licensed Parameters in this Program: 3

Program **SDW**

Parameter	EPA Method	Billing Code	Cert Date
Radium 228	EPA 904	RADIO	
Uranium	U-02	RADIO	

Total Licensed Parameters in this Program: 2

Program **WW**

Parameter	EPA Method	Billing Code	Cert Date
Gross Alpha	EPA 900	RADIO	01/15/09
Gross Beta	EPA 900	RADIO	01/15/09
Radium 226	EPA 903.1	RADIO	01/15/09
Total Radium	EPA 903.0	RADIO	01/15/09

Total Licensed Parameters in this Program: 4

Instruments	Quantity	Date
COUNTERS FOR RADIOACTIVITY	25	12/30/10

Softwares
BEACKMAN - COUNTERS FOR RADIOACTIVITY
Cannberra

Arizona Department of Health Services
Office of Laboratory Licensure, Certification & Training
250 North 17th Avenue, Phoenix, AZ 85007

Thursday, February 13 2014

AZ License: **AZ0538**

Lab Director: **Mr. John R. Kern**

Lab Name: SVL Analytical, Inc.
Phone: (208) 784-1258
Fax: (208) 783-0983

Program **HW**

Parameter	EPA Method	Billing Code	Cert Date
Aluminum	EPA 6010B	MTL3	09/29/98
Antimony	EPA 6010B	MTL3	09/29/98
Antimony	EPA 6020A	MTL1	02/13/14
Arsenic	EPA 6010B	MTL3	09/29/98
Arsenic	EPA 6020A	MTL1	02/13/14
Barium	EPA 6010B	MTL3	09/29/98
Barium	EPA 6020A	MTL1	02/13/14
Beryllium	EPA 6010B	MTL3	09/29/98
Beryllium	EPA 6020A	MTL1	02/13/14
Boron	EPA 6010B	MTL3	04/24/03
Cadmium	EPA 6010B	MTL3	09/29/98
Cadmium	EPA 6020A	MTL1	02/13/14
Calcium	EPA 6010B	MTL3	09/29/98
Cation-Exchange Capacity Of Soils	EPA 9080	MISC23	12/05/06
Cation-Exchange Capacity Of Soils	EPA 9081	MISC23	12/08/97
Chromium	EPA 6020A	MTL1	02/13/14
Chromium, Total	EPA 6010B	MTL3	09/29/98
Cobalt	EPA 6010B	MTL3	09/29/98
Cobalt	EPA 6020A	MTL1	02/13/14
Copper	EPA 6010B	MTL3	09/29/98
Copper	EPA 6020A	MTL1	02/13/14
Cyanide	EPA 9012B	MISC2	12/05/06
Dissolved In Water	EPA 3005A	PREP1	12/05/06
Ignitability (Flash Point)	EPA 1010A	HAZ2	12/05/06
Iron	EPA 6010B	MTL3	09/29/98
Lead	EPA 6010B	MTL3	09/29/98
Lead	EPA 6020A	MTL1	02/13/14
Lithium	EPA 6010B	MTL3	09/29/98
Magnesium	EPA 6010B	MTL3	09/29/98
Manganese	EPA 6010B	MTL3	09/29/98
Manganese	EPA 6020A	MTL1	02/13/14
Mercury	EPA 7470A	MTL5	02/15/00
Mercury	EPA 7471A	MTL5	03/28/96
Molybdenum	EPA 6010B	MTL3	09/29/98
Nickel	EPA 6010B	MTL3	09/29/98
Nickel	EPA 6020A	MTL1	02/13/14
Ph (Hydrogen Ion)	EPA 9045D	NIA2	12/05/06
Phosphorus	EPA 6010B	MTL3	04/24/03
Potassium	EPA 6010B	MTL3	09/29/98

AZ License: AZ0538 **Lab Name: SVL Analytical, Inc.**

Program HW

Parameter	EPA Method	Billing Code	Cert Date
Sediments, Sludges And Soils	EPA 3050B	PREP1	12/05/06
Selenium	EPA 6010B	MTL3	09/29/98
Silica	EPA 6010B	MTL3	04/24/03
Silver	EPA 6010B	MTL3	09/29/98
Silver	EPA 6020A	MTL1	02/13/14
Sodium	EPA 6010B	MTL3	09/29/98
Splp	EPA 1312	HAZ5	10/30/97
Strontium	EPA 6010B	MTL3	09/29/98
Tclp	EPA 1311	HAZ5	03/28/96
Thallium	EPA 6010B	MTL3	09/29/98
Thallium	EPA 6020A	MTL1	02/13/14
Tin	EPA 6010B	MTL3	09/29/98
Titanium	EPA 6010B	MTL3	04/24/03
Total Metals	EPA 3010A	PREP1	12/05/06
Total Metals	EPA 3020A	PREP1	06/24/08
Total Recoverable In Water	EPA 3005A	PREP1	12/05/06
Vanadium	EPA 6010B	MTL3	09/29/98
Zinc	EPA 6010B	MTL3	09/29/98
Zinc	EPA 6020A	MTL1	02/13/14

Total Licensed Parameters in this Program: 58

Program SDW

Parameter	EPA Method	Billing Code	Cert Date
Alkalinity	SM 2320B	NIA1	03/28/96
Aluminum	EPA 200.7	MTL3	02/15/00
Antimony	EPA 200.8	MTL1	12/29/04
Arsenic	EPA 200.8	MTL1	12/29/04
Barium	EPA 200.7	MTL3	03/28/96
Barium	EPA 200.8	MTL1	12/29/04
Beryllium	EPA 200.7	MTL3	09/29/98
Beryllium	EPA 200.8	MTL1	12/29/04
Bromide	EPA 300.0	NIIIA1	02/24/06
Cadmium	EPA 200.7	MTL3	04/23/02
Cadmium	EPA 200.8	MTL1	12/29/04
Calcium	EPA 200.7	MTL3	03/28/96
Carbon, Total Organic	SM 5310B	MISC1	04/24/03
Chloride	EPA 300.0	NIIIA1	03/28/96
Chromium Total	EPA 200.7	MTL3	03/28/96
Chromium Total	EPA 200.8	MTL1	07/26/05
Color	SM 2120B	NIA4	02/19/08
Copper	EPA 200.7	MTL3	03/28/96

Arizona Department of Health Services
Office of Laboratory Licensure, Certification & Training
250 North 17th Avenue, Phoenix, AZ 85007

Thursday, February 13 2014

AZ License: AZ0538 **Lab Name: SVL Analytical, Inc.**

Program SDW

Parameter	EPA Method	Billing Code	Cert Date
Copper	EPA 200.8	MTL1	07/26/05
Corrosivity	SM 2330B	NIA2	02/15/00
Cyanide	EPA 335.4	MISC2	09/29/98
Fluoride	EPA 300.0	NIIIA1	03/30/96
Hardness	EPA 200.7 CA&MG	MTL3	02/24/06
Hardness	SM 2340B	MTL3	12/05/06
Hydrogen Ion (Ph)	SM 4500-H B	NIA2	12/05/06
Iron	EPA 200.7	MTL3	03/28/96
Lead	EPA 200.8	MTL1	12/29/04
Magnesium	EPA 200.7	MTL3	02/15/00
Manganese	EPA 200.7	MTL3	03/28/96
Manganese	EPA 200.8	MTL1	12/29/04
Mercury	EPA 245.1	MTL5	03/28/96
Nickel	EPA 200.7	MTL3	09/29/98
Nickel	EPA 200.8	MTL1	12/29/04
Nitrate	EPA 300.0	NIIIA1	03/28/96
Nitrite	EPA 300.0	NIIIA1	09/29/98
Odor	SM 2150B	NIA4	02/19/08
Orthophosphate	SM 4500-P E	NIIB4	04/23/02
Residue, Filterable (Tds)	SM 2540C	NIA2	09/29/98
Selenium	EPA 200.8	MTL1	12/29/04
Silica	EPA 200.7	MTL3	02/15/00
Silver	EPA 200.7	MTL3	03/28/96
Silver	EPA 200.8	MTL1	12/29/04
Sodium	EPA 200.7	MTL3	09/29/98
Specific Conductance	SM 2510B	NIA2	12/05/06
Strontium	EPA 200.7	MTL3	03/28/96
Sulfate	EPA 300.0	NIIIA1	03/28/96
Surfactant (Mbas)	SM 5540C	NIIA1	02/15/08
Thallium	EPA 200.8	MTL1	12/29/04
Turbidity, Ntu: Nephelometric	EPA 180.1	NIA2	03/28/96
Uranium	EPA 200.8	MTL1	11/01/05
Zinc	EPA 200.7	MTL3	03/28/96
Zinc	EPA 200.8	MTL1	12/29/04

Total Licensed Parameters in this Program: 52

Program WW

Parameter	EPA Method	Billing Code	Cert Date
Acidity	SM 2310B	NIIA1	03/28/96
Alkalinity, Total	SM 2320B	NIA1	03/28/96
Aluminum	EPA 200.7	MTL3	03/28/96

AZ License: AZ0538 **Lab Name: SVL Analytical, Inc.**

Program WW

Parameter	EPA Method	Billing Code	Cert Date
Ammonia	EPA 350.1	NIIB1	04/10/01
Antimony	EPA 200.7	MTL3	03/28/96
Antimony	EPA 200.8	MTL1	12/29/04
Arsenic	EPA 200.7	MTL3	03/28/96
Arsenic	EPA 200.8	MTL1	12/29/04
Barium	EPA 200.7	MTL3	03/28/96
Barium	EPA 200.8	MTL1	12/29/04
Beryllium	EPA 200.7	MTL3	03/28/96
Beryllium	EPA 200.8	MTL1	12/29/04
Boron	EPA 200.7	MTL3	03/28/96
Bromide	EPA 300.0	NIIIA1	03/11/05
Cadmium	EPA 200.7	MTL3	03/28/96
Cadmium	EPA 200.8	MTL1	12/29/04
Calcium	EPA 200.7	MTL3	03/28/96
Carbon, Total Organic (Toc)	SM 5310B	MISC1	12/05/06
Chemical Oxygen Demand	EPA 410.4	DEM3	12/05/06
Chloride	EPA 300.0	NIIIA1	03/28/96
Chromium Total	EPA 200.7	MTL3	03/28/96
Chromium Total	EPA 200.8	MTL1	12/29/04
Chromium, Hexavalent	SM 3500-CR D	MTL8	12/05/06
Cobalt	EPA 200.7	MTL3	03/28/96
Cobalt	EPA 200.8	MTL1	12/29/04
Color	SM 2120B	NIA4	12/29/06
Copper	EPA 200.7	MTL3	03/28/96
Copper	EPA 200.8	MTL1	12/29/04
Cyanide, Total	EPA 335.4	MISC2	03/21/12
Fluoride	EPA 300.0	NIIIA1	12/11/97
Gold	EPA 231.2	MTL1	02/15/00
Hardness	SM 2340B	MTL8	12/05/06
Hydrogen Ion (Ph)	SM 4500-H B	NIA2	12/05/06
Iron	EPA 200.7	MTL3	03/28/96
Kjeldahl Nitrogen	EPA 351.2	NIIB4	03/20/07
Lead	EPA 200.7	MTL3	03/28/96
Lead	EPA 200.8	MTL1	12/29/04
Lithium	EPA 200.7	MTL3	04/23/03
Magnesium	EPA 200.7	MTL3	07/10/96
Manganese	EPA 200.7	MTL3	03/28/96
Manganese	EPA 200.8	MTL1	12/29/04
Mercury	EPA 245.1	MTL5	03/28/96
Molybdenum	EPA 200.7	MTL3	03/28/96
Molybdenum	EPA 200.8	MTL1	12/29/04

AZ License: AZ0538 **Lab Name: SVL Analytical, Inc.**

Program WW

Parameter	EPA Method	Billing Code	Cert Date
Nickel	EPA 200.7	MTL3	03/28/96
Nickel	EPA 200.8	MTL1	12/29/04
Nitrate (As N)	EPA 300.0	NIIIA1	03/28/96
Nitrate-Nitrite (As N)	EPA 300.0	NIIIA1	02/19/08
Nitrate-Nitrite (As N)	EPA 353.2	NIB1	04/03/02
Nitrite (As N)	EPA 300.0	NIIIA1	03/28/96
Orthophosphate	SM 4500-P E	NIIB4	04/23/02
Phosphorus, Total	SM 4500-P E	NIIB4	12/05/06
Potassium	EPA 200.7	MTL3	03/28/96
Residue Filterable	SM 2540 C	NIA2	09/29/98
Residue Nonfilterable	SM 2540D	NIIA1	12/05/06
Residue Total	SM 2540B	NIIA1	03/20/07
Residue Volatile	EPA 160.4	NIIA1	04/10/01
Selenium	EPA 200.7	MTL3	03/28/96
Selenium	EPA 200.8	MTL1	12/29/04
Silica, Dissolved	EPA 200.7	MTL3	03/28/96
Silver	EPA 200.7	MTL3	03/28/96
Silver	EPA 200.8	MTL1	12/05/04
Sodium	EPA 200.7	MTL3	03/06/97
Specific Conductance	EPA 120.1	NIA2	03/28/96
Strontium	EPA 200.7	MTL3	03/28/96
Sulfate	EPA 300.0	NIIIA1	03/28/96
Sulfide	SM 4500-S F	MISC1	12/05/06
Thallium	EPA 200.7	MTL3	03/28/96
Thallium	EPA 200.8	MTL1	12/29/04
Tin	EPA 200.7	MTL3	03/28/96
Turbidity, Ntu	EPA 180.1	NIA2	03/23/98
Vanadium	EPA 200.7	MTL3	03/06/97
Vanadium	EPA 200.8	MTL1	12/29/04
Zinc	EPA 200.7	MTL3	02/15/00
Zinc	EPA 200.8	MTL1	12/29/04

Total Licensed Parameters in this Program: 75

Instruments	Quantity	Date
INDUCTIVELY COUPLED PLASMA SPECTROMETER	5	02/22/10
ION CHROMATOGRAPH	3	03/30/96
AUTOMATED AUTOANALYZER	3	03/03/09
INDUCTIVELY COUPLED PLASMA/MASS SPECTROMETER	2	02/23/11
MERCURY ANALYZER	2	03/03/09
ATOMIC ABSORPTION SPECTROPHOTOMETER	1	03/06/12

Arizona Department of Health Services

ENVIRONMENTAL LABORATORY LICENSE

Issued to:

Laboratory Director: **John R. Kern**
Owner/Representative: **Wayne R. Sorensen**

SVL Analytical, Inc.
AZ0538

is in compliance with Environmental Laboratory's applicable standards for the State of Arizona and maintains on file a List of Parameters for which the laboratory is certified to perform analysis.

PERIOD OF LICENSURE FROM: 04/22/2014 TO: 04/21/2015

GREAT SEAL OF THE STATE OF ARIZONA 1912

Steven D. Baker, Chief
Office of Laboratory Licensure & Certification
Bureau of State Laboratory Services

Arizona Department of Health Services
Office of Laboratory Licensure, Certification & Training
250 North 17th Avenue, Phoenix, AZ 85007

Thursday, February 13 2014

AZ License: **AZ0538**

Lab Director: **Mr. John R. Kern**

Lab Name: SVL Analytical, Inc.
Phone: (208) 784-1258
Fax: (208) 783-0983

Program **HW**

Parameter	EPA Method	Billing Code	Cert Date
Aluminum	EPA 6010B	MTL3	09/29/98
Antimony	EPA 6010B	MTL3	09/29/98
Antimony	EPA 6020A	MTL1	02/13/14
Arsenic	EPA 6010B	MTL3	09/29/98
Arsenic	EPA 6020A	MTL1	02/13/14
Barium	EPA 6010B	MTL3	09/29/98
Barium	EPA 6020A	MTL1	02/13/14
Beryllium	EPA 6010B	MTL3	09/29/98
Beryllium	EPA 6020A	MTL1	02/13/14
Boron	EPA 6010B	MTL3	04/24/03
Cadmium	EPA 6010B	MTL3	09/29/98
Cadmium	EPA 6020A	MTL1	02/13/14
Calcium	EPA 6010B	MTL3	09/29/98
Cation-Exchange Capacity Of Soils	EPA 9080	MISC23	12/05/06
Cation-Exchange Capacity Of Soils	EPA 9081	MISC23	12/08/97
Chromium	EPA 6020A	MTL1	02/13/14
Chromium, Total	EPA 6010B	MTL3	09/29/98
Cobalt	EPA 6010B	MTL3	09/29/98
Cobalt	EPA 6020A	MTL1	02/13/14
Copper	EPA 6010B	MTL3	09/29/98
Copper	EPA 6020A	MTL1	02/13/14
Cyanide	EPA 9012B	MISC2	12/05/06
Dissolved In Water	EPA 3005A	PREP1	12/05/06
Ignitability (Flash Point)	EPA 1010A	HAZ2	12/05/06
Iron	EPA 6010B	MTL3	09/29/98
Lead	EPA 6010B	MTL3	09/29/98
Lead	EPA 6020A	MTL1	02/13/14
Lithium	EPA 6010B	MTL3	09/29/98
Magnesium	EPA 6010B	MTL3	09/29/98
Manganese	EPA 6010B	MTL3	09/29/98
Manganese	EPA 6020A	MTL1	02/13/14
Mercury	EPA 7470A	MTL5	02/15/00
Mercury	EPA 7471A	MTL5	03/28/96
Molybdenum	EPA 6010B	MTL3	09/29/98
Nickel	EPA 6010B	MTL3	09/29/98
Nickel	EPA 6020A	MTL1	02/13/14
Ph (Hydrogen Ion)	EPA 9045D	NIA2	12/05/06
Phosphorus	EPA 6010B	MTL3	04/24/03
Potassium	EPA 6010B	MTL3	09/29/98

AZ License: AZ0538 **Lab Name: SVL Analytical, Inc.**

Program HW

Parameter	EPA Method	Billing Code	Cert Date
Sediments, Sludges And Soils	EPA 3050B	PREP1	12/05/06
Selenium	EPA 6010B	MTL3	09/29/98
Silica	EPA 6010B	MTL3	04/24/03
Silver	EPA 6010B	MTL3	09/29/98
Silver	EPA 6020A	MTL1	02/13/14
Sodium	EPA 6010B	MTL3	09/29/98
Splp	EPA 1312	HAZ5	10/30/97
Strontium	EPA 6010B	MTL3	09/29/98
Tclp	EPA 1311	HAZ5	03/28/96
Thallium	EPA 6010B	MTL3	09/29/98
Thallium	EPA 6020A	MTL1	02/13/14
Tin	EPA 6010B	MTL3	09/29/98
Titanium	EPA 6010B	MTL3	04/24/03
Total Metals	EPA 3010A	PREP1	12/05/06
Total Metals	EPA 3020A	PREP1	06/24/08
Total Recoverable In Water	EPA 3005A	PREP1	12/05/06
Vanadium	EPA 6010B	MTL3	09/29/98
Zinc	EPA 6010B	MTL3	09/29/98
Zinc	EPA 6020A	MTL1	02/13/14

Total Licensed Parameters in this Program: 58

Program SDW

Parameter	EPA Method	Billing Code	Cert Date
Alkalinity	SM 2320B	NIA1	03/28/96
Aluminum	EPA 200.7	MTL3	02/15/00
Antimony	EPA 200.8	MTL1	12/29/04
Arsenic	EPA 200.8	MTL1	12/29/04
Barium	EPA 200.7	MTL3	03/28/96
Barium	EPA 200.8	MTL1	12/29/04
Beryllium	EPA 200.7	MTL3	09/29/98
Beryllium	EPA 200.8	MTL1	12/29/04
Bromide	EPA 300.0	NIIIA1	02/24/06
Cadmium	EPA 200.7	MTL3	04/23/02
Cadmium	EPA 200.8	MTL1	12/29/04
Calcium	EPA 200.7	MTL3	03/28/96
Carbon, Total Organic	SM 5310B	MISC1	04/24/03
Chloride	EPA 300.0	NIIIA1	03/28/96
Chromium Total	EPA 200.7	MTL3	03/28/96
Chromium Total	EPA 200.8	MTL1	07/26/05
Color	SM 2120B	NIA4	02/19/08
Copper	EPA 200.7	MTL3	03/28/96

Arizona Department of Health Services
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Thursday, February 13 2014

AZ License: AZ0538 **Lab Name: SVL Analytical, Inc.**

Program SDW

Parameter	EPA Method	Billing Code	Cert Date
Copper	EPA 200.8	MTL1	07/26/05
Corrosivity	SM 2330B	NIA2	02/15/00
Cyanide	EPA 335.4	MISC2	09/29/98
Fluoride	EPA 300.0	NIIIA1	03/30/96
Hardness	EPA 200.7 CA&MG	MTL3	02/24/06
Hardness	SM 2340B	MTL3	12/05/06
Hydrogen Ion (Ph)	SM 4500-H B	NIA2	12/05/06
Iron	EPA 200.7	MTL3	03/28/96
Lead	EPA 200.8	MTL1	12/29/04
Magnesium	EPA 200.7	MTL3	02/15/00
Manganese	EPA 200.7	MTL3	03/28/96
Manganese	EPA 200.8	MTL1	12/29/04
Mercury	EPA 245.1	MTL5	03/28/96
Nickel	EPA 200.7	MTL3	09/29/98
Nickel	EPA 200.8	MTL1	12/29/04
Nitrate	EPA 300.0	NIIIA1	03/28/96
Nitrite	EPA 300.0	NIIIA1	09/29/98
Odor	SM 2150B	NIA4	02/19/08
Orthophosphate	SM 4500-P E	NIIB4	04/23/02
Residue, Filterable (Tds)	SM 2540C	NIA2	09/29/98
Selenium	EPA 200.8	MTL1	12/29/04
Silica	EPA 200.7	MTL3	02/15/00
Silver	EPA 200.7	MTL3	03/28/96
Silver	EPA 200.8	MTL1	12/29/04
Sodium	EPA 200.7	MTL3	09/29/98
Specific Conductance	SM 2510B	NIA2	12/05/06
Strontium	EPA 200.7	MTL3	03/28/96
Sulfate	EPA 300.0	NIIIA1	03/28/96
Surfactant (Mbas)	SM 5540C	NIIA1	02/15/08
Thallium	EPA 200.8	MTL1	12/29/04
Turbidity, Ntu: Nephelometric	EPA 180.1	NIA2	03/28/96
Uranium	EPA 200.8	MTL1	11/01/05
Zinc	EPA 200.7	MTL3	03/28/96
Zinc	EPA 200.8	MTL1	12/29/04

Total Licensed Parameters in this Program: 52

Program WW

Parameter	EPA Method	Billing Code	Cert Date
Acidity	SM 2310B	NIIA1	03/28/96
Alkalinity, Total	SM 2320B	NIA1	03/28/96
Aluminum	EPA 200.7	MTL3	03/28/96

AZ License: AZ0538 **Lab Name: SVL Analytical, Inc.**

Program WW

Parameter	EPA Method	Billing Code	Cert Date
Ammonia	EPA 350.1	NIIB1	04/10/01
Antimony	EPA 200.7	MTL3	03/28/96
Antimony	EPA 200.8	MTL1	12/29/04
Arsenic	EPA 200.7	MTL3	03/28/96
Arsenic	EPA 200.8	MTL1	12/29/04
Barium	EPA 200.7	MTL3	03/28/96
Barium	EPA 200.8	MTL1	12/29/04
Beryllium	EPA 200.7	MTL3	03/28/96
Beryllium	EPA 200.8	MTL1	12/29/04
Boron	EPA 200.7	MTL3	03/28/96
Bromide	EPA 300.0	NIIIA1	03/11/05
Cadmium	EPA 200.7	MTL3	03/28/96
Cadmium	EPA 200.8	MTL1	12/29/04
Calcium	EPA 200.7	MTL3	03/28/96
Carbon, Total Organic (Toc)	SM 5310B	MISC1	12/05/06
Chemical Oxygen Demand	EPA 410.4	DEM3	12/05/06
Chloride	EPA 300.0	NIIIA1	03/28/96
Chromium Total	EPA 200.7	MTL3	03/28/96
Chromium Total	EPA 200.8	MTL1	12/29/04
Chromium, Hexavalent	SM 3500-CR D	MTL8	12/05/06
Cobalt	EPA 200.7	MTL3	03/28/96
Cobalt	EPA 200.8	MTL1	12/29/04
Color	SM 2120B	NIA4	12/29/06
Copper	EPA 200.7	MTL3	03/28/96
Copper	EPA 200.8	MTL1	12/29/04
Cyanide, Total	EPA 335.4	MISC2	03/21/12
Fluoride	EPA 300.0	NIIIA1	12/11/97
Gold	EPA 231.2	MTL1	02/15/00
Hardness	SM 2340B	MTL8	12/05/06
Hydrogen Ion (Ph)	SM 4500-H B	NIA2	12/05/06
Iron	EPA 200.7	MTL3	03/28/96
Kjeldahl Nitrogen	EPA 351.2	NIIB4	03/20/07
Lead	EPA 200.7	MTL3	03/28/96
Lead	EPA 200.8	MTL1	12/29/04
Lithium	EPA 200.7	MTL3	04/23/03
Magnesium	EPA 200.7	MTL3	07/10/96
Manganese	EPA 200.7	MTL3	03/28/96
Manganese	EPA 200.8	MTL1	12/29/04
Mercury	EPA 245.1	MTL5	03/28/96
Molybdenum	EPA 200.7	MTL3	03/28/96
Molybdenum	EPA 200.8	MTL1	12/29/04

AZ License: AZ0538 **Lab Name: SVL Analytical, Inc.**

Program WW

Parameter	EPA Method	Billing Code	Cert Date
Nickel	EPA 200.7	MTL3	03/28/96
Nickel	EPA 200.8	MTL1	12/29/04
Nitrate (As N)	EPA 300.0	NIIIA1	03/28/96
Nitrate-Nitrite (As N)	EPA 300.0	NIIIA1	02/19/08
Nitrate-Nitrite (As N)	EPA 353.2	NIB1	04/03/02
Nitrite (As N)	EPA 300.0	NIIIA1	03/28/96
Orthophosphate	SM 4500-P E	NIIB4	04/23/02
Phosphorus, Total	SM 4500-P E	NIIB4	12/05/06
Potassium	EPA 200.7	MTL3	03/28/96
Residue Filterable	SM 2540 C	NIA2	09/29/98
Residue Nonfilterable	SM 2540D	NIIA1	12/05/06
Residue Total	SM 2540B	NIIA1	03/20/07
Residue Volatile	EPA 160.4	NIIA1	04/10/01
Selenium	EPA 200.7	MTL3	03/28/96
Selenium	EPA 200.8	MTL1	12/29/04
Silica, Dissolved	EPA 200.7	MTL3	03/28/96
Silver	EPA 200.7	MTL3	03/28/96
Silver	EPA 200.8	MTL1	12/05/04
Sodium	EPA 200.7	MTL3	03/06/97
Specific Conductance	EPA 120.1	NIA2	03/28/96
Strontium	EPA 200.7	MTL3	03/28/96
Sulfate	EPA 300.0	NIIIA1	03/28/96
Sulfide	SM 4500-S F	MISC1	12/05/06
Thallium	EPA 200.7	MTL3	03/28/96
Thallium	EPA 200.8	MTL1	12/29/04
Tin	EPA 200.7	MTL3	03/28/96
Turbidity, Ntu	EPA 180.1	NIA2	03/23/98
Vanadium	EPA 200.7	MTL3	03/06/97
Vanadium	EPA 200.8	MTL1	12/29/04
Zinc	EPA 200.7	MTL3	02/15/00
Zinc	EPA 200.8	MTL1	12/29/04

Total Licensed Parameters in this Program: 75

Instruments	Quantity	Date
INDUCTIVELY COUPLED PLASMA SPECTROMETER	5	02/22/10
ION CHROMATOGRAPH	3	03/30/96
AUTOMATED AUTOANALYZER	3	03/03/09
INDUCTIVELY COUPLED PLASMA/MASS SPECTROMETER	2	02/23/11
MERCURY ANALYZER	2	03/03/09
ATOMIC ABSORPTION SPECTROPHOTOMETER	1	03/06/12

ARCADIS

Laboratory Quality Assurance Plans

Environmental

Laboratory Quality Assurance Plan

(LQAP)

Laboratory Quality Assurance Plan (LQAP)

Revision 16

August 16, 2012

ALS

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Fort Collins, CO 80524

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Approved by:

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Operations Manager

Robert P. Di Rienzo
Quality Assurance Manager

Steve Workman
Technical Manager

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BIBLIOGRAPHY

Appendices use in conjunction with the LQAP are documents routinely revised and do not constitute a revision to the LQAP. If you require an appendix referenced in this document please contact your project manager or quality assurance department for the most current version.

1. INTRODUCTION

This Laboratory Quality Assurance Plan (LQAP) describes the policies, procedures and accountabilities established by ALS Environmental (ALS) to ensure that the environmental test results reported from the analysis of air, water, soil, waste, and other matrices are reliable and of known and documented quality. This document describes the quality assurance and quality control procedures followed to generate reliable analytical data.

This LQAP is designed to be an overview of ALS operations. Detailed methodologies and practices are written in ALS Standard Operating Procedures (SOPs). Where appropriate, ALS SOPs are referenced in this document to direct the reader to more complete information. A list of current SOPs is found in Appendix H.

ALS maintains certifications pertaining to various commercial and government entities. Each certification requires that the laboratory continue to perform at levels specified by the programs issuing certification. Program requirements can be rigorous; they include semiannual performance evaluations as well as annual audits of the laboratory to verify compliance.

The State of Utah has primacy in administering certification of this laboratory to perform EPA methods. Thus, the Utah State Health Department certifies ALS to perform EPA methods under Utah Rule R444-14. For that reason, reference is made to Utah Rule R444-14 in this LQAP.

ALS is a full service environmental and radiochemistry laboratory, performing analyses for organic, inorganic, and radiological constituents in a variety of matrices. ALS specializes in serving the Department of Energy (DOE), Department of Defense (DoD), and architect-engineering firms. ALS routinely provides hardcopy data packages and electronic data deliverables that are easily validated by external validators.

The management team at ALS applies an integrated approach to quality assurance, client service, and efficient operations that enables ALS to produce compliant data that meet or exceed all technical and service requirements as prescribed by our clients. This Laboratory Quality Assurance Plan (LQAP) defines ALS's quality assurance (QA) program, and communicates ALS's goals, values and policies regarding quality, ethical conduct, data integrity, and optimized operations. ALS management is committed to continual improvement by implementing the management systems set forth in this LQAP and the following documents: ISO 17025;2005, TNI 2009, DoD QSM and DOE QSAS.

Documents and forms used in the laboratory may still have previous ownership names like ATI, PAI, Paragon Analytical, DataChem or DCL. These former names can be used until revisions to specific documents are needed.

1.1 MISSION STATEMENT

To provide analytical services to help our customers make informed decisions.

1.2 VISION STATEMENT

To be recognized as a global market leader.

1.3 QUALITY POLICY

ALS is committed to producing legally defensible analytical data of known and documented quality acceptable for its intended use and in compliance with the Safe Drinking Water Act, the Clean Water Act, and the Resource Conservation and Recovery Act. This LQAP is designed to satisfy the applicable requirements of the State of Utah and other state certification programs. ALS complies with the National Environmental Laboratory Accreditation Conference (TNI) standards.

ALS corporate management has committed its full support to provide the personnel, facilities, equipment, and procedures required by this LQAP.

ALS management is committed to improvements of the management systems through compliance with TNI 2009 and ISO 17025:2005 ALS management is also committed to compliance with project related requirements including DOECAP QSAS and DoD QSM Gray Boxes.

ALS management reviews its operations on an ongoing basis and seeks input from staff and clients to make improvements. See section 12.1.5 of this plan for details.

It is the policy of ALS that all employees shall be familiar with all Quality documentation.

Within this framework, ALS performs analyses in strict accordance with promulgated methodologies, including:

- USEPA, SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods;
- USEPA, Methods for Chemical Analysis of Waters and Wastes (MCAWW);
- USEPA, Methods for Determination of Metals in Environmental Samples;

- American Public Health Association (APHA), Standard Methods for the Examination of Water and Wastewater (SM);
- USEPA, Methods for Determination of Organic Compounds in Drinking Water;
- American Society for Testing and Materials (ASTM), Annual Book of ASTM Standards, Volume 11 – Water and Environmental Technology;
- American Society for Testing and Materials (ASTM), Annual Book of ASTM Standards, Volume 12 – Nuclear Energy;
- USDOE, Environmental Measurements Laboratory (EML), Procedures Manual (HASL-300);
- USEPA, Eastern Environmental Radiation Facility (EERF), Radiochemistry Procedures Manual;
- USDOE, Radiological and Environmental Sciences (RESL), Procedures Manual;
- USEPA, Prescribed Procedures for Measurement of Radioactivity in Drinking Water; and
- US, Code of Federal Regulations (40 CFR).

1.4 STATEMENT ON WASTE, ABUSE AND FRAUD

ALS is committed to achieving our goals in the most efficient and effective manner possible, thus avoiding wasteful use of resources. This is accomplished by assuring the proper utilization of ALS's purchased materials and equipment, and time and ability of our personnel. *Any ALS employee, who has any suggestion or concern regarding ALS's practices, is encouraged to discuss his/her idea or question with the Operations Manager, the Quality Assurance Manager, and/or the Laboratory Director*. A means of confidentially reporting concerns anonymously is also available. Grievances and allegations of unethical conduct will be fully investigated, and appropriate actions taken.

Training regarding ALS's Waste, Abuse and Fraud policies is provided to every new staff member, and to all employees lab-wide as an annual refresher. ALS's policies regarding waste, abuse and fraud are included in ALS SOP 143 and CE-GEN-001**.**

1.5 CODE OF ETHICS AND DATA INTEGRITY STATEMENTS

ALS is responsible for creating a work environment that enables all employees to perform their duties in an ethical manner. *It is ALS's expectation that all employees exhibit professionalism and respect for clients and each other in all interactions and tasks.* ALS requires that each employee abide by the following guidelines:

- Every ALS employee is responsible for the propriety and consequences of his or her actions. Each employee shall conduct him or herself in a professional manner towards all clients, regulators, auditors, vendors, and other employees. Professional conduct relates to honesty, integrity, respect, and tolerance for cultural diversity.

- Every ALS employee shall perform all assigned duties in accordance with ALS's established quality assurance policies and quality control procedures that have been developed to ensure conformance with contractual and regulatory requirements.

- ALS expects all employees to use professional judgment and to document all situations thoroughly. It is the responsibility of each ALS employee to consult the Operations Manager or Quality Assurance Manager when atypical or unusual situations occur and to disclose and document the decision-making process. Every employee must disclose any instance of noncompliance. ALS reports all noncompliance issues affecting data to the client.

- It is the responsibility of each ALS employee to report any suspicion of unethical conduct to the Quality Assurance Manager or the Laboratory Director.

Procedures addressing Ethics and Data integrity provide assurance that a highly ethical approach to testing is a key component of all laboratory planning, training and implementation of methods. See ALS SOPs 143 and CE-GEN-001.

Strict adherence to ALS's Code of Ethics and Data Integrity is essential to the reputation and continued health of our business. All ALS employees are required to acknowledge their responsibility and intent to behave in an ethical manner by attesting to the requirements described in procedures and annual refresher training is conducted.

1.6 REVIEW, REVISION, DISTRIBUTION AND HIERARCHY OF QA DOCUMENTS

Current copies of pertinent quality assurance guidance documents, such as ALS's LQAP, the TNI Standards, ISO 17025:2005, the US DOE Quality Systems for

Analytical Services (QSAS), the US DoD Quality Systems Manual (QSM) and others, are posted to the ALS network so that they are accessible to every employee. Laboratory Standard Operating Procedures (SOPs) and other method references are also posted to the network for lab-wide employee access. Project-specific requirements are disseminated to the laboratory via Laboratory Information Management Systems (LIMS) program specifications (discussed further below).

ALS recognizes a hierarchy of guidance that provides for comprehensive definition, yet flexible coverage, thus enabling both overall program and site-specific needs to be met. An overview explaining this hierarchy is given below and in ALS SOP 143. **SOP 926** provides detailed guidance on the review, revision, and distribution of laboratory-generated controlled documents.

1.6.1 LABORATORY QUALITY ASSURANCE PLAN

The LQAP is an encompassing controlled-document that describes theALS quality assurance programs and policies. All systems, policies, and procedures have been developed and implemented in accordance with applicable USEPA requirements, regulations, and guidance; the current TNI standards; and requirements set forth in various client quality assurance documents and contractual specifications. This document has been prepared in accordance with these referenced documents, as well as others, cited in the attached **Bibliography**. The LQAP is intended to provide a 'quality requirements framework', including quality control (QC) procedures to be followed in the absence of project-specific requirements (note that project-specific requirements are communicated to laboratory staff via LIMS program specifications, which are discussed subsequently).

The Quality Assurance Manager (QAM) bears primary responsibility for ensuring that the LQAP meets industry standards. Proposed revisions to the LQAP are approved by key laboratory personnel. Following approval, the QAM posts the revised LQAP to the ALS network and revision to LQAP is documented in LIMS. The LIMS notifies personnel of all revised documents. It is the requirement of all employees to read and update reading records for all assigned controlled documents. Archival records of all LQAP iterations are maintained by the Quality Assurance Department.

1.6.2 STANDARD OPERATING PROCEDURES

The second kind of controlled-document in the hierarchy of quality assurance guidance are the Standard Operating Procedures (SOPs). An SOP defines the QA/QC requirements for each method and describes in

detail how personnel perform procedures and evaluate data. SOPs pertaining to general practices (e.g., standards, temperature monitoring, etc.), administrative procedures (e.g., procurement of supplies and materials, etc.) and health & safety requirements (e.g., ALS Safety Modules and the Chemical Hygiene Plan), are also maintained by ALS. It is ALS's intent that the information contained in our SOPs is both method-compliant, and accurately reflect actual practice. *Suggestions for SOP content clarification or revision are encouraged.* SOPS are published to the network when approved.

The LIMS notifies personnel of all revised documents. It is the requirement of all employees to read and update reading records for all assigned controlled documents

This process of revision, approval and distribution is established in the ALS SOP 926. A list of current SOPs is provided in **Appendix H**. The Quality Assurance Department manages the review, revision and controlled distribution of documents and maintains associated records.

1.6.3 LABORATORY MANAGEMENT INFORMATION SYSTEMS (LIMS) PROGRAM SPECIFICATION

The last and most specific controlled-document in this hierarchy is the LIMS program specification. The LIMS program specification is a distillation of client Quality Assurance Project Plan (QAPjP) or contractual requirements, prepared electronically by the ALS Project Manager (PM), in collaboration with the QAM and applicable operations management. This custom program specification, along with the associated LIMS test code nicknames, contain directives and controls that govern testing and reporting data. The program specification is often limited in scope and addresses only those QA/QC criteria required for a specific project. *When the client's requirements differ from those stated in the SOPs and/or LQAP, the project-specific LIMS program specification requirements supersede the others.* ***It is the responsibility of all personnel who work with samples or data to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of the samples or data.***

2. LABORATORY ORGANIZATION AND RESPONSIBILITIES

This section provides an overview of ALS organization and defines key personnel, their responsibilities, and the lines of communication between these employees. An organization chart that illustrates reporting relationships is provided in **Appendix B**.

ALS policy is to perform work for clients in the most efficient manner possible, avoiding waste of resources and undue pressure on employees. It is the role of both ALS management and employees to ensure that work for clients is performed most efficiently and effectively by properly utilizing ALS purchased materials, equipment, and the time and ability of personnel.

2.1 GENERAL REQUIREMENTS FOR LABORATORY PERSONNEL

ALS maintains sufficient personnel to perform analytical services for our clients. Each employee must have a combination of experience and education that enables him or her to demonstrate a specific knowledge of his or her job function, and a general knowledge of laboratory operations, test methods, QA/QC procedures, and records management. *All personnel are responsible for complying with the requirements that pertain to his/her assigned duties.*

2.2 KEY PERSONNEL

Education, experience and skill requirements for these positions are addressed in job descriptions (Title). Functional responsibilities are further discussed below.

In the event of a temporary absence, key personnel must notify other key staff of their absence and reassign their duties to another employee (deputy) who will perform the assigned duties. For example, a PM may assign another PM to cover his or her duties; Group Leader may assign a senior chemist to cover his or her duties; and the Operations Manager may assign a Manager to cover his or her duties.

2.1.1 LABORATORY DIRECTOR

The Laboratory Director (Laboratory Director) is responsible for:

- All laboratory operations, including: business functions such as marketing, sales and financial issues.Providing input and support to proposal processes, including interacting with the Sales, Technical and Quality Assurance staff, to ensure that the laboratory is capable of complying with client and regulatory requirements;

- Supervising all personnel through Management staff, who ensure that QA/QC procedures are being performed and that any nonconformances or discrepancies are documented and remedied properly and promptly;

- Ensuring that corrective actions relating to Findings from internal and external audits are completed in a timely fashion;
- Ensuring that the laboratory has the appropriate resources and facilities to perform analytical services;
- Ensuring that sufficient numbers of qualified personnel are employed to supervise and perform the work of the laboratory;
- Defining the minimum level of education, experience, and skills necessary for all positions in the laboratory;
- Ensuring that only those vendors and supplies that are of adequate quality are used; and
- Directing the performance of the annual Managerial Review.

2.1.2 OPERATIONS MANAGER

The Operations Manger reports to the Laboratory Director, and exercises day-to-day supervision of laboratory personnel, procedures, and reporting of results. The Operations Manager (and/or his designee) is responsible for:

* Technical functions such as sample control, preparation, analysis, data management; and quality assurance;
* Providing technical education and training to personnel, authorizing personnel with appropriate educational and/or technical background perform all tests for which the laboratory is accredited, and providing documentation of employee capability and training., and ensuring that training and documentation are up to date;
* Monitoring QA/QC standards of performance, including ensuring that corrective actions are developed, documented, and implemented for all external and internal audit Findings, PT study failures, and other corrective actions;
* Monitoring the validity of the analyses performed and data generated in the laboratory to ensure the production of compliant data, including, contributing to and/or overseeing data review processes;

* Ensure that SOPs are compliant with promulgated methodologies and reflect current practice;

* Providing input to the Laboratory Director regarding methodologies, personnel resources, software, and instrumentation; and assisting in the evaluation and/or development of new methods and technologies that improve ALS's ability to meet clients' needs;

* Reviewing RFPs and assisting in the preparation and submission of proposals; and

* Interacting with the Quality Assurance, Information Systems, and Health and Safety Departments to ensure that the laboratory is capable of complying with client and regulatory requirements.

2.1.3 QUALITY ASSURANCE MANAGER

The Quality Assurance Manager (Manager) reports to the Laboratory Director and is independent of daily operation and production requirements. Therefore, the QAM is able to evaluate data objectively and perform assessments without production influence. *The QAM has authority to stop work if systems are sufficiently out of control to compromise the integrity of the data generated.*

The QAM shall have documented training and/or experience in QA/QC procedures; knowledge of quality systems as defined by TNI and other management systems standards; and a general knowledge of the analytical test methods for which data review is performed.

The QAM (and/or designee) is responsible for:

- Defining and implementing the quality system;

- Developing and maintaining a pro-active program for prevention and detection of improper, unethical, or illegal practices (e.g., single- or double-blind proficiency testing studies, electronic data audits, maintaining documents that identify appropriate and inappropriate laboratory and data manipulation practices);

- Ensuring continuous improvement of laboratory procedures via training, control charts, proficiency testing studies, internal audits, and external audits;
- Coordinating the laboratory's participation in state and Federal certification programs;
- Scheduling the review and distribution and maintaining distribution records of controlled documents, including plans (e.g., LQAP, etc.) and SOPs;
- Reviewing, when requested, Requests For Proposal (RFPs) to ensure ALS compliance with required QA/QC practices;
- Facilitating external audits;
- Overseeing or conducting internal audits of the entire operation annually (technical, management system, data, electronic);
- Coordinating, preparing and approving external and internal audit responses and corrective actions;
- Managing the laboratory's participation in proficiency testing (PT) studies;
- Reviewing nonconformances and approving corrective actions;
- Reviewing QC limits per established procedures;
- Ensuring that Detection Limit studies are performed and documented per requirements;
- Managing the reference standards used in the calibration and/or verification of support equipment (e.g., weights, thermometers, balances);
- Revising the LQAP annually in accordance with industry standards;
- Maintaining an archival system for quality records; and

- Maintaining technical and quality assurance training records, including employee competency to perform testing.

2.1.4 HEALTH & SAFETY MANAGER/RADIATION SAFTETY OFFICER (RSO)

The Health & Safety Manager/Radiation Safety Officer (RSO) (Safety Officer) reports to the Laboratory Director. This Manager is responsible for establishing and monitoring adequate systems, procedures and training to ensure that the laboratory staff, facilities and operational activities conducted, function in a manner that minimizes employee risk of illness and injury, is compliant with all applicable regulations pertaining to matters of safety and health, and that limits the financial liability of the corporation as it relates to these matters. As RSO, this Manager is also responsible for discharging the duties and requirements prescribed by ALS's Radioactive Materials License.

Key responsibilities of the Health & Safety Manager/RSO (and/or designee) include:

- Ensuring that all employees have sufficient training to perform their job without unnecessary risk of illness or injury, providing health and safety, including radiation safety, training for new employees, and maintaining health and safety-related training records;

- Providing procedural guidance in the form of the Chemical Hygiene Plan (CHP), Radiation Protection Plan (RPP), Respiratory Protection Plan (ResPP), Emergency and Contingency Plan (ECP) and Health and Safety SOPs, and ensuring that these guidances are reviewed by laboratory staff;

- Ensuring that the laboratory facilities are maintained and operated in a safe manner, including:

  (a) Performing routine safety inspections of all operational areas;

  (b) Performing routine radiation surveys and managing the radiation dosimetry program; and

  (c) Performing personal monitoring, as indicated, for chemical and other exposures.

- Maintaining the laboratory's Colorado Radioactive Materials License and ensuring compliance with the terms of the license. Included in this responsibility are:

    (a) Procuring and managing radioactive sources and standards;

    (b) Maintaining the laboratory's radioactive materials inventory, which also includes directing prescreen analyses that provide initial characterization of potential sample radioactivity;

    (c) Overseeing permitted low level radioactive materials releases to the sanitary sewer; and

    (d) Ensuring that radioactive materials waste is transported in accordance with all Federal and state regulations, and is transferred only to facilities that possess a radioactive materials license.

2.1.5 FACILITIES/WASTE COMPLIANCE MANAGER (SAFETY OFFICER)

The Facilities/Waste Compliance Manager (Safety Officer), reports to the Laboratory Director. This Manager is responsible for day-to-day management of the building and serves as the primary point of contact for all matters related to waste collection and disposal.

The Facilities/Waste Compliance Manager (and/or designee) is responsible for:

- Coordinating heating, ventilation, and air-conditioning (HVAC) systems operation and maintenance;
- Maintaining the uninterruptible power supply (UPS) and coordinating maintenance and repairs to the electrical system;
- Maintaining the in-house vacuum system;
- Coordinating repairs to the building (e.g., doors, locks, windows, cabinetry);
- Maintaining the building's security and fire alarm system;

- Interfacing with fire inspectors; and responding to security and fire alarms on a 24-hour basis;
- Implementing waste reduction procedures;
- Managing the accumulation of radioactive waste in the laboratory;
- Developing and maintaining Satellite Accumulation Areas (SAAs) and 90-Day Storage Areas;
- Overseeing all waste disposal operations performed by ALS, including (1) ensuring compliance with Federal, state, and local regulations for waste handling and disposal in accordance with RCRA, TSCA, and radioactive waste disposal regulations; (2) managing hazardous waste shipments to Temporary Storage and Disposal Facilities (TSDFs); (3) managing sanitary sewer releases; and (4) managing sample archives and the return of samples and sample residues to clients;
- Training personnel on proper techniques for sample handling and waste disposal, according to standards implemented by Federal, state, and local authorities and maintaining associated training records; and
- Supervising the Sample Receiving Department.

2.1.6 INFORMATION SYSTEMS MANAGER

The Information Systems (IS) Manager (Manager) reports to the Laboratory Director. This Manager is responsible for administering the network, maintaining data recovery systems, and for managing personal computing (PC) equipment and peripherals, thus supporting instrumentation and LIMS. The IS Manager (and/or designee) is responsible for:

- Managing and maintaining the laboratory computer system. This function includes determining and purchasing appropriate hardware and verifying that its function meets intended objectives, establishing network server structure, and developing and implementing proper maintenance and backup procedures;

- Procuring, configuring and maintaining all printers and copiers;
- Serving as a technical resource on computer-related issues;
- Documenting related operating procedures through SOPs, manuals or other proprietary documentation;
- Supervising recovery of all systems in the event of a disaster;
- Along with the Laboratory Information Systems Manager, analyzing information flow in the laboratory and suggesting the most effective hardware, applications software, and/or programming changes as solutions to meet long-term customer requirements; also, implementing those changes in data acquisition and management by purchasing hardware or software, where software is not developed internally; and
- Maintaining and implementing existing and future communications systems, including all internet and telephone systems.

2.1.7 LABORATORY INFORMATION MANAGEMENT SYSTEMS MANAGER

The Laboratory Information Management Systems (LIMS) Manager reports to the Laboratory Director, and bears the primary responsibility for the LIMS, which serves the needs of the technical, business, and management functions of the laboratory.

Key responsibilities of the LIMS Manager (and/or designee) include:

- Designing and developing information systems that relate to data capture and reporting;
- Maintaining and supporting applications that access LIMS and maintaining and supporting database back-end applications used for LIMS;
- Documenting changes and procedures through SOPs, manuals or other proprietary documentation;
- Developing software, as needed, using the appropriate tools, and per industry standard methodologies and validations;

- Overseeing and assisting with the implementation, testing and verification of upgrades made to instrument software;

- Coordinating all efforts to automate and improve electronic systems and processes throughout the laboratory;

- Developing interfaces necessary to achieve the requirements for client-specified electronic data deliverables (EDDs), and managing all deliverable formats provided to clients (hardcopy, electronic); and

- Providing training, as applicable, for all LIMS-related applications.

2.1.8 PROJECT MANAGER

- Project Managers report to the Client Services Manager. *The Project Manager serves as the primary point of contact between clients and ALS.* Each PM (and/or designee) is responsible for:

- Managing and coordinating the laboratory's performance after contract award, by defining technical and service requirements for personnel via LIMS, and interacting with clients and laboratory personnel to ensure that technical criteria and client service needs are met, including monitoring holding times (if appropriate) and deliverable deadlines, for all project sample analyses;

- Reviewing and approving any nonconformances reported by the laboratory and notifying the client, if appropriate, and communicating with clients pro-actively to ensure that all client service and technical concerns are resolved promptly;

- Reviewing all final reports for completeness, compliance with project requirements, clerical accuracy, and reasonableness;

- Generating, as directed by prompts provided in ALS's proprietary EDD generator, and transmitting EDDs to their clients as required;

- Ensure communications with the clients are in compliance with ALS SOP 997 "Client Communication"; and

- Communicating to the Operation Manager any potential need for new or improved capabilities based on clients' feedback.

2.1.9 GROUP LEADER

- Coordinating and approving the purchase of reagents, standards, glassware, and equipment that meet requirements
- Maintaining current, compliant MDL studies for all methods, matrices, analytes, columns, and instruments
- Assigning job tasks and prioritizing analyses;
- Developing and implementing a preventive maintenance program for instrumentation in their laboratory, and ensuring that all equipment is maintained, serviced, and properly calibrated;

2.2 GENERAL TECHNICAL PERSONNEL

A chemist (analyst) or technician reports to the Operations Manager or Group Leader. This employee performs work in accordance with ALS's controlled documents (e.g., SOPs, LQAP, etc.) and project-specific requirements as defined by the applicable LIMS specification. *ALS believes that quality begins at the bench.* Accordingly, these employees are key contributors to ALS's success.

A chemist or technician is responsible for:

* Demonstrating proficiency in the analyses for which they are responsible ***before*** analyzing samples (e.g., performing acceptable Initial Demonstration of Capability), and documenting this demonstration of proficiency in accordance with ALS Procedure 150;
* Performing analyses, recording all data accurately, directly, and promptly, and interpreting and reviewing data according to established procedures;
* Read and understand all assigned SOPs and plan documents;
* Complying with all QA/QC requirements that pertain to their job function;
* Complying with all health, safety, and waste disposal requirements, as applicable;

* Maintaining and repairing instrumentation;

* Demonstrating good house-keeping practices;

* Disclosing all instances of nonconformances promptly and in writing using the NCR process (**SOP 928**); and

* Participating in training sessions.

3. QUALITY ASSURANCE INDICATORS AND OTHER MEASUREMENT PARAMETERS

ALS' objective is the development and implementation of policies and procedures that provide results of known, documented, and appropriate quality. This LQAP defines general policies for the analysis, documentation, evaluation, validation, and reporting of data. Specific, detailed procedures for chain-of-custody, calibration of instruments, analysis, reporting, quality control, audits, preventative maintenance, and corrective actions, are provided in SOPs as listed in **Appendix H**.

In order to produce data of known, documented, and appropriate quality, ALS:

- maintains an effective quality assurance program that measures and verifies laboratory performance;

- provides for a Quality Assurance Department that is independent of the operational groups and that has stop-work authority, and that has the responsibility and authority to audit the laboratory and develop and enforce corrective actions;

- evaluates technical and service requirements of all analytical services requests before accepting samples from a client/project. This evaluation includes a review of facilities, instrumentation, staffing, turnaround times, and any project-specific quality control or reporting requirements;

- provides sufficient flexibility to allow controlled changes in routine methodology in order to achieve client-specific data requirements as prescribed in client documents and contracts;

- documents initial demonstration of capability (IDOC) and continuing demonstration of capability (CDOC) for all methods according to Appendix C of the TNI standards;

- performs all analyses according to promulgated methods or methods developed and validated by ALS and documented in SOPs;

- recognizes as soon as possible and discloses and corrects any factors that adversely affect data quality; and

- maintains complete records of sample submittal, raw data, laboratory performance, and completed analyses to support reported data.

3.1 DATA QUALITY INDICATORS

Data Quality Indicators (DQIs) are qualitative and quantitative statements developed by data users that specify the quality of data from field and laboratory data collection activities in order to support specific decisions or regulatory actions. The DQIs describe *what* data are needed, *why* the data are needed, and *how* the data will be used to address the problem being investigated. DQIs also establish qualitative and quantitative goals that allow the data user to determine whether the data are of sufficient quality for the intended application.

The principal DQIs are **precision**, **accuracy** (bias), **representativeness**, **completeness**, and **comparability** (i.e., the PARCC parameters). The following sections define and describe the application of these parameters. The QA/QC protocols used for the majority of analyses are adopted from SW-846 and 40 CFR methodologies, the USEPA Organics and Inorganics CLP SOWs, and various radiochemistry guidances, which contain detailed descriptions of the quality control measures routinely employed.

3.1.1 PRECISION

Precision is an expression of the reproducibility or degree of mutual agreement among independent measurements as the result of repeated application of the same process under similar conditions.

Analytical precision is a measurement of the variability associated with duplicate or replicate analyses of the same sample in the laboratory. Analytical precision is determined by the analysis of matrix spike/matrix spike duplicates (MS/MSD), laboratory control sample pairs (LCS/LCSD), or by unspiked duplicate samples (DUPs). Total precision is a measurement of the variability associated with the entire sampling and analysis process, and is determined by analysis of duplicate or replicate *field* samples, thus incorporating the variability introduced by both the field and laboratory operations.

Precision is independent of bias or accuracy, and reflects only the degree to which the measurements agree *with one another*, not the degree to which they agree with the true or accepted value of the parameter measured. Precision for chemistry analyses is typically expressed as relative percent difference (RPD), as defined below:

$$RPD(\%) = \frac{X_1 - X_2}{(X_1 + X_2)/2} \quad (100)$$

where:

RPD = Relative Percent Difference

X_1, X_2 = analyte value of sample 1 and sample 2

Precision, for radiochemical analyses, is typically measured in terms of Duplicate Error Ratio (DER), calculated as follows:

$$DER = \frac{|S - D|}{2 * \sqrt{\sigma^2_S + \sigma^2_D}}$$

where:

DER = Duplicate Error Ratio

S, D = analyte values of (S)ample and (D)uplicate

σ = One Sigma error value associated with sample result

RPDs or DERs are compared to the control limits established for the analysis method, or other quality control criteria as prescribed in the applicable LIMS program specification. Precision objectives vary per analytical method. Sample homogeneity/non-homogeneity is an important factor that influences the precision of duplicate sample results.

3.1.2 ACCURACY

Accuracy is an expression of agreement between the measured and known or accepted reference values.

Accuracy is typically measured by determining the percent recovery of known target analytes (i.e., a surrogate or matrix spike) that are spiked into a field sample or reagent water or simulated solid matrix (laboratory control sample). Surrogate recovery is reported and is used to assess method performance for each sample analyzed for volatile and semivolatile organic compounds. For organic and inorganic parameters, the stated accuracy objectives apply to spiking levels at or near the midpoint of the calibration curve. For radiochemical analyses, the spiking levels for the control spikes may vary from five to fifty times the method reporting limit.

Percent recovery is calculated as:

$$R(\%) = \frac{(C_1 - C_2)(100)}{C_3}$$

where:

R% = Spike amount recovered
C_1 = Concentration of analyte in spiked sample
C_2 = Concentration of analyte in unspiked sample
C_3 = Concentration of spike added

Acceptance limits are usually based upon established laboratory performance for similar samples. Other quality control criteria may be prescribed in the applicable LIMS program specification. Recoveries outside the established limits may indicate some assignable cause other than normal measurement error, and the need for corrective action. This corrective action may include reanalysis of the quality control sample, recalibration of the instrument, reanalysis of the affected samples in the batch, re-preparation of samples in the batch, or flagging and qualifying the data as suspect if the problem cannot be resolved. For contaminated samples, recovery of matrix spikes may depend on homogeneity, matrix interference, and dilution requirements for quantitation.

Both accuracy and precision are calculated for each batch and the associated sample results must be interpreted by considering theses specific measures. The quality assurance objectives for precision and accuracy are to achieve the quality control acceptance criteria specified in the appropriate analytical procedure.

For organic analyses, precision and accuracy are determined by using matrix spike and matrix spike duplicate samples and/or surrogate spike compounds and laboratory control samples. For inorganic analyses, precision and accuracy are determined by using duplicate samples or matrix spike duplicate samples (precision) and matrix spike and laboratory control samples (accuracy). For radiological analyses, precision and accuracy are determined from the results of duplicate samples or matrix spike duplicate samples (precision), laboratory control sample duplicates (precision) and laboratory control samples (accuracy).

Samples identified as field blanks cannot be used for duplicate or matrix spike sample analyses.

QC limits for accuracy and precision may be developed from intra-laboratory historical data or adopted from prescribed limits required by the client. If quality control acceptance criteria do not exist for a given method, then the laboratory may establish advisory control limits derived from a minimum of four data points. Until verified by a statistically significant data population, the control limits will be considered as advisory limits only, and the laboratory will not automatically initiate reanalysis if these limits are not achieved. See Section 9.3 for further discussion of control limits and control charts.

Bias describes the systematic error of a measurement process that causes errors in one direction from the true value. Sources of bias include incomplete homogenization before subsampling and incomplete extraction of target analytes. Calibration drift, which is the nonrandom change in a measurement system over time, is another example of systematic error, and is detectable by the periodic measurement of calibration check standards. *Bias is **not** equivalent to accuracy.*

3.1.3 REPRESENTATIVENESS

Representativeness is a qualitative element. It expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition within a defined spatial and/or temporal boundary.

Sample handling protocols (e.g., holding times, storage, preservation and transportation) have been developed to preserve the representativeness of the samples. Proper documentation establishes that quality control protocols have been followed, and sample identification and integrity are ensured. *ALS makes every attempt to ensure that the aliquots taken for analysis are homogenous and representative of the samples received.*

3.1.4 COMPARABILITY

Comparability is a qualitative expression of the confidence with which one data set can be compared to another. Comparability is achieved by:

- following established, standardized, and approved sample collection techniques and analytical methods;
- achieving holding times;

- reporting results in common units;
- using consistent detection levels; and
- reporting data according to consistent rules.

See Chapter 10 of this LQAP for further discussion of standard units typically used to report various analytical parameters.

3.1.5 COMPLETENESS

Completeness is an expression of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Completeness is the percentage of measurements that are judged to be usable (i.e., that meet project-specific requirements). Completeness goals are defined in the site sampling and analysis plan, QAPjP or contract, and vary with the size and complexity of the project. Completeness goals of 80-95% are traditionally accepted as realistic. ALS's objective is 100% completeness for samples unaffected by matrix interferences.

3.2 TRACEABILITY

Traceability is the extent to which results can be substantiated by hard-copy documentation, electronic or computer-generated data calculations, computer software, and data generation. Traceability documentation exists in two forms: (1) that which links final numerical results to authoritative measurement standards, and (2) that which explicitly describes the history of each sample from collection to analysis. Measurement traceability is further discussed in Chapter 7 of this LQAP.

3.3 SENSITIVITY

The term sensitivity is used in a broad sense to describe the various limits that enable a laboratory to meet project-specific data quality objectives (DQOs). These limit types include: instrument detection limit (IDL), method detection limit (MDL), method quantitation limit (MQL) or method reporting limit (RL), contract-required detection limit (CRDL), and contract-required quantitation limit (CRQL).

3.3.1 IDL AND LOD

The IDL is a minimum value that addresses the detection capability of the ICP instrument *only*, hence IDL studies are performed on a per analyte per instrument basis. These IDL studies must be conducted on whenever there is a significant change in instrument components or reagents.

The LOD (Detection Limit or MDL) is a minimum value that addresses the detection capability for the sample preparation procedures and the instrument. Hence, ALS performs LOD studies for each preparatory and determinative method combination, matrix, instrument, and analytical column. LOD studies are ongoing in each batch of samples tested. LOD studies are also required for method validation, and whenever the basic chemistry of a procedure changes.

LOD (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. LODs are determined using ALS SOP 329.

An MDL study is not performed for radiological analyses, or any components for which spiking solutions are not available or relevant (e.g., pH, ignitability, etc.). Reporting limits for these kinds of parameters, where applicable, are established based on the laboratory's knowledge of extraction efficiency, instrument sensitivity, and experience with the procedure. **SOP 329** provides additional information about LOD studies.

Results calculated between the MDL and the LOQ (RL) contain a significant amounts of error. Therefore, values reported between the LOD and LOQ(RL) are qualified as estimated – 'J' flagged for organic parameters, 'B' flagged for inorganic parameters. Also, LOD values are based on an interference-free matrix, and cannot evaluate the effects of sample matrix. Therefore, established LODs may not be achievable in some environmental matrices.

3.3.2 LOQ (RL)

ALS defines LOQ as the analyte concentration at or above which the laboratory's precision and accuracy requirements can be routinely demonstrated and achieved. The statistical error associated with this region of a calibration curve is significantly smaller than that associated with the region near the MDL. The LOQ values for most analytes reported by ALS are numbers that are approximately 30% of the LOD for those analytes. It is ALS's policy to analyze a calibration standard at or below the LOQ when performing an initial calibration.

The LOQ is the lowest level that can be reliably measured by a laboratory with defined limits of precision and bias. The precision and bias at the LOQ is associated with Reporting Limits verification (RVS)

samples analyzed. The USEPA CLP SOW uses the terms CRDL and CRQL to describe *contractually-required* levels of reporting.

3.4 MINIMUM DETECTABLE CONCENTRATION (RADIOCHEMISTRY)

The minimum detectable concentration (MDC) is used for radiochemical procedures and is defined as the concentration at which there is a 95% confidence that an analyte signal will be distinguishable from an analyte-free sample.

The general formula for calculating the MDC is based on calculations derived by Curie (Curie, L.A., "Limits for Qualitative Detection and Quantitative Determination," Analytical Chemistry 40(3); pp. 586-693; 1968) and is calculated as follows:

$$MDC = \frac{(4.65\ X\ \sigma_b) + 2.71}{T * K}$$

where:

MDC = Minimum Detectable Concentration

σb = Standard deviation of the measurement background

T = Sample count time

K = Factor for incorporating efficiency, abundance, aliquot yield, ingrowth and decay, and activity conversion factors

3.5 MEASUREMENT UNCERTAINTY

3.5.1 ANALYTICAL UNCERTAINTY

Uncertainty is associated with most of the results obtained in the laboratory testing conducted by ALS. It is meaningful to estimate the extent of the uncertainty associated with each result generated by the laboratory. It is also useful to recognize that this measurement uncertainty is likely to be much less than that associated with sample collection activities. In practice, the uncertainty of a result may arise from many possible sources. ALS has considered the relative contribution of major sources of error. The approach adopted by the laboratory to estimate uncertainty resulted in the conclusion that many sources of error are insignificant compared to the processes of sample preparation, calibration, and instrumental measurement. The uncertainty associated with these processes can be estimated from quality control data. Accordingly, ALS estimates uncertainty from data derived from quality control samples carried through the entire analytical process. Each estimate of uncertainty is associated with a specific combination of analytical method and sample matrix.

The ALS Standard Operating Procedure 998 gives details of how uncertainty in the analytical process is estimated, calculated and reported if required.

3.5.2 TOTAL PROPAGATED UNCERTAINTY FOR RADIOCHEMISRY

Total propagated uncertainty (TPU), is a summation of the various uncertainties present in a measurement process, and is an integral part of every reported radiochemical value. TPU, reported as ±TPU, is the expressed estimated measure of the total uncertainty inherent in that reported radiochemical result.

The components of the TPU are classified as either random or systematic. Random uncertainties, also called counting uncertainties (CU), derive from the statistically random (normally distributed) nature of radioactive decay, and are estimated as the square root of the total number of counts acquired during analysis. In cases where the chemical yield is determined by the analysis of a radioactive tracer, the yield uncertainty (YU) is also a random uncertainty, and is estimated as the square root of the total number of tracer counts acquired. CU and YU are calculated in activity units to afford comparability to the sample result.

Systematic uncertainties are attributable to actual errors in the measurement of a physical quantity. For example, if a balance has an accuracy of $\pm$0.1%, the results of those gravimetric measurements are not normally distributed, but rather are assumed to be biased by that amount. Estimates of systematic uncertainties in laboratory processes are somewhat subjective, but should be supported by empirical data whenever possible. Systematic uncertainties associated with the preparation of a sample are called preparation uncertainties (PU), and are defined based on the number of volumetric and gravimetric measurements, quantitative transfers, etc. Systematic uncertainties associated with the analysis, called instrument uncertainties (IU), include biases associated with sample positioning, standard values, calibration coefficients, etc. PU and IU are typically provided as a percentage of the final result. To afford comparability to sample results, PU and IU are expressed in activity units by multiplying the percentage by the sample activity (A).

All contributions to TPU are considered to be independent of each other, and the individual contributions are combined as the square root

of the sum of the squares (see equation below). The final TPU result is expressed in activity units, such as

pCi/g or pCi/L.

$$TPU = \sqrt{CU^2 + YU^2 + (A * PU)^2 + (A * IU)^2}$$

TPU is expressed as a value at a specific confidence interval. The default convention at ALS is to provide the TPU at the 2-sigma confidence interval. This asserts approximately a 96% confidence level that the actual sample value is within the reported uncertainty range of the calculated result. **SOP 708** provides more information about the calculation and use of TPU.

3.6 QUALITY ASSURANCE PROJECT PLAN (QAPjP) EXCEPTIONS

As a result of the unknown nature of environmental samples prior to analysis, ALS has minimal control over analytical and quality control complications that result from sample matrix conditions. These conditions may include highly concentrated samples that contain target compounds of interest and/or non-target components; high organic content (both natural and synthetic); and extremes in pH, viscosity, solubility, etc. Each of these conditions may require a different approach.

Analysis for some samples may be achieved through the use of reduced aliquot sizes. Some sample matrices may require the laboratory to use cleanup and/or dilution techniques in order to analyze the sample by the desired protocol. Unfortunately, reduction of analysis aliquot or diluting a sample necessitates raising reporting limits (RLs) or MDCs, and often adversely impacts the calculation of surrogate, tracer, and matrix spike compound recoveries.

ALS has the responsibility to identify matrix interferences that preclude the generation of 'compliant' data. This determination may be made by demonstrating reproducibility (i.e., reanalysis of the affected sample) to show that the quality control measurement failure resulted from sample matrix conditions beyond the laboratory's control and not as a result of analytical error. For example, if the surrogate or tracer recoveries are outside of control limits, then samples may be re-extracted and/or reanalyzed. Repeated non-compliant results indicate that sample matrix probably prevented the laboratory from reporting results deemed compliant.

Analytical projects containing particularly "dirty" samples (i.e., highly contaminated with target compounds and/or matrix co-extractives) will often fail to meet pre-established completeness goals (set forth in the QAPjP), when prior

site history does not reveal the matrix constituents issues. Although the laboratory performs all analytical testing and cleanup procedures by the prescribed protocols, the results obtained may not meet validation criteria as a result of elevated reporting limits or the frequency at which surrogate, internal, tracer, or matrix spike recoveries fail to meet acceptance limits. In cases where the laboratory is unable to meet quality control criteria as a result of sample matrix complications, results that are qualified by data validation guidelines may still be useful to the end user of the data.

ALS is committed to adhering to the method requirements and quality control procedures prescribed by our clients. ALS strives to produce compliant data, however, uncertainties associated with environmental samples may preclude the laboratory's ability to generate fully compliant data. ALS will not assume responsibility for conditions beyond our reasonable control that directly impact the "validity" versus the usability of the associated analytical data generated by the laboratory.

4. SAMPLE CONTAINERS, PRESERVATION, HANDLING, HOLDING TIMES

Defining the magnitude and nature of an environmental problem, and developing an appropriate solution, requires the collection of representative samples for laboratory analysis and data evaluation. The objective of field sampling is to remove a small portion of an environment that is representative of the entire body. *Analytical methods have been standardized, but the results of analyses are only as good as the sampling protocol and the sample preservation and handling methods.* Defining sampling procedures and the quality elements applicable to environmental testing is beyond the scope of this document, and beyond the responsibility of the laboratory.

Although the laboratory is not responsible for sample collection, it is responsible for maintaining the integrity of the sample after receipt. After the sample has been collected, the constituents of the sample must remain as close as possible to the field condition (i.e., degradation must be prevented). The length of time that these constituents will remain stable is related to their character and the preservation method used. Preservation is accomplished by the addition of chemical preservatives and/or storage at a controlled temperature, and by the strict observation of prescribed maximum holding time allowances. **Appendix C** lists sample container types, preservation requirements, and holding times.

4.1 FIELD SUPPORT

Unless not required by the client, sample kits are prepared at the laboratory to provide the client with all sample containers, preservatives and documentation needed for the analyses needed for a project. ALS provides shipping containers, custody documents, custody seals, clean sample bottles, labels, applicable high-purity chemical preservatives for water samples, and trip blanks to support field-sampling events. Hard-sided, insulated, "picnic" coolers are typically used to

transport samples from the field to the laboratory. These coolers meet or exceed all protocol requirements (i.e., USDOT, USEPA, ASTM) for shipping. ALS **SOP 205** provides further information on sample kits.

4.2 SAMPLE CONTAINERS

ALS provides certified clean (I-Chem 300™, Eagle Pitcher Level 1, or equivalent) sample bottles for sample collection. Used sample bottles are never used by the laboratory. The Sample Receiving Department maintains certificates of cleanliness that are provided by the vendor for all sample bottles. These certificates are provided to the client upon request. Containers are stored in clean areas, away from laboratory processes, to prevent exposure to fuels, solvents, and other contaminants.

4.3 SAMPLE PRESERVATION AND HOLDING TIMES

ALS provides the required chemical preservatives for water samples and, upon request, "blue ice" packs, for thermal preservation during transport. Typically, high quality reagent grade chemical preservatives (i.e., acids, solutions, etc.) are added to individual sample bottles, as appropriate per method and US Department of Transportation (DOT) requirements. Only trace metals grade nitric acid is used for preservation of metals or radiochemical samples, as applicable. It is the responsibility of those collecting the samples to properly use these materials (e.g., don't rinse or overfill container such that the preservative is washed out), and to ensure that chemical preservation requirements are met, and proper preservation techniques (chilling) are performed. Holding times begin with the collection of samples and continue until analysis is complete. See **Appendix C** for a summary of container, preservation and holding time requirements specific to various analyses and matrices.

4.4 SAMPLE RECEIPT SCHEDULE

ALS receives samples six days of the week, Monday through Saturday. ALS requests that clients ship samples for delivery within one day of collection, and give advance notice to the laboratory regarding shipment of RUSH samples or samples with short hold time requirements. Shipping containers received at the laboratory on holidays or after business hours are placed in a walk-in refrigerator and opened on the next business day, unless other arrangements are made in advance.

4.5 CHAIN-OF-CUSTODY

Chain-of-custody (COC) documentation begins with field sampling and continues through laboratory analysis and disposal. A chain-of-custody record that identifies all individuals who handle the sample is used to establish an intact, continuous record of the physical possession, storage, and disposal of collected samples, including their aliquots, extracts or digestates. The chain-of-custody

record is initiated in the field by field personnel who complete a COC form listing all samples. This form contains the following information and remains with the samples during transport:

- client project name and project location;
- field sample number/identification;
- date and time of sample collection;
- matrix;
- container type and number of containers for each sample;
- preservative;
- analysis requested;
- sampler's remarks and signature;
- signature of person relinquishing samples and date and time relinquished;
- custody seal number (if applicable); and
- designation of matrix spike/matrix spike duplicate (MS/MSD) samples (optional).

  Note that contingent upon the sample matrix and analysis to be performed, additional sample volume may need to be submitted to accommodate MS/MSD analyses.

All transfers of samples, except directly between commercial couriers, must be recorded on the chain-of-custody form via the "relinquished" and "received by" sections. All information, except signatures, should be clearly printed.

The USEPA National Enforcement Investigations Center (NEIC) defines evidence of custody as:

- in one's actual possession, or
- in one's view, after being in one's physical possession, or
- having been in one's possession and then locked or sealed to prevent tampering, or
- kept in a secure area, restricted to authorized personnel only.

To ensure that sample custody objectives of traceability are achieved for every project, the chain-of-custody initiated in the field, is continued and maintained

internally throughout the laboratory per the requirements specified in **SOP 318.** Internal chain-of-custody begins with sample acceptance and login (**SOP 202**), is maintained as samples are distributed for use throughout the laboratory (further discussed in LQAP Section 4.10), and concludes with final sample disposition (i.e., return to the client or disposal). ALS applies a unique barcode to each sample bottle received, and maintains several scanners and PCs throughout the laboratory to document and assist with sample, aliquot, extract and digestate movement throughout the facility. This electronic process is accomplished through LIMS, which retains records of all sample and fraction transactions made.

4.6 SAMPLE ACCEPTANCE POLICY

ALS' sample acceptance policy requires that a sample meet the following conditions:

- The sample shall be completely documented (sample identification, location, date and time of collection, collector's name, preservation type, sample type, any special remarks concerning the sample);
- The sample shall be identified by a unique identifier using durable labels completed in indelible ink;
- The sample shall be collected in adequate volume;
- The sample shall be collected in an appropriate container;
- The sample shall be delivered to the laboratory with at least one-half the holding time remaining;
- The sample shall not exceed allowed radioactivity levels; and
- The sample shall not show signs of contamination, breakage, or leakage.

Sample receipt discrepancies are documented by Sample Receiving Department personnel on the Condition of Sample Upon Receipt, Form 201 (SOP 008), which is forwarded to the Project Manager as part of the workorder folder. Where samples do not meet the criteria stated above, the Project Manager requests information from the client before proceeding. If the client can provide the information and, in cases of compromised sample integrity, directs the laboratory to proceed, then data acquired from the sample(s) analysis is reported and the problems noted during sample receipt are disclosed in the narrative of the final data report.

In support of the protection of employee health and of ALS's radioactive materials license, ALS observes prescreening protocols that designate or determine samples with radioactive content. Detailed procedures for conducting

radiological survey of incoming sample packages are given in **SOP 008**, further details regarding prescreening protocols are given in **SOP 703**.

4.7 SAMPLE RECEIPT PROTOCOLS

Upon receipt of the field samples at the laboratory, personnel ensure that sample bottles are maintained according to storage requirements, and in a manner that does not contaminate the samples (see section 4.9 for further details).

Ascension numbers that increment serially each month of the year are applied as workorder number assignments. Following sample arrival and initial screen for USDOT compliance and removable radioactivity, sample receiving personnel inspect the sample and record any discrepancies using Form 201 (**SOP 008**). The following information is documented:

- client and project name, as applicable;
- presence/absence and condition of (i.e., intact, broken) custody seals on the shipping containers;
- presence/absence of chain-of-custody and completeness;
- sample condition (intact, broken, leaking);
- presence/absence of removable sample tags;
- agreement/non-agreement between the sample labels, tags, chain-of-custody, and any other client documentation;
- receipt of adequate sample volume;
- sample temperature, where applicable;
- presence/absence of headspace in VOA and ^{222}Radon vials; and
- chemical preservation, where applicable.

Sample temperature is verified upon receipt by measuring the temperature of the temperature blank (if available) or by measuring the temperature of a representative samples(s) with an infrared (IR) temperature device. See **SOP 210** for instructions and procedures related to IR temperature guns. Samples that require thermal preservation are considered acceptable if the temperature upon arrival is between just above freezing to 6ºC. Samples that require thermal preservation but are hand-delivered to the laboratory immediately after collection, may not meet the temperature requirement. If the hand-delivered sample is packed in ice, then Sample Receiving personnel record its temperature and note that the chilling process was initiated.

4.8 SAMPLE LOGIN POLICIES AND PROCEDURES

After completing sample receipt procedures, the following sample information and analytical requests are entered into LIMS under the unique workorder number assigned:

- client name, contact, address, phone number;
- ALS Project Manager;
- date and time of sample receipt;
- unique laboratory identifier for each sample;
- sample description, including date/time of collection;
- analyses requested (LIMS calculates holding times for each analysis);
- program specification or other special instructions, if applicable; and
- due date.

In general, a group of received samples is assigned one workorder number in LIMS. Each sample container is assigned a unique ALS identifier (barcode) that is placed on each container. This unique identification includes all samples, subsamples, and subsequent extracts and/or digestates.

See **SOP 202** for additional information about sample login and distribution.

4.9 SAMPLE STORAGE

Samples requiring thermal preservation are stored in designated refrigerated storage areas that are maintained just above freezing to 6ºC,. Freezer storage areas are maintained at freezing to ¯20ºC,. The temperature of refrigeration units is monitored continuously using electronic min/max thermometers and recorded each business day, near to the beginning of the work shift. If the temperature exceeds the prescribed range, then corrective action is taken and documented immediately, and the client notified, if appropriate; see **SOP 326** for further details. Directives for corrective action pertaining to catastrophic failure of cooling units (as well as laboratory ovens, etc.) are included in ALS's Emergency and Contingency Plan (ECP).

Samples are stored away from all standards, reagents, food and other sources of contamination. Samples are stored in such a manner as to prevent cross-contamination. For example, pure product or potentially contaminated samples are tagged as "hazardous" and stored within a secured area, separate from other samples. ALS provides designated sample storage areas according to the following parameter groups: metals, inorganics (WetChem), semivolatile organics, volatile organics, fuels, and radiochemical analyses.

Samples having suspected radioactive activity and scheduled also for stable chemical analyses are refrigerated. Samples to receive tritium analyses are refrigerated. Samples designated for radiochemistry analyses *only*, with the exception of tritium, are segregated and maintained at ambient temperature.

To effectively monitor the storage and potential contamination of volatile organic samples, ALS observes a refrigerator blank program (detailed in **SOPs 511, 512**).

To provide for the safe containment of sample material that could be released as a result of sample container failure, all samples are stored in secondary containment bins. These secondary containment bins are of a sturdy and inert nature, and are sufficient in size to fully contain the sample(s) in the event of a spill, leak or breakage. The bin(s) may be uniquely identified (labeled) to assist in locating samples via the chain-of-custody system. The bins are thoroughly cleaned between uses.

4.10 SAMPLE ACCESS

It is ALS's policy that neither samples nor data may be released to unauthorized personnel. In order to ensure that this policy is maintained, the laboratory facilities are maintained under controlled access and are restricted to authorized personnel only (see **SOP 132** for further details pertaining to building security).

As discussed previously in this section, ALS personnel follow strict sample handling and internal chain-of-custody procedures to ensure the integrity of all data generated. Limited access electronic controls in LIMS further protect the validity of the data results. Samples are scanned and transacted in LIMS when they are removed from a storage area for preparation or analysis. The sample ID, analyst, date, time, and location are recorded with each transaction. Likewise, the samples are scanned and transacted in LIMS upon their return to the storage unit. Barcode scanning and LIMS transaction is also observed for the return of sample remainders to the client, and for disposal (see LQAP Section 4.13). ALS **SOP 318** contains internal chain-of-custody details; procedures for sample return to the client are described in **SOP 027**.

4.11 SAMPLE HOMOGENIZATION AND SUBSAMPLING

Obtaining a representative aliquot of sample for testing is critical to the representativeness of the analytical results obtained. Proper subsampling techniques, particularly for solid matrices, are a component of each bench employee's technical instruction. Sample homogenization procedures prior to radiochemical analysis are prescribed in **SOP 736.** Representative subsampling procedures for stable chemistry analyses is prescribed in **SOP 336**.Client and method specified procedures for homogenization or aliquotting may also be defined in the applicable LIMS program specification.

4.12 SUBCONTRACTING ANALYTICAL SERVICES

ALS strives to identify the need to subcontract specific analytical procedures during the bid response process. Analyses may also need to be subcontracted, however, in cases of emergency where the ability to meet sample holding time criteria is endangered. In these instances, ALS compiles a list of qualified subcontract laboratories that are suitable to perform the needed analyses, then submits the list to the client for selection and approval. If TNI certified analyses are to be subcontracted, the subcontract laboratory must also hold TNI certification for the analyses that are to be conducted. The same concept regarding subcontract laboratory qualifications may apply for other program samples (e.g., DOD laboratory approval status is required for the analyses to be conducted in the case of DOD samples that must be subcontracted for analysis). Note that for subcontracted DOD sample analyses, the subcontract laboratory must receive project-specific approval from the DOD client before any samples are analyzed.

ALS's Project Manager must receive permission from the client, in writing, before the subcontract laboratory can be procured and samples forwarded to the laboratory. At a minimum, the specific terms of the subcontract laboratory agreement must include:

- analytical method required (e.g., SW-846, 40 CFR, etc.);
- number and type of samples expected;
- project-specific quality control requirements;
- deliverables required (hardcopy, electronic);
- laboratory certifications required;
- price per analysis; and
- turnaround time requirements.

See **SOP 103** for guidance on evaluating a subcontract laboratory's qualifications. Detailed procedures pertaining to submitting samples to a subcontract laboratory are provided in **SOP 103**.

4.13 SAMPLE DISPOSAL

After completion of sample analysis and submission of the project report, unused portions of samples are retained by the laboratory for a minimum of 30 days or as designated by client and contract requirements from date of invoice. Samples are disposed or returned to the client according to the nature of the samples and the client's specifications. ALS documents and retains all conditions of disposal and correspondence between all parties concerning the final disposition of the sample.

Samples, digestates, leachates, extracts, and process waste that are characterized as hazardous, radioactive, or mixed waste are disposed in accordance with Federal and state laws and regulations. ALS maintains records to demonstrate that all disposal efforts were conducted in compliance with these laws and regulations. This documentation includes the unique sample identity, date of disposal, nature of disposal (e.g., sample depleted, sample disposed in hazardous waste facility, sample disposed in mixed waste facility, sample returned to client); and name of the individual responsible for disposal.

5. LABORATORY FACILITIES

Appendix E contains a diagram of the ALS laboratory facility. ALS maintains constant and consistent test conditions throughout the facility (e.g., temperature, air purification, lighting). All entrances and exits are wired to a laboratory-wide security system that is monitored continuously. Access to the laboratory area from the front offices is restricted by means of keypad locks requiring numeric security code entry. Visitors must sign in at the front desk and must be escorted at all times (some vendors are allowed access without continuous escort, in order to facilitate repairs or deliveries). Further details pertaining to building security are provided in **SOP 132**.

The following sections highlight areas of the laboratory that are involved with sample receipt, handling, preparation, and analysis of samples.

5.1 SAMPLE RECEIPT AREAS

ALS's sample receiving area consists of a large dedicated room of more than 500 ft^2. It contains fume extraction and radiation survey equipment to safely handle incoming radioactive and mixed waste samples. There is an outside access door to facilitate sample delivery and shipping of sample kits. Adjacent to the sample receiving area is the bottle storage room and the radioactivity prescreening lab.

5.2 SAMPLE STORAGE AREAS

ALS's sample receiving area has a walk-in cooler and a freezer that are used for temporary storage of samples that require thermal preservation. In addition, there are several designated sample storage locations throughout the laboratory that are used to store samples scheduled for specific analyses (see section 4.9 for further details).

5.3 SAMPLE PREPARATION AREAS

The laboratory has nine sample preparation/extraction/digestion areas. These areas are divided as follows: six radiochemistry preparation laboratories; two organics extraction laboratories; and one metals digestion laboratory. The total floor space of these six laboratories is approximately 4500 ft^2.

Laboratory preparation procedures are segregated as much as possible to minimize the potential for contamination, maximize processing efficiency, and maintain analytical integrity. Rigorous cleaning of glassware (**SOPs 334** and **720**) and apparatus ensures that cross-contamination is minimized. Each laboratory area has a dedicated or locally shared HVAC system that continuously exchanges the laboratory air with filtered and conditioned outside air. There are 34 laboratory hoods in the six sample preparation areas, and each sample preparation area has at least one hood that is capable of maintaining an average face velocity of 100 feet per minute.

5.4 STANDARDS PREPARATION AREAS

A dedicated radiochemical standards preparations room, and an organics standards preparation area are maintained. Metals and inorganic standards are stored independently from sample storage areas and are prepared in their respective laboratory areas.

5.5 ANALYTICAL LABORATORIES

The ALS facility houses a volatile organics analysis (VOAs) laboratory that is on an upper level of the building, away from all other laboratory operations. The ALS facility also houses one general chemistry (WetChem) laboratory, two radiochemical counting rooms, a total organic carbon (TOC) laboratory area, two gas chromatograph (GC) laboratory area, a semivolatile organic compounds (SVOCs) laboratory, and a metals laboratory that contains separate inductively coupled plasma (ICP), mercury, and inductively coupled plasma/mass spectrometry (ICP/MS) rooms.

5.6 OTHER LABORATORY AREAS

Other areas of the ALS facility include a tank room for compressed gasses, several waste management areas, telephone and computer storage rooms, staff offices, Reporting Group and Reports Management data processing rooms, and various scanning/reproduction and supply storage areas.

5.7 DEIONIZED WATER SYSTEM

Within the laboratory, there are two main deionized (DI) water distribution systems available for glassware cleaning, bulk reagent preparation, and general use. One system is located in the janitor's area and serves the radiochemistry side of the facility (ASTM Type II water generated). The other system is located adjacent to the metals laboratory area and serves the stable chemistry side of the facility (ASTM Type I water generated). These DI water systems are capable of continuously delivering water that meets the requirements specified for the ASTM water type, and are monitored and documented each business day to ensure that the water meets these criteria. ALS also maintains a third treated water system that is used to support washing of stable chemistry laboratory glassware.

DI water is defined as municipal tap water that has been treated by passing it through a particulate filter, activated carbon unit, cation exchange resin, anion exchange resin, mixed bed resin, and a final "polishing" cartridge. This water contains no detectable heavy metals or inorganic compounds of interest, and is free of organic compounds of analytical interest above ALS's routine reporting limits. Additionally, a benchtop Millipore Synergy 185™ unit is available for laboratory use should further finishing be desired.

SOP 319 provides detailed information pertaining to ALS's DI water systems, including discussions of independent monthly testing to verify that electronic readouts of water quality are accurate, maintenance by a vendor contractor, and corrective measures to be taken should water quality degrade to below acceptable limits.

6. ANALYTICAL PROCEDURES

ALS is capable of analyzing various matrices, including surface and groundwater, drinking water, soil, sediment, vegetation, tissue, filter and aqueous and solid wastes. ALS does not routinely perform analyses on air (non-particulate), however, analysis of these matrices may be available through our sister laboratories. Analyses are performed using promulgated methodologies as requested by the client and their regulators, and as required by ALS's certifying authorities. *New iterations of established methodologies are evaluated on an ongoing basis and implemented as client needs dictate.* Analytical procedures are conducted in strict adherence with SOPs that describe the preparation, analysis, review and reporting of samples. In some cases, these SOPs may also describe proprietary methods developed by ALS and used per the client's request. A list of ALS's analytical capabilities is presented in **Appendix C.** A list of ALS's SOPs is provided in **Appendix H**. References for analytical procedures used are presented in the attached **Bibliography**. ALS also, upon request, develops and validates procedures that are more applicable to a specific client objective.

6.1 ANALYTICAL METHODS

Selection of the appropriate method is dependent upon data usage and regulatory requirements. ALS may modify existing methods in order to:

- achieve project-specific objectives;
- incorporate modifications or improvements in analytical technology;
- address unusual matrices not covered in available methods; and
- provide analytical capabilities for an analyte for which there are no promulgated methodologies.

ALS discloses method modifications to our clients by providing the appropriate SOP for review.

6.2 METHOD COMPLIANCE

Compliance is the proper execution of recognized, documented procedures that are either approved or required. Strict adherence to these procedures is necessary to provide data acceptable to a regulatory body of competent jurisdiction in a specific regulatory context.

Compliance is, however, separate from, but not inconsistent with, technical scientific quality. ALS understands that the expectations of our clients commonly include the assumption that data and reports will satisfy a regulatory purpose and will be found acceptable and compliant with regulatory requirements.

6.3 NON-STANDARD METHOD VALIDATION

When a non-promulgated method (i.e., methods other than EPA, ASTM, etc.) is required for specific projects or analytes of interest, or when the laboratory develops a procedure, the laboratory must establish the validity of the method prior to extracting or analyzing a client's samples. *Validity is established by meeting criteria for precision and accuracy. See ALS SOP 999 for method validation protocols.*

7. MEASUREMENT TRACEABILITY AND CALIBRATION

ALS follows a well-defined calibration routine for all instruments and equipment. Calibration may be performed by laboratory personnel using certified reference materials traceable to NIST or equivalent certified materials, or by external calibration agencies or equipment manufacturers. The discussion in this section of the LQAP is general in nature because the requirements for calibration are instrument or equipment and method specific. Details of calibration procedures and requirements can be found in ALS's standard operating procedures (SOPs), analytical methods and operations manuals.

A list of all major instrumentation available at ALS is provided in **Appendix G**. The Quality Assurance Department maintains this list.

7.1 TRACEABILITY OF CALIBRATION

ALS's program of calibration and/or verification and validation of equipment must ensure that, wherever possible, measurements performed by the laboratory are traceable to national standards of measurement. ALS requests and maintains calibration certificates (e.g., weights, thermometers, balances) that demonstrate traceability to national standards of measurement. If traceability to national standards of measurement is not available or applicable, then ALS provides evidence of correlation of results (e.g., verifying an in-line resistivity meter by

reading the system's output with a conductivity meter; participating in a PT studies).

7.2 REFERENCE STANDARDS OF MEASUREMENT

ALS uses reference standards of measurement (such as Class S weights or NIST-traceable thermometers) for calibration verification purposes only (i.e., these reference standards are not available to laboratory staff for general use). Reference standards of measurement are calibrated by an ISO 17025 Calibration Laboratory. Reference thermometers are calibrated every two years. Reference weights are certified every five years. Certificates of vendor calibration are maintained by the Quality Assurance Department.

The certified reference standards are then used to annually verify other measurement devices (e.g., laboratory thermometers, laboratory weight sets) in-house. The in-house verification efforts are managed by the Quality Assurance Department. All items so verified are tagged with a sticker indicating the unique identity of the device, the date of verification and the initials of the technician who performed the verification, and the date the verification is valid through. Procedures for the in-house verification of thermometers are given in **SOP 923**. Procedures for the verification of weight sets are given in **SOP 901**.

7.3 TRACEABILITY OF STANDARDS, SOLVENTS AND REAGENTS

ALS purchases the highest quality standards, solvents, and reagents appropriate to the analytical methodologies employed. The vendor must supply a Certificate of Analysis, Certificate of Purity, or equivalent. These certificates are maintained by the department using the materials.

With the exception of extraction solvents, each department documents the date of receipt, date opened and an expiration date for all standards and reagents by labeling the original container, or certificate and/or by entering this information into ALS's Standards and Reagents database.

Each department is responsible for the preparation, documentation, storage and disposal of its chemicals. Standards preparation information is documented by entry in ALS's Standards and Reagents database. The following information, needed to maintain traceability of the standard, is recorded for each standard:

- date of receipt of reference standard;
- unique internal identification number and traceability to purchased stock or neat compounds, as applicable (i.e., vendor/lot numbers; unique ALS identifier);
- date of preparation;

- name of preparer;
- amount of reference material used;
- volume/identity of reagents and solvents used;
- final volume;
- concentration;
- expiration date of the stock and prepared standards.

See **SOP 300** for additional information about standards preparation, storage, and expiration. Verification (re-verification) of radiochemical standards is also addressed in **SOP 710**.

7.4 GENERAL REQUIREMENTS FOR CALIBRATION

Each calibration is dated and documented to ensure that it is traceable to the method, instrument, date of analysis, analyte, concentration, and response. Sufficient information must be documented to permit reconstruction of the calibration. Acceptance criteria for calibrations must comply with method requirements.

7.5 INSTRUMENT CALIBRATION

This section defines the essential elements of initial instrument calibration (ICAL) and continuing instrument calibration verification (CCV). These procedures ensure that the data will be of known, documented, and appropriate quality for a given application. *Samples yielding concentrations that exceed the upper limit of the calibration curve shall be diluted and reanalyzed, if possible, to bring the results within the calibrated range. Results of samples outside the known calibration range, above or below, must be reported as qualified values and discussed in the case narrative.*

Initial instrument calibration is used for quantitation and continuing instrument calibration verification is used to confirm the validity of the initial calibration. The following items are required of both initial and continuing instrument calibrations:

- The details of the instrument calibration procedures, including evaluation and acceptance criteria, and corrective measures to be taken in the event that these acceptance criteria are not met, must be included or referenced in the test method SOP.

- Sufficient raw data records must be retained to allow reconstruction of the instrument calibration (e.g., calibration date, test method, instrument,

date of analysis, name of analyst, concentration of standard(s), response, response factor).

Additional essential elements of initial as well as continuing instrument calibrations are discussed below.

7.5.1 INITIAL INSTRUMENT CALIBRATION

The following items are essential elements of initial instrument calibration:

- Samples must be quantitated from the ICAL, unless the reference method states otherwise.
- The initial calibration range must consist of at least the minimum number of calibration points specified by the reference method. If the reference method does not specify the number of calibration standards, then the minimum number is two, not including blanks or a zero standard. Exception: multi-component analytes, such as chlordane, toxaphene or Aroclors, may be analyzed using a one-point calibration, per SW-846 guidance, if so requested by the client.
- The lowest calibration standard must be above the detection limit (MDL) and at or below the RL (i.e., the method reporting limit must be within the calibrated range of the method).
- Calibration standards must include concentrations at or below the regulatory limits, if these limits are known to the laboratory.
- Criteria for the acceptance of an initial instrument calibration must be established (e.g., RSD, correlation coefficient, etc.).
- If ICAL results are outside acceptance criteria, then corrective action must be performed, and the instrument recalibrated before analyzing samples.
- Exclusion of initial calibration points without technical justification is not allowed (poor injection or power failure are valid reasons to exclude a calibration point).

- All reported target analytes and surrogates must be included in the initial calibration.

- The ICAL must be verified (see section 7.5.3) before samples can be analyzed.

7.5.2 CONTINUING INSTRUMENT CALIBRATION

A continuing calibration verification (CCV) standard must be analyzed with the frequency prescribed in the reference method, or as dictated by the applicable LIMS program specification (typically within every 12hr time period). For example:

- When an ICAL is not performed on the day of analysis, then validity of the initial calibration must be verified with an acceptable CCV prior to sample analysis.

- A CCV must be repeated at the beginning and end of each analytical sequence. (For GC/MS methods that use an internal standard, only one CCV must be analyzed before each analytical sequence). Some methods additionally prescribe that a CCV must be analyzed after every 10 (or 20) samples analyzed.

The following items are essential elements of continuing instrument calibration:

- With the exception of multi-component analytes, all reported target analytes must be included in the continuing instrument calibration standard.

- Criteria for the acceptance of a CCV must be established (e.g., %D, %Drift, from the initial calibration).

- If the CCV results exceed acceptance criteria, then corrective actions must be performed. If routine corrective action procedures do not produce a second consecutive CCV within acceptance criteria, then a new calibration must be performed and successfully verified.

Additional aspects of calibration verification are discussed below.

7.5.3 CALIBRATION VERIFICATIONS

All ICALs must be verified with a ***second source*** standard obtained from a different manufacturer/vendor and traceable to a national standard, when available. If a different manufacturer/vendor is not available, the laboratory must request a different lot number of the standard.

In most cases, a second-source initial calibration verification (ICV) standard is analyzed immediately after the ICAL and before any samples are analyzed. However, analysis of an ICV is not required, if the continuing calibration verification (CCV) standard is from a second source.

Sample data associated with an unacceptable calibration verification standard may be reported as qualified data in the following cases:

- When the acceptance criteria for the CCV is exceeded high (i.e., high bias), and only non-detects were determined for the affected analyte(s) in associated samples, then those non-detects may be reported.
- When the acceptance criteria for the CCV is exceeded low (i.e., low bias), then these sample results may be reported if they exceed a maximum regulatory limit.
- When the acceptance criteria for the CCV are exceeded (high or low), and the effect on the system from previous sample analysis is substantiated (e.g., by reanalysis or sample response characteristics on a different detector), then the sample results may be reported.

Other levels of concentrations and frequencies of analysis for calibration checks (ICVs, CCVs) may be required by specific client programs. These requirements, which supercede method, SOP or LQAP requirements otherwise stated, are communicated to the laboratory staff via LIMS program specifications.

8. PREVENTIVE MAINTENANCE AND REPAIR OF EQUIPMENT

ALS maintains an organized maintenance program that is broader than the particular instruments or devices a specific employee may operate or is familiar with. The objective of

ALS's equipment maintenance program is to provide a structure of care that prevents quality control failures and minimizes lost productivity that results from equipment malfunction or failure. Within this program are provisions for corrective actions, maintaining spare parts, and a contingency plan in the event of catastrophic failure (e.g., loss of power for a significant period of time).

See Appendix G for a comprehensive list of ALS's equipment.

ALS's maintenance program is based on equipment manufacturer's recommendations, operator training guidance, and other considerations (e.g., sample throughput). The established maintenance program applies to all laboratory primary instrumentation, as well as support equipment (see Section 8.6 for a definition of what constitutes support equipment). Provisions for documenting all routine and non-routine instrument equipment maintenance and repairs are also established within the maintenance program.

Responsibilities for applying ALS's maintenance program rests with the department that utilizes the equipment, the Quality Assurance Department bears responsibility for certain support equipment such as balances, ovens, refrigerators, freezers, and temperature measurement devices. Only authorized personnel are permitted to perform maintenance.

Culturally, ALS makes a distinction between 'operational' and 'routine' maintenance that external parties generally do not. ALS considers the normal/typical things that operators do to keep the equipment functioning properly (e.g., septum replacement, reagent refill, etc.), as 'operational' maintenance, and does not generally view these tasks as routine maintenance events that require specific documentation in a dedicated maintenance log. ALS's view is that the fact that the equipment is performing properly and yielding acceptable QC results, evidences that these maintenance tasks were performed as needed. ALS's maintenance system does, however, provide for attestations that this maintenance was performed, where applicable. In contrast, ALS defines routine maintenance as those things done in-house only periodically (i.e., that are beyond what is performed as usual 'operational' maintenance), that are short of vendor repair (e.g., annual GFPC drawer evaluation).

Documentation requirements are discussed further in Section 8.4 below.

Note that ALS does not consider 'priming', or analysis of solvent blanks, which generally get recorded in the instrument run log, as maintenance.

8.1 MAINTENANCE SCHEDULES

In general, ALS performs maintenance as needed (including preventive considerations). Certain aspects of routine maintenance are considered to be 'operational', and are performed each time the instrument is run. Other maintenance is performed 'periodically' (e.g., roughly monthly, contingent upon sample throughput). Each instrument operator is responsible for the performance

of their own instrument, and may perform maintenance duties at their discretion. For these reasons, ALS's culture is not one of 'scheduled' maintenance, in the traditional (calendar) sense. Consequently, although the Group Leader provides oversight, it is not necessary or practicable to create formal maintenance schedules, or to have maintenance performance synchronized within the department.

ALS maintains service contracts for most major analytical equipment, including gas and high-performance liquid chromatographs, mass spectrometers, liquid scintillation counters, and cold vapor atomic absorption and inductively coupled plasma spectrophotometers. Preventive maintenance is included in most of these service contracts. Service contracts that include preventive maintenance are also retained for ALS balances and the DI water system.

8.2 SETTINGS

ALS's equipment list (Appendix G) depicts the following information: a) the identity and type of equipment and its software; b) the equipment's serial number or other unique identification; c) the current location; d) the date received and date placed in service (if available); and e) the condition when it was received (e.g., new, used, reconditioned).

While it is true that some settings (e.g., detector wavelength) may be stipulated in reference methods, most instrument settings are not specifically prescribed, as they are instead, dictated by acceptable outcome (e.g., peak resolution, etc.). In a similar vein, ALS provides typical instrument settings in the associated determinative SOP, but actual settings may vary contingent upon instrument performance and contributing factors, such as ambient conditions and operator subjectivity.

For the most part (i.e., not applicable to some types of equipment), instrument configuration and settings information is captured electronically by the instrument's 'method' files. Typically there is an 'acquisition' method file and a 'quantitation' method file that together, control the manner in which the data are obtained and subsequently calculated. These instrument files are archived via established laboratory electronic backup protocols (Form 159 – IS / LIMS Policy Statement), and are retrievable, thus providing for the reconstruction of data. The utilization of proper settings is evidenced by analytical data and QC results that meet performance criteria.

8.3 TRENDS

The dominant focus of trending contained in pertinent guidance documents relates to the generation of acceptable 'at on-set' and 'continuing' method QC checks. Concurrent with these requirements, ALS's culture for trending observation

labwide consists of ensuring that acceptable instrument checks are generated, and that the system is not producing any artifacts at levels of concern, prior to analyzing sample sets.

The expertise of the operator is a major component in effective equipment operation. Experienced operators develop an intuitive sense as to how their instrument is performing. Generally this sense is not based on a specific indicator, as there may be many contributing factors to that particular indicator, but rather on an accumulation of queues (similar to those factors that would be considered during the troubleshooting process). Because this type of expertise does not lend itself well to documentation, ALS emphasizes cross-training to ensure consistent data generation, and the retention of 'corporate knowledge'. See section 11.4.

8.4 EQUIPMENT DOCUMENTATION REQUIREMENTS

Analysts are responsible for maintaining calibration/verification and maintenance records of all instruments and equipment involved in the creation of the analytical data they generate. Considerations of maintenance, settings and trends, and their documentation, vary widely contingent upon the type of equipment, how automated it is, and the degree of sample throughput. Documentation can be accomplished by various means, electronically and via hardcopy. For example, ICP, ICP/MS and CVAA routine maintenance is entered into the instrument's PC and printed out in the raw data header, while service contract maintenance and repair are documented in hardcover logbooks. Labwide, dedicated hardcover maintenance logbooks are assigned to each piece of major ALS instrumentation, however, the manner in which equipment documentation is recorded, is at the discretion of the work group. It is not ALS's intent to unify or centralize maintenance information.

Although the manner of record keeping varies, in order to provide a clear and complete history of repairs and maintenance associated with the instrument, each entry may, but not limited to, include the following elements:

- the date of the maintenance or repair:
- the reason for the maintenance or repair (e.g., was this action taken to correct a problem or was this action routine instrument maintenance);
- a full description of the maintenance or repair conducted;
- the name of the analyst or vendor who performed the maintenance or repair;

- reference that it was verified that the equipment is operating properly before being placed back in service (SOP 317), and where this information can be found; and

- the initials of the analyst making the entry and date of entry.

Where applicable, the identity of the reference material used as an instrument check must also be recorded, and where applicable, a statement as to the calibration's expiration must also be made.

Details regarding equipment documentation are also provided in SOP 303. Note that maintenance logs are included in monthly logbook review.

Table 8.1 (Maintenance Snapshot) following provides a brief summary of laboratory equipment, an overview of associated maintenance performed, and comments regarding how associated maintenance documentation is accomplished.

8.5 CORRECTIVE ACTIONS, SPARE PARTS, CONTINGENCY PLAN

8.5.1 CORRECTIVE ACTIONS

Corrective measures for failed QC checks are given in the associated determinative SOP. General procedures for removing equipment from service and placing new or repaired equipment into service, are provided in SOP 317. Detail regarding corrective measures and repair for support equipment failures (e.g., ovens, cooling units, pipets, DI water system), are discussed in SOPs 320, 326, 321 and 319, respectively. Actions to be taken in the event of catastrophic failure are discussed in Section 8.5.3 below.

ALS maintains service contracts (preventive maintenance, repair) for most major analytical equipment. Some equipment (particularly some support equipment) does not lend itself to repair and would likely be replaced instead, per requirements given in SOP 127.

8.5.2 SPARE PARTS

An adequate inventory of spare parts is required to minimize equipment downtime. This inventory should include those parts and supplies that:

- are subject to frequent failure;

- have limited useful lifetimes, or

- cannot be obtained in a timely manner should failure occur.

departments are responsible for maintaining an adequate inventory of necessary spare parts for all major instruments and equipment items. Examples of spare parts maintained for major instrumentation include: septa, inserts, columns, tube fittings, filaments, source parts, and traps.

8.5.3 CONTINGENCY PLAN

In the event of a catastrophic instrument failure, ALS will make every effort to analyze samples within holding times by alternate means. If the redundancy in instrumentation is insufficient to handle the affected samples, then the Group Leader will notify the Project Manager immediately. In turn, the PM will notify the client to discuss options that will ensure successful completion of the project.

ALS will also take appropriate mitigating steps and notify the client should significant power, cooling unit, etc. failures occur that create circumstances which could adversely impact the client's sample results. An automated system is in place to notify computer support and operations. should a power outage of significant duration occur. However, any employee who notes an outage or unit failure is responsible for contacting the appropriate manager., who will in turn direct the necessary actions. The specific course of action taken is dependent upon the nature and extent of the failure. General procedures to be followed in the event of catastrophic failure are provided as an appendix to ALS's Emergency and Contingency Plan (ECP).

8.6 SUPPORT EQUIPMENT

ALS defines support equipment as all those devices which are not the primary determinative instrument defined by the analytical method, which support laboratory operations and would contribute to the testing uncertainty. Support equipment includes balances, ovens, refrigerators, freezers, water baths, temperature measurement devices, and mechanical (e.g., Eppendorf ™ pipets. Support equipment affecting the uncertainty of testing results is calibrated or verified, typically annually, within the applied range of use. NIST-traceable references must be used when available, and the results of the calibration/verification are documented and within the specifications required of the application for which the equipment is intended.

Because automatic dispensing devices used to deliver solvents or reagents (e.g., for sample preservation and extractions) are not used to deliver critical volumes, these devices are exempt from daily verification.

Additionally, ALS has procedures for the following support equipment:

Deionized (DI) water systems (SOP 319)

Health physics equipment

Glassware - given in SOPs 334 and 720.

Mechanical Pipettes, SOP 321.

Because automatic dispensing devices used to deliver solvents or reagents (e.g., for sample preservation and extractions) are not used to deliver critical volumes, these devices are exempt from daily verification.

Certificates of Accuracy are acquired from the manufacturer and are retained on file within each department using glass microliter syringes.

The following SOPs provide additional information about calibration and verification of support equipment:

- **SOP 305** -- balance calibration and verification
- **SOP 320** -- monitoring and recording of oven temperatures
- **SOP 326** -- monitoring refrigerator and freezer temperatures.

9. QUALITY CONTROL PROCEDURES

ALS' quality control program provides a systematic process that enables the laboratory to evaluate and control the validity of analytical results, by measuring and monitoring accuracy and precision by method and matrix; by developing control limits and using these limits to detect errors or out-of-control events; and by requiring corrective actions to prevent or minimize the recurrence of these events. ALS observes QC procedures to ensure that sample data meet laboratory and client quality objectives.

The purpose of preparing and analyzing QC samples is to demonstrate accuracy and precision of the sample data and efficacy of the method for the target analytes being investigated. Acceptance criteria may be dictated by reference methods or by project requirements. All assessments of QC data are performed after all rounding and significant figure truncations have been performed.

For all analyses performed by ALS, the QC concepts and samples described in the following sections are mandatory. Determinative SOPs contain a Table that summarizes the types and frequency of QC samples, acceptance criteria, and corrective actions required. Observation of maximum holding time allowance is discussed in LQAP Chapter 4.

9.1 DEFINITION OF BATCH

9.1.1 PREPARATION BATCH

A preparation batch consists of as many as 20 field samples of the same or similar matrix, that are prepared together by the same analyst(s) within a limited or continuous time period, following the same method, and using the same kind of equipment and same lots of reagents. Each batch must contain the appropriate number and kind of method control samples (e.g., MB, LCS) and matrix-specific QC samples (e.g., MS/MSD, DUP). Cleanup procedures may be included as part of the preparation batch. All field and QC samples in the batch should be subjected to the same preparation and cleanup procedures.

9.1.2 ANALYSIS BATCH

The analysis batch (or sequence) consists of samples that are analyzed together within the same or continuous time period, on the same instrument, and processed using the same calibration. Each analysis sequence must contain the appropriate number and kind of standards and samples as defined by the method. If samples from a preparation batch are analyzed in multiple analysis batches, extended method control and matrix-specific QC samples need not be analyzed with every analysis batch.

Where no sample pre-treatment (such as extraction or digestion) is required prior to analysis (e.g., analysis of volatile organic compounds, anions analysis by ion chromatography, etc.), the preparation batch and analysis sequence are equivalent.

9.2 PREPARATION BATCH QC SAMPLES AND STANDARDS – DEFINITION AND USE

The results of quality control samples provide an estimate of accuracy and precision for the preparation and analysis steps of sample handling. The following sections describe the QC information provided by each of these analytical measurements.

9.2.1 METHOD BLANK

A method blank (MB) consists of an aliquot of well-characterized, controlled, or certified matrix (e.g., reagent water, Ottawa sand, solid reference material, boiling chips) that is processed through the entire sample preparation, cleanup, and analysis procedure. For radiochemical analyses, a suitable blank solid matrix has not been identified; therefore, reagent water is routinely used for the blank for

most solid matrices. The volume or weight of the blank must be approximately equal to the sample volume or weight processed for sample analyses.

The purpose of the MB is to demonstrate that interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware, are known and minimized. A method blank should not contain target analytes at or above the reporting limit, unless otherwise permitted in the method. Other maximum blank contamination control criteria may apply, as indicated in the associated LIMS program specification.

While some methods may require background correction, sample results are typically not corrected for blank contamination.

9.2.2 LABORATORY CONTROL SAMPLE

A Laboratory Control Sample (LCS) consists of an aliquot of well-characterized, controlled, certified matrix (e.g., reagent water, sand, solid reference material, Teflon™ chips) that is spiked with analytes of interest and processed through the sample preparation, cleanup, and analysis procedure.

The purpose of the LCS is to provide an estimate of bias based on recovery of the compounds from the clean, controlled matrix, and to demonstrate that the laboratory is performing the method within accepted guidelines without potential non-matrix interferences.

Where sample pretreatment is not required, such as with ion chromatography or gamma spectroscopy analysis, or the analysis of volatile organic compounds, the ICV standard or other appropriate control standard may be employed as the LCS.

An LCS for methods with extensive lists of analytes that may interfere with one another may include a limited number of analytes, but the analytes included must be representative of as many analytes as is practical.

Other client-specific QC requirements may be prescribed in the applicable LIMS program specification. The requirements set forth in the LIMS program specification supercede those stated in the method, SOP or LQAP.

9.2.3 MATRIX SPIKE/MATRIX SPIKE DUPLICATE

A matrix spike (MS) or matrix spike duplicate (MSD) is a field sample to which known concentrations of target analytes are added before the sample is processed. The purpose of MS/MSD samples is to assess the performance of the method for a particular matrix and to provide information about the sample's homogeneity. Results of the MS/MSD samples are evaluated in relation to the method QC samples to determine the effect of the matrix in regards to accuracy and precision. Sample results are not corrected for MS/MSD excursions.

To generate MS/MSD pairs for any analysis, there must be an adequate volume/weight of field sample available. Inadequate sample volumes preclude the possibility of generating this pair of QC samples. ALS asks clients to designate the sample to be used for MS/MSD analysis to ensure that adequate sample volumes are collected.

For some analyses, changing the composition of the sample in any way invalidates the analysis to be performed (e.g., hardness, alkalinity, pH). Therefore, an MS/MSD pair cannot be generated for these analyses. Normally, duplicate sample aliquots are analyzed in order to generate an estimate of the method's precision.

Other client-specific quality control requirements may be prescribed in the applicable LIMS program specification. The requirements set forth in the LIMS program specification supercede those stated in the method, SOP or LQAP.

9.2.4 SAMPLE DUPLICATE

A sample duplicate (DUP) is a second representative portion of sample that is carried through the preparation, cleanup and analysis process. Results for the duplicate sample are compared to the initial sample analysis results as a means of evaluating precision. For organic analyses, the MS/MSDs fulfill this function. The degree of sample homogeneity directly impacts the integrity of the sample duplicate analysis.

Precision criteria for sample duplicate analyses are those prescribed in the reference method and/or SOP, unless otherwise superceded by client-specific requirements contained in the applicable LIMS program specification.

9.2.5 SURROGATES

Surrogates are organic compounds that are similar to the target analytes, but are unlikely to be present in actual field samples. They are introduced into all field and QC samples in a batch prior to sample preparation, and provide an estimate of bias based on recovery of similar compounds, for a given extraction technique and analysis method combination. Sample results are not corrected for surrogate recoveries.

Acceptance criteria for surrogates are those prescribed in the reference method and/or SOP, unless otherwise superceded by client-specific requirements contained in the applicable LIMS program specification.

9.2.6 CHEMICAL YIELD MONITORS OR ISOTOPIC TRACERS

Chemical yield monitors are used in radiochemical analyses and provide information similar to the surrogate spikes discussed above. The primary difference between a chemical yield monitor and a surrogate is that sample results are corrected for chemical yield recoveries and not corrected for surrogate recoveries. A chemical yield monitor is a substance that has similar chemical characteristics as the parameter being measured. It is introduced into all field and QC samples in a batch during the preparation procedure. Chemical yield monitors provide information regarding the performance of a method on a sample-by-sample basis.

Chemical yield monitors are evaluated against established laboratory control limits. These ALS default control limits may be superceded by other quality control criteria specified in the applicable LIMS program specification.

9.3 CONTROL CHARTS

Control charts are a tool that can assist the laboratory in evaluating process control and trends. Control charts are used as a visual queue giving warning before a measurement system drifts into an out-of-control situation. Information such as radiochemical calibration parameters, results of daily efficiency checks, etc. can be documented in control charts. Accuracy control charts, discussed further below, that contain method LCS (and surrogate, as applicable) performance information, are managed through LIMS. Although the QAM is responsible to annually review LCS information, and determine is significant change to a method or process has occurred. The QAM then notifies technical management is the mean and standard deviation of LCS data show significant change (>10%). QC limits can be updated after review by technical personnel as

appropriate.LCS information is accessible to *all* bench personnel **for their consideration,** through LIMS.

Further discussions of control charts and control limits and other considerations such as outlier rejection and trend evaluation follow below.

9.3.1 ACCURACY CONTROL CHARTS

Accuracy (recovery) for a batch can be evaluated by plotting the individual percent recovery points for analytes on a control chart or comparing the values against the current control limits. If the spike recovery values for the current analytical batch meet the acceptance criteria for that method, then the data point (and batch) are accepted. See Appendix A for general process and the QC Table of each determinative SOP for further details as to the appropriate corrective actions to be taken for controlled failures.

If fewer than 20 data points for a method, matrix, and analyte combination are acquired, then control charts yield advisory limits.

9.3.2 CONTROL LIMITS

Control limits for each controlled analyte are calculated, and can be updated, using ALS's LIMS. The recovery values from all data processed within a specified date range, are used to calculate the control limits and compile the control chart. **Standard outlier tests, based on the population number evaluated (e.g., Dixon n=<20; Grubbs n=3-147; etc.), per their restrictions/requirements, may be applied.**

The upper and lower control limits of the control chart are designated as the value equal to the average recovery plus or minus three times the standard deviation (i.e., 99% confidence interval).

The upper and lower warning limits for the control chart are designated as the value equal to the average recovery plus or minus two times the standard deviation (i.e., 95% confidence interval).

The average recovery, standard deviation, minimum value, maximum value, and population are displayed on each control chart.

Control limits are updated as needed (e.g., acquisition of a sufficient number of data points to establish meaningful control limits for a newly implemented method; if deemed appropriate as a result of a corrective

action investigation; etc.). The frequency with which control limits are updated may vary for different methods. Generally, intra-laboratory historical control limits are not updated more than once per year.

9.3.3 OUTLIER REJECTION

For the generation of control charts, and other quality control data that monitor the laboratory's performance, it is essential to prevent spurious or erroneous data from being incorporated. It may be necessary to reject data as an outlier to prevent an adverse effect on the values being calculated.

See SOP 329 for further details regarding the processing of MDL studies and evaluation of outliers.

9.3.4 TREND EVALUATION

In addition to evaluating individual batch QC results against control limits, QC results from successive batches are also evaluated for possible trends. See section 11.4.

9.4 SECOND COLUMN OR SECOND DETECTOR CONFIRMATION

Second column or detector confirmation is performed for several GC methods. Whenever two dissimilar chromatography columns or two detectors of a different nature are available for a given method, the laboratory performs second column or second detector confirmation analysis to confirm the identity of target analytes in field samples. When second column analysis is performed for any chromatography technique, the following policies apply:

- Every attempt will be made to calibrate the second (confirmatory) column in the same manner as the quantitative (primary) column. The same initial and continuing calibration standards will be analyzed on the confirmation column in the same manner as the quantitation column. The purpose of this dual calibration requirement is to allow the possibility of reporting quantitative results from the confirmation column if interferences on the primary column prevent accurate target analyte quantitation.

- For chromatographic techniques, the determination of target analytes in a sample depends solely on peak retention times observed in both primary and secondary column chromatograms. If target analyte peaks are present at the proper retention times in both confirmation and quantitation column chromatograms at levels above the MDL, then ALS considers this analyte to be confirmed.

- In general, ALS reports a single value from the two columns based on client requirements. In the absence of client requirements ALS reports the higher value of the two columns.

  If no interferences are present, and an analyte's value from either the primary or secondary column is greater than the reporting limit but between the MDL and the reporting limit on the other column, then ALS reports the higher value that is greater than the reporting limit for that analyte.

9.5 MANUAL RE-INTEGRATION POLICIES AND PROCEDURES

Many data collection systems allow the analyst to reprocess data, thereby allowing for the manual re-integration of analyte peaks. ALS makes every attempt to optimize peak integration parameters; however, manual reprocessing of data must be performed to correct a data system's integration error (e.g., incorrect or missed peak assignment, over- or under-integration of area). Manual re-integrations may not be performed solely to meet initial or continuing calibration criteria or any QC criteria (e.g., tuning, or surrogate or spiking compound recovery).

Whenever a manual integration is performed, the analyst performing this process must include a hardcopy of the original and re-integrated peak in the final data report. In addition, the analyst must initial and date the re-integrated page and document the reason for re-integration on the printout. The re-integration must be documented in the case narrative.

Further details regarding manual integration procedures are given in **SOP 939**.

10. DATA REDUCTION, VALIDATION AND REPORTING

Data transfer and reduction are essential functions in summarizing information to support conclusions. It is essential that these processes are performed accurately and are followed by multiple reviews before data are submitted to the client. All analytical data generated by ALS are extensively reviewed for accuracy and completeness. The data validation process consists of data generation, reduction, and multiple levels of review, as described below.

10.1 DOCUMENTATION OF RAW DATA

Where possible, raw data are captured and processed electronically using verified software programs (see **SOPs 709 and 1400** for further information regarding software verification).

To facilitate manual documentation of raw data (where suitable LIMS benchsheet interfaces do not yet exist), ALS creates custom logbooks comprised of forms or benchsheets that are tailored to contain the information required to adequately

document the process being performed, and the associated data. The Quality Assurance Department controls these forms and benchsheets, and issues bound and paginated logbooks to the laboratory as needed via controlled distribution.

As applicable, hardcover, bound laboratory notebooks (most frequently used for instrument maintenance logs or Project Manager notebooks) are also issued via controlled distribution to laboratory staff as needed.

The manually recorded raw data are entered into the laboratory logbook directly, promptly, and legibly in indelible ink. All raw data entries must, at a minimum, contain the following information:

- the initials of the individual who performed the process;
- the date the process was performed;
- the methodology used; and
- the identity of all samples or standard solutions that were employed in carrying out the process.

Raw data must be maintained as part of the laboratory's records. Raw data not only includes instrument outputs, but sample preparation, standard materials documentation, and equipment maintenance information as well. Raw data may be archived electronically or as hardcopy.

10.2 CORRECTION OF ERRORS IN DOCUMENTS

During the course of processing and reviewing sample preparations and analysis results, it may be necessary to correct documentation errors. Detailed requirements for the correction of manual documentation errors are prescribed in **SOP 303**; the correction of electronic information is governed by LIMS controls and audit trails. In summary, manual entries may not be obliterated by erasure, use of correction fluid, or other means. In order to maintain the integrity of the documentation generated by the laboratory, changes to hardcopy documentation must be made in the following manner:

- A single line must be struck through the error so that the original text remains legible;
- As applicable, a corrected entry must be made adjacent to the error; and
- The person making the change must initial and date the corrective entry.

If not clearly evident, the reason for the data change must be indicated.

10.3 DATA REDUCTION

ALS analysts perform data reduction. This process consists of interpreting instrument results and verifying calculated concentrations in samples from the raw data. The complexity of the data reduction is dependent on the specific analytical method and the number of discrete operations involved in obtaining a measurement (e.g., digestions, dilutions, cleanups, concentrations). The analyst calculates the final reportable values from raw data or enters all necessary raw data into the LIMS so that the LIMS can calculate the final reportable values.

Data are reduced according to protocols described in SOPs and method-specific review checklists. Computer software used for data reduction is validated before use and verified regularly by manual calculations. All information used in calculation is recorded in order to facilitate reconstruction of the final results (e.g., raw data, calibration files, tuning records, results of standard additions, interference check results, sample response, and blank or background-correction protocols). Information about the preparation of the samples is maintained in order to facilitate reconstruction of the final results (e.g., weight or volume, percent moisture for solids, extract volume, dilution factor).

Copies of all raw data and the calculations used to generate the final results, as recorded in hardbound laboratory notebooks, spreadsheets, electronic data files and LIMS record files, are retained in the project file to allow reconstruction of the data reduction process.

10.4 REPORTING OF SAMPLE RESULTS

Sample results are reported either on an “as-received” basis, or in units of dry-weight measure. The number of significant figures reported is consistent with the limits of uncertainty inherent to the analytical method. In most cases, results are reported to no more than two or three significant figures. Analytical problems, and/or any modifications of referenced methods are noted in the data package case narrative.

Standard units appropriate to the analytical method are used to report all sample results. Measurements for radiochemical analyses are reported in units of activity such as:

- picocuries per liter (pCi/L), aqueous; or picocuries per gram (pCi/g), solid matrix samples.
- disintegrations per minute per liter (dpm/L) or disintegrations per minute per gram (dpm/g).
- Becquerels per liter (Bq/L) or Becquerels per gram (Bq/g).

It should be noted that one (1) Curie is equal to 2.22 X 10^{12} dpm; and is also equal to 3.7 X 10^{10} Bq.

Standard units for inorganic and organic analyses are units of mass per volume (aqueous samples), or mass per weight (solid matrix samples). For example, Wet Chemistry parameters such as hardness, total organic carbon (TOC), etc., are typically reported in milligrams per liter (mg/L) or milligrams per kilogram (mg/kg). Metals results for liquid samples may be reported as mg/L or as micrograms per liter (µg/L). Some methods have specific reporting units mandated by their analysis technique. For example, pH is reported as pH units, and specific conductance is reported as milli-Siemens (mmho/cm) or micro-Siemens (µmho/cm).

10.5 DATA REVIEW

ALS employs multiple levels of data review. All data generated and reduced follow review protocols specified in laboratory SOPs (such as **SOPs 052** and **715**), and method-specific checklists. The preparatory technician and analyst who generate the analytical data perform a **Level 1** review of the data for correctness and completeness. This data review verifies that:

- the appropriate SOPs have been followed;
- any special sample preparation or analytical requirements that were communicated to the laboratory via the LIMS program specification have been met;
- all sample preparation information is correct and complete;
- all analysis information is correct and complete;
- QC samples meet criteria for frequency, accuracy and precision;
- all calculations, conversions, and data transfers are accurate;
- all documentation is present and complete, including benchsheets and/or run logs, any applicable NCRs, and documentation and presentation of manual integrations per SOP 939, as applicable.

Procedures for handling unacceptable data are discussed subsequently (LQAP Section 10.6).

Following completion of the Level 1 Review, the analyst then forwards the data to the Group Leader or another qualified reviewer whose function is to provide an

independent **Level 2** review of the data. In addition to the elements evaluated in the Level 1 review described above, the Level 2 reviewer verifies that:

- the calibration data are scientifically sound, appropriate to the method, and completely documented;
- qualitative identification of target analytes is correct;
- quantitative results are correct.

The Level 2 reviewer selects a sample and verifies it to the benchsheet. If no errors are found, then the review is considered complete. If any problems are discovered, then additional samples are verified to the benchsheet with the process continuing until no additional errors are found or until the data package has been reviewed in its entirety. The Level 2 review is documented by recording the date and initials of the reviewer on the checklist employed. This sign-off signifies that the data are approved for release and a final report is prepared.

Once the final report is prepared, an additional overall technical review is performed before it is routed to the Project Manager for a **Level 3** review. The intent of this review is to verify that the report is complete and that the data meet the overall objectives of the project.

Each step of the review process involves evaluation of data quality based on both the results of the QC data and the professional judgment of those conducting the analysis and/or review. This application of technical knowledge and experience to the evaluation of the data is essential in ensuring that data produced are consistently of known, documented, and appropriate quality.

10.6 PROCEDURES FOR HANDLING UNACCEPTABLE DATA

All QC information is recorded in the same format, with the same units, as that of the associated sample results. It is the analyst's responsibility to evaluate QC data against applicable prescribed limits. See Appendix A for guidance on method QC evaluation. When an analysis of a QC sample (e.g., MB, LCS, CCV, etc.), indicates that the associated samples do not meet requirements, the analyst must immediately notify the Group Leader. The Group Leader then consults with the PM (and QAM, as applicable) to determine whether or not the affected samples must be re-prepped and/or re-analyzed, and/or if specific corrective action needs to be taken before additional analysis may proceed. A Nonconformance Report (NCR) as discussed in Chapter 11 of this LQAP, is initiated per **SOP 928**, as applicable. If the non-compliant data cannot be corrected, then the affected results must be flagged as discussed below, and the discrepancy disclosed in the data package case narrative.

10.7 DATA REPORTING

Data reports contain final sample results, the methods of analysis used and limits of detection, and QC data. The extent of supportive data included (e.g., benchsheets, run logs, calibration data, instrument raw data printouts, etc.), is contingent upon the type of report contracted by the client.

Results of subcontracted data are clearly indicated as subcontract laboratory results when incorporated into the final data package report.

10.7.1 FACSIMILE OR IMAGED REPORTS

For projects that require rapid turnaround of sample analysis results, the laboratory may provide a facsimile or imaged e-mail attachment to the client, followed by the full data report at a later date. If the analysis results provided by facsimile or imaged e-mail attachment have undergone the same review processes followed for final data packages, then this forwarded report indicates that the sample analysis results are final. However, if the accelerated turnaround time requirements preclude a full review/validation of the sample data, then the report is marked as "PRELIMINARY" to indicate that results may change as the review process is completed.

10.7.2 HARDCOPY DATA PACKAGES

The format and content of a data report is dependent upon project specifications, and it is beyond the scope of this document to describe project-specific report requirements. In the absence of client-specified data package deliverables, the following sections describe the items that must be included in all data reports.

10.7.2.1 COVER LETTER

Items contained in the cover letter include:

- the client's name and address;
- ALS's name and address, name of contact and telephone number;
- a tabular presentation of field/client sample ID, ALS Sample ID, date received, matrix, and date collected. This item is typically presented as an attachment, the Sample Cross Reference Table;
- a list of each analysis performed and total number of pages for each analytical report;

- identification of all test data provided by a subcontract laboratory;
- a discussion of previously submitted or partial reports that pertain to the samples discussed in the current report; and
- the signature of ALS's Project Manager or designee.

10.7.2.2 REPORT FORMAT

Analysis reports are presented in tabular format, and consistent significant figures and units of measurement are used. The following information is included in each report:

- laboratory name, client name, project name and/or number;
- client/field sample ID and ALS sample ID;
- date of sample receipt, date and time of sample collection, and date/time of sample preparation and/or analysis;
- sample matrix;
- reporting units and identification of whether the sample results are reported on an "as-received" or dry weight basis;
- method reference for the parameter analyzed and method reporting limits;
- identification of numerical results with values below the method reporting limit;
- case narrative that identifies test methods, describes any deviation from the method or contractual requirements, additions or exceptions to the SOP, and discloses any conditions that may affect the quality of the results;
- identification of sample results that did not meet sample acceptance criteria;
- footnotes or qualifiers referenced to specific data (as applicable) and explanations or keys to flags and abbreviations used;

- surrogate and tracer recoveries, where applicable;
- where applicable, a statement of the estimated uncertainty of the test result; and
- a signature and title, or equivalent electronic identification, of the personnel who accepts responsibility for the content of the report, and the date of issue.

If a report is reissued, the amendments must clearly state that the report is reissued. The cover letter and case narrative must describe why the report has been reissued and which sample results have been reissued.

10.7.2.3 QC REPORTS

Each final report includes QC reports that summarize results from the associated LCS, MB, and matrix QC samples. Additional QC samples may be prepared and reported to comply with project-specific requirements.

10.7.2.4 DATA QUALIFIERS – FLAGGING CODES

Whenever the data quality objectives of the LQAP are not met, the associated sample results must be flagged with the appropriate flagging codes. These codes are applied only in the event that the laboratory cannot generate (through reanalysis) fully compliant data. If sample values are reported outside the calibration range of the method or unreliable interferences exist in the sample, then descriptive codes are applied to the result.

Data qualifiers are added by the laboratory prior to reporting the analysis results. The laboratory appends data qualifiers to each environmental field sample based on an evaluation of all available QC information (e.g., MS/MSD samples, laboratory blanks, LCSs, calibration verification standards, etc.). Analytical batch comments are added to the narrative section of each data report to explain any nonconformance or other issues.

Other flagging practices may be observed if so dictated by the applicable LIMS program specification.

10.7.3 ELECTRONIC DATA DELIVERABLES (EDDS)

The electronic data deliverables generated by the laboratory are project-specific and are produced in a format specified by the client. *Information presented in corresponding fields of the hardcopy report and EDD are identical as both are generated from LIMS.* Before submitting the EDD file, the Project Manager or designee verifies that the EDD is complete and meets the client's format requirements. All EDDs are submitted to the client on computer disks or are transmitted electronically.

10.8 RECORDS AND DATA STORAGE

Records provide the direct evidence and support for the necessary technical interpretations, judgments, and discussion concerning laboratory results. These records, particularly those that are anticipated to be used as evidentiary data, provide the historical evidence needed for later review and evaluation. Records must be legible, identifiable, and retrievable. They must be protected against damage, deterioration, fire, theft, vermin, and loss. Though only 5-year retention is required by TNI, ALS retains all records for a minimum of seven (7) years, or as otherwise specified per the client's contract.

Laboratory records include the following kinds of documentation:

- personnel qualifications, experience, and training;
- correspondence between ALS and clients;
- quality assurance records (e.g., retired SOPs and LQAPs, PT study results, internal and external audit reports and responses);
- contents of laboratory logbooks;
- equipment maintenance records;
- traceability of standards, solvents and reagents;
- instrument checks and calibrations;
- raw data;
- final data reports; and
- sample management records (e.g., sample login, field and internal chain-of-custody, storage, disposal).

10.8.1 ELECTRONIC RECORDS

ALS employs a multi-level system that addresses both the frequent backup of sample results (in LIMS) and the periodic backup of raw data (from both networked and non-networked instruments).

Additionally, the software that ALS uses for these backups, contains a disaster recovery module that allows for the complete recovery of the backup database, in its entirety. In short, ALS's LIMS is backed up hourly, and, along with all network servers, is additionally backed up to tape each business day. As indicated in the IS and LIMS Policy Statement (SOP 143 and SOP 1401), instrument backups are performed approximately monthly. Contingent upon the volume of analysis, the frequency of backup might vary.

Backup of the instrument computers is done centrally by the IS Manager if the instrument computer is on the network. It is the responsibility of the operator\user to coordinate a convenient time for both the IS Manager and the user for non-network instrument backup. The instruments that are not on the network are backed up using portable devices. These devices, as well as media, are checked out from the IS Manager, then are returned to the IS Manager for safe storage.

An electronic archive for maintaining final project reports was implemented in 2001. Upon completion of a workorder, all data reports are scanned to create image files that are catalogued and saved to a dedicated server that is backed up daily as described above. The scanned images remain available on the network for review should any questions regarding the data arise.

10.8.2 TRANSFER OF RECORDS

In the event that the laboratory changes ownership, the responsibility for the retention of records in accordance with the guidelines established in this LQAP, is conferred to the new owner. Should ALS go out of business, ALS will inform our clients in writing of this business decision, and that the transfer of records to the client must be in compliance with state, regulatory and legal records retention times.

10.9 CLIENT INQUIRIES/COMPLAINTS

The focal point of contact with the client is the ALS Project Manager. If a complaint or any circumstance raises doubt concerning ALS's compliance with its policies or procedures, or with the requirement of a method or quality system, it is the Project Manager who initiates investigation and follows through to resolution. The QAM, Operations Manager, and Laboratory Director are made aware of, and involved in, the resolution process as needed. Documentation of the complaint and its resolution are maintained as part of the project records. Where resubmission of data is required and/or implementation of preventive measures is

necessary, it is processed (**SOP 928**), through the QAM. ALS will respond to all complaints in a timely fashion.

10.10 CONFIDENTIALITY

All laboratory results and associated raw data are confidential and may not be released to or discussed with any party other than the client who requested the analytical services. Access to laboratory records and LIMS is limited to laboratory personnel, on a restricted basis, based on need (i.e., job function). Records are available for an accrediting authority's on-site review, and records specific to the client (as well as quality system records) are available to the client for client audits. ALS requires that auditors will honor our clients' and ALS's confidentiality requirements, and will not discuss any results, documents, or records viewed during the course of an audit.

Confidentiality is included as a component of ALS's ethics training, which is provided to each person as they join the ALS staff, and annually, as a refresher training, thereafter.

11. CORRECTIVE ACTION, PREVENTIVE ACTION AND IMPROVEMENT

Corrective action is necessary when any measurement system fails to meet the requirements of this LQAP, the appropriate SOP or project-specific instructions, or whenever an error is detected. Items that may need corrective action range from a minor problem such as an analyst failing to initial a form, to a major problem such as a chemist preparing a sample using the wrong reference method.

Corrective actions fall into two general categories: short-term and long-term. Short-term corrective actions are those that can be applied immediately. Examples include: having an analyst initial a form where the initial was missed, or correcting an error in a logbook entry per procedures described in SOP 303. Long-term corrective actions are those that require a clarification of practice or a change in policy in order to effectively resolve the problem. Corrective actions must be completed by the date designated by the QA Department (i.e., within 21 calendar days or less, unless otherwise provided for). Associated SOPs may need to be revised and republished for long-term corrective actions, laboratory staff must be re-trained in accordance with the updated procedures.

11.1 RESPONSIBILITIES FOR CORRECTIVE ACTION INITIATION

The type of corrective action taken is coordinated by the Operations , Quality Assurance and applicable Project Managers. A controlled Nonconformance Report is used to document the corrective action. *Any* individual who notes a problem or deviation is responsible for initiating the NCR in a timely manner.

It is the responsibility all personnel who work with samples to note any discrepancies or nonconformances that occur with sample handling. It is the

responsibility of the chemists who prepare samples for analysis to document any problems that are noted during sample preparation. It is the analyst's responsibility to monitor the proper functioning of the analytical system prior to, during and following sample analysis. To accomplish this, various DQIs as discussed in Chapter 3 of this LQAP are monitored and evaluated against laboratory established or project-specific QA/QC requirements. If the evaluation reveals that any of the QC acceptance criteria are not met, then the analyst must immediately correct the problem. When an acceptable resolution cannot be achieved and/or data quality is negatively impacted, the analyst must notify the Operations and Project Managers and must initiate an NCR (**SOP 928**) immediately. Per the guidance contained in SOP 928, the laboratory shall notify all affected clients of potential data quality issues in a timely manner, and corrective actions taken to resolve the issue shall be completed in a reasonable timeframe, with documentation submitted to the client.

11.2 ALS NONCONFORMANCE AND CORRECTIVE ACTION PROCESS

Non-conformances are reported (documented) electronically through a LIMS interface that is available to all staff. The individual who discovered the problem or deviation is responsible for initiating the next sequential NCR in LIMS. Note that in addition to documenting laboratory sample or test issues, NCRs are also used to address client inquiries, and to investigate Performance Test (PT) sample failures.

Documented on the NCR are the initials of the initiator and descriptions of the method, workorder(s) and samples affected; the type, content and extent of the problem noted; the probable cause and the root of the problem (if known); measures taken to prevent recurrence; the specific corrective actions taken and their outcome; and the final disposition/resolution of the data.

As described in **SOP 928**, the processing of the NCR flows from the initiator, to their Group Leader and the relevant Project Manager(s), and finally to the Quality Assurance Manager. In this manner, a consensus is achieved as to what specific corrective actions are to be taken. The Project Manager, at his or her discretion, may or may not contact the client to discuss options based on the nature of the nonconformance. Whether or not the client is contacted is noted on the NCR, if the client is contacted, the Project Manager documents who was contacted and when. The Project, Operations and Quality Assurance Managers electronically sign and date the NCR, documenting their final approval and verification of the disposition of the data. The LIMS provides for delegation of signature authority as needed to cover key staff outages.

The LIMS, which is subject to ALS's frequent backup protocols, maintains an archive of all NCRs generated. In this manner, NCRs are retained as part of the

laboratory's electronic records. Also, contingent upon the level of data deliverable specified by the client, a copy of the associated NCR report is included in the analytical data package.

Corrective actions that require follow-up, including those initiated by internal or external audits and systematic non conformances, are catalogued in a separate database that tracks audit findings, root cause, corrective actions, follow up for effectiveness, and closure. This database is managed by the QA Department but is available to all staff on a read-only basis.

11.3 IMPROVEMENT AND PREVENTIVE ACTION

At ALS, improvement of the quality systems and preventive action is effected through an ongoing systems review by management using input from all staff.

ALS actively seeks employee and client input for improvements through surveys and questionnaires. ALS maintains a process improvement website for employees to provide suggestions for improvements. For clients, ALS provides surveys and feedback on services provided. These automated systems report directly to the laboratory director for input into the management review process.

Preventive actions include preventive instrument maintenance as listed in all ALS Testing SOPs. These actions are documented in run logbooks and maintenance logbooks.

The laboratory Non conformance system within the LIMS identifies events as non conformance or incidence. The incidence is considered a potential non conformance and is evaluated along with all events for needed potential improvements to the ALS testing processes.

Management and key personnel review strategic goals and necessary improvements through a planning process (Balanced Scorecard). This process and review of actions items is available in monthly reports for the laboratory to corporate operations. All employees are asked to participate these goal setting sessions on a regular basis.
The top laboratory management team conducts an ongoing review of the operations and quality system. This review process includes daily, weekly and monthly status meetings.

11.4 IDENTIFICATION OF TRENDS IN QC DATA

Preventive Actions using QC sample trending although not required is available to help prevent non compliance QC situations from occurring.

While a trend is not necessarily an out-of-control situation in itself, it can provide an early warning of a condition that can cause the system to go out of control. Trending can be used for calibration, equipment, reagents, and various other routine processes in the laboratory. ALS analytical SOPs describe in detail the assessment of batch and sample QC data in the laboratory.

The following conditions are trends that can initiate action and/or monitoring.

- A series of seven successive points on the same side of the mean
- A series of five successive points going in the same direction
- A cyclical pattern of QC sample results
- Two successive points between warning limits and control limits

ALS relies on analytical staff to identify trends in analytical systems and processes. Quality Assurance and laboratory personnel can produce control charts as needed to help assess trends but this activity in itself is not preventive and is only used to verify trends exist. The occurrence of a trend does not invalidate data that are otherwise in control. However, trends do require attention to determine whether a cause can be assigned to the trend so that appropriate preventive action can be undertaken.

Long term trends in control limits are evaluated yearly by Quality Assurance and technical operations as per ALS LQAP Section 9.3.1.

Process for identification of trends in QC data

Control limits are guides used for data evaluation. Verifying that QC sample values are not trending ensures that the method may continue to be used for the analysis of field samples. If an undesirable trend appears in the analytical QC data, field sample data for samples analyzed with the QC samples might also be trending in the same manner.

A trend in method QC data might be indicated if one or more of the following situations exist:

- A series of seven successive points on the same side of the mean
- A series of five successive points trending in the same direction
- Two consecutive points outside of warning limits

To identify a trend in surrogate, tracer and carrier recovery data, all values for a preparation batch must be evaluated collectively as a single event, since the values were generated during the same preparation event. Trends should be evaluated between preparation batches and not on any single sample.

LIMS can provide control charts for review to verify that trends exist but is not a tool used for trend identification. It is the responsibility of the analyst to review data for trends.

Evaluation of Significance

After a trend has been identified, the significance of the trend must be evaluated. An individual trend in data might, or might not, be a cause for action, particularly in the case of a single analyte in a multi-analyte method.

Examples:

1) Seven points (values of 97% – 100%) on the same side of the chart mean (value of 96%), with a warning limit at 104% and a control limit at 109%.

   Evaluation: Consistent data, less than one standard deviation from the chart mean. No action required.

2) Five successive points (values of 88% – 96%) moving in the same direction, with a chart mean of 94% and an upper control limit of 109%.

   Evaluation: Data moving across the chart mean, within one standard deviation from the chart mean, data are in the middle of the performance range of the method. No action required.

3) Five successive points (values of 94% – 107%) moving in the same direction, with a chart mean of 94% and an upper control limit of 109%.

   Evaluation: Data moving away from the chart mean, nearing the control limit. Action while not required should be implemented to keep the procedure from going out-of-control.

If data exhibit a sufficiently significant trend to require corrective action, the cause of the trend must be determined.

Questions to be considered in the evaluation of a data trend and the determination of the cause of the trend might include (but are not limited to) the following:

- Five Why Root Cause Analysis

- Is this trend representative of the entire method?
- Is this trend limited to a single analyte in a multi-analyte method?
- Is this trend exhibited in the data of several analytes in a multi-analyte method, and is the same general trend observed for each analyte?
- What is the time period of the trend (i.e., a week, several weeks, several months)?
- What changes in the analytical system have occurred during the time period to which the trend applies?
- Are new personnel involved?
- Is different instrumentation involved?
- Were new or different standard solutions introduced?
- Was there a change in the analytical protocol or method?
- Has instrument sensitivity or response changed dramatically?
- Has instrument maintenance been performed recently?
- Have there been any changes in method reagents (i.e., brand, lot)?
- Have there been any matrix effects carried over from difficult samples?

Assignment of Significance

Following the identification of a data trend (as indicated above) and the evaluation of the trend for significance, a decision must be made that the level of significance does or does not require action.

At the time of quality control sample data evaluation, the evaluator must make a decision based upon personal judgment. Criteria can determine whether a trend exists, but judgment must be used in the determination of the significance of that trend.

If the data trend is determined to not pose a threat to the quality of *immediate future analytical data*, or does not reasonably indicate that the analytical method might begin to produce data that could be anomalous, the level of significance is INSIGNIFICANT.

If the data trend is determined to not pose a threat to the quality of *immediate analytical data* such that no action is required, but does possibly indicate that the analytical method may begin to produce data that could be anomalous, the level of significance should be MONITORED by technical personnel.

If the data trend is determined to possibly or reasonably pose a threat to the quality of *future analytical data*, and reasonably indicates that the analytical method may begin to produce data that could be anomalous, the level of significance is SIGNIFICANT, and actions must be initiated to prevent out of control events.

Resolution Procedure

Following identification of a trend and an assignment of a level of significance, future action regarding the trend must be determined.

If a data trend is evaluated as significant, laboratory personnel responsible for data trend evaluation must promptly inform all analysts involved in work related to the significant trend that the trend exists and that action must be initiated to prevent its reoccurrence and correct it.

All activities related to a significant trend will be documented in normal analysis records.

Laboratory personnel are required to initiate action to correct a significant data trend related to their work.

The trending rules used by ALS are in the following table. In most instances experience chemists identify trends and take action upon reviewing analytical data.

RULE	DESCRIPTION	POSSIBLE PREVENTIVE ACTIONS
Above Warning Limits	Two of three data points above warning limits	Check Calibration and Spiking Solutions Instrument Maintenance
Below Warning Limits	Two of three data points below warning limits.	Check Calibration and Spiking Solutions Instrument Maintenance
Above Mean	Seven consecutive data points	Check Calibration and Spiking

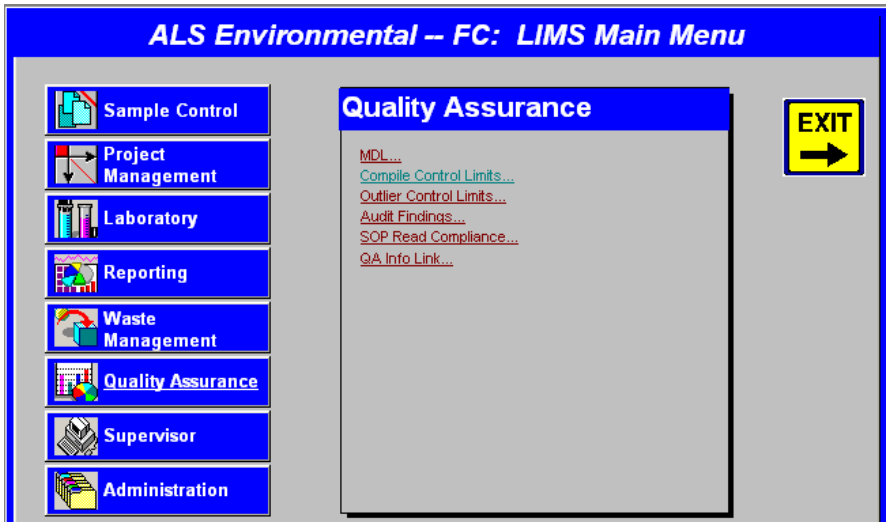
RULE	DESCRIPTION	POSSIBLE PREVENTIVE ACTIONS
	above the mean	Solutions Instrument Maintenance
Below Mean	Seven consecutive data points below the mean	Check Calibration and Spiking Solutions Instrument Maintenance
Ascending Data	Seven consecutive data points in ascending direction	Check Calibration and Spiking Solutions Instrument Maintenance
Descending Data	Seven consecutive data points in descending direction	Check Calibration and Spiking Solutions Instrument Maintenance

Procedure for producing Control Charts to verify trends are present

LIMS Main Menu

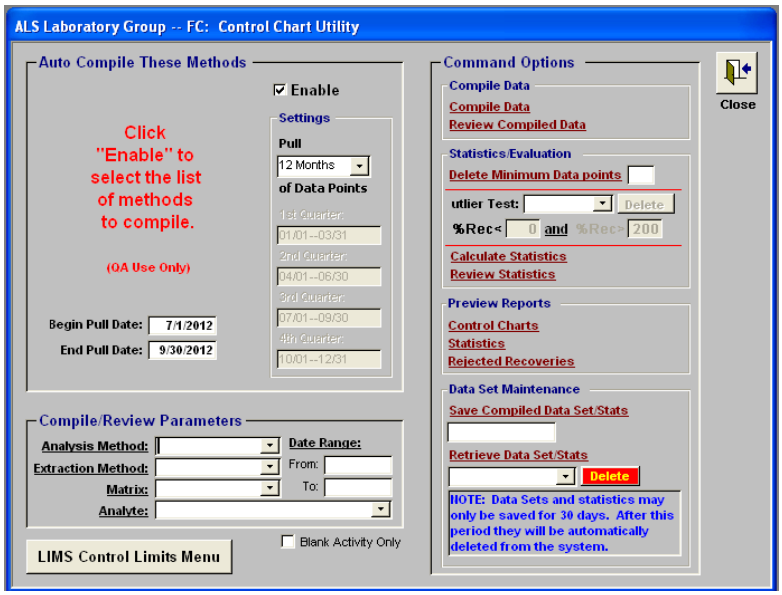
From Quality Assurance Menu

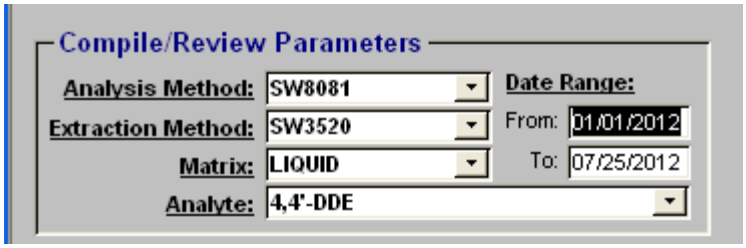
Select Compile Control Limits

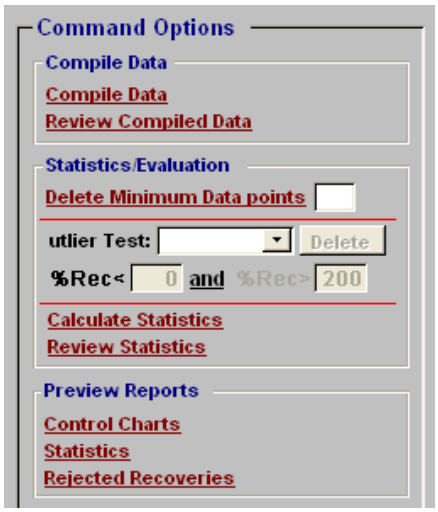


Compile Control Utility Menu
In the Compile/Review Parameters Box
Select Analysis Method, Extraction Method, Matrix, Analyte and Date Range (Use no more than the last 12 months)
In the Command Option Box (In Sequence)

Compile Data
Calculate Statistics
Control Charts







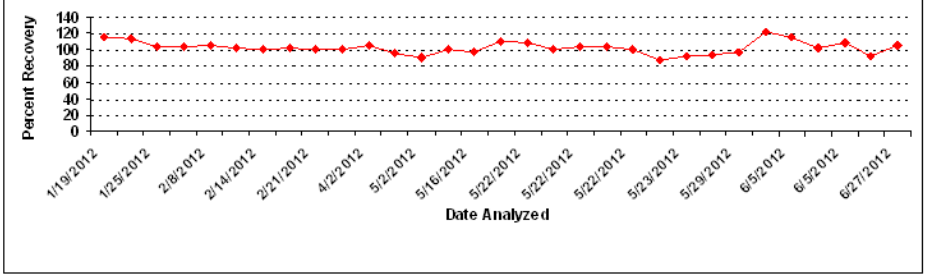
Control Charts By Analytical Test

Outlier Test:

TEST: Analysis Method: SW8081
Extraction Method: SW3520
Matrix: LIQUID
Analyte: 4,4'-DDE

Outlier Test: NONE

		2 Sigma		3 Sigma	
N: 31		-	+	-	+
Mean: 102.6		87.22	118.01	79.52	125.70
SD: 7.70					
Min: 87					
Max: 122					



Parameters for this control chart report:

Analytical Method:	SW8081	Min. Data Points:	#Error
Extraction Method:	SW3520	Include Unval. Results:	#Error
Matrix:	LIQUID	Lower Rec. Limit:	0%
Analyte:	4,4'-DDE	Upper Rec. Limit:	200%
Begin Date:	01/01/2012	Outlier Removal:	#Error
End Date:	07/25/2012		

12. AUDITS

12.1 INTERNAL AUDITS

Periodic evaluations conducted by the Quality Assurance Department and the analysis of Proficiency Test (PT) samples are two types of internal audits used to assess and document the performance of laboratory staff and processes. Audit documentation constitutes a permanent record of the conformance of ALS's measurement systems to quality system requirements.

Internal audits include both technical and systems audits, and are performed periodically per an annual schedule developed and maintained by the Quality Assurance Department. Considerations taken into account in developing the internal audit schedule include, but are not limited to, requests made by the Laboratory Director; the scheduled occurrence of external audits; as needed to support a specific project's requirements; to verify the continued effectiveness of corrective actions previously taken; or in response to an identified need to evaluate compliance in any area of laboratory operations. The intention of the internal audit schedule is to provide for the evaluation of each laboratory area or system at least once annually, thereby providing an overview of laboratory operations. Form 168 or other audit questionnaire may be used as a guide to conduct and document internal audits. Each year, the internal audits conducted are compiled into the annual Quality Systems Audit (QSA), which is discussed subsequently (LQAP Section 12.1.3).

All internal audits are conducted by QA staff or designees who, by experience, are deemed to be knowledgeable in the area assessed. The assigned auditor identifies the scope, time frame and expected duration of the audit, and communicates this information to the applicable Group Leader. The auditor reviews relevant information such as regulations, contract requirements, published procedures, SOPs, etc., prior to the audit. The criteria set forth in these applicable guidances establish the basis of the audit. These reference materials may also be used as auditor's aids.

The audit is conducted in an efficient and professional manner. Findings, Observations and comments are communicated to the Operations Manager.

Short-term corrective actions may be taken at the time an item is noted, or an appropriate long-term corrective action plan may be developed. An audit is considered to be closed-out when deficiencies have been satisfactorily corrected.

An audit report summarizing the Determinations made and the corrective actions taken or planned is compiled; the original auditor's notes are customarily included as an attachment of the audit report. The outcome of the audit is communicated to

the Laboratory Director. Internal audit corrective actions requiring follow up are tracked in a LIMS Table that is available for viewing to all laboratory personnel. The QAM oversees satisfactory completion of corrective measures taken. Internal audit records are maintained by the Quality Assurance Department.

See **SOP 937** for additional information pertaining to internal audit procedures.

12.1.1 INTERNAL TECHNICAL AUDITS

Operational functions that may be reviewed during a technical audit may include, but are not limited to:

- Adherence to SOPs and compliance with promulgated method requirements during sample preparation and analysis;
- Maintenance of internal chain-of-custody;
- Proper preparation, storage, use and documentation of standards;
- Performance and documentation of instrument maintenance;
- Performance and documentation of data review;
- Evaluation of documentation practices pertaining to benchsheet and logbook entries, Nonconformance Report (NCR) generation and analyst demonstration of capability.

12.1.2 INTERNAL SYSTEM AUDITS

Examples of elements that may be reviewed as a system audit may include, but are not limited to:

- An assessment of the SOP process, including procedures for submitting and approving revisions, update and distribution of SOPs, tracking of employee SOP assignments and sign-offs, SOP electronic file management, and archiving of older SOP iterations and records.
- LIMS data capture and reporting processes.
- Sample handling, storage and disposal practices, including maintenance of sample storage areas, sample tracking and internal chain-of-custody documentation, duration of retention, and disposal designation and documentation.

- Use of ALS's Standards and Reagents database.
- Performance and documentation of laboratory logbook review.

12.1.3 ANNUAL QUALITY SYSTEMS AUDIT

A lab-wide review of conformance to ALS's quality system is conducted annually by the QA Manager or designee(s) as required by the TNI Standard. The annual Quality Systems Audit (QSA) shall be managed, conducted and reported according to the audit procedures described above. Inputs to the QSA may include, but are not limited to, summaries of the following: Nonconformance Reports (NCRs), Proficiency Testing (PT) study results, deficiencies noted during data review, internal audit Determinations, and Determinations made via external audits.

12.1.4 PROFICIENCY TESTING STUDIES

ALS participates in agency studies and/or contracts approved vendors to provide PT samples in accordance with a schedule developed and maintained by the Quality Assurance Department. Participation in PT studies enables ALS to demonstrate capability for continued accreditation, competency in a newly developed method, or the effectiveness of corrective actions taken.

ALS participates in the following inter-laboratory proficiency testing studies:

- Water Supply (WS) -- twice annually
- Water Pollution (WP) -- twice annually
- Soil/Hazardous Waste and UST -- twice annually
- Radiochemistry -- twice annually
- US Department of Energy (USDOE) Mixed Analyte Performance Evaluation Program (MAPEP) -- twice annually

These PT studies support various regulatory programs (SDWA, CWA, RCRA) and require that the laboratory perform analyses per various methodologies (e.g., EPA 600 series, MCAWW, ASTM, SW-846), matrices and analytes. Analyte lists include: volatile organics, semivolatile organics, organochlorine pesticides, polychlorinated

biphenyls, organophosphorous pesticides, phenoxyacid herbicides, petroleum hydrocarbons, metals, minerals, nutrients and radionuclides. The analyses of PT samples are conducted in-house, in the manner prescribed by the provider, and within the turnaround time stipulated. The PT samples are distributed to the laboratory and are processed by qualified analysts who routinely perform the analytical method.

PT study results are evaluated by the Quality Assurance Department and the department as they become available. The NCR and corrective action process as described in Chapter 11 of this LQAP, is used to address any deficiencies that are noted. An archive of PT study reports, maintained by the QA Department, is posted to the network for lab-wide access.

12.1.5 ANNUAL MANAGERIAL REVIEW

A lab-wide Managerial Review is performed annually. The Managerial Review assesses operational effectiveness in terms of meeting ALS's business goals. It is a tool used to document and facilitate the consideration and introduction of needed operational changes and improvements.

The Managerial Review is performed by a designee under the direction of the Laboratory Director. The general techniques of scoping, assessment interview, reporting and follow-up as described in the internal audit procedures discussed above and outlined in SOP 937, are used to conduct the annual Managerial Review. The contents of the annual Managerial Review are considered to be confidential. A confidential footer must, therefore, appear as a component of the annual Managerial Review report.

Inputs to the Managerial Review may include, but are not limited to the following: a snapshot summary of product generated (i.e., number of samples analyzed and the types of analyses performed), various business assessment reports (e.g., TAT, on- time delivery), output from the annual QSA (i.e., problem areas identified), interview of laboratory staff, and presentation of items discussed during strategic planning sessions and/or Manager's meetings.

12.2 EXTERNAL AUDITS

External audits may be performed by a state or Federal agency or a client as part of an ongoing certification process. Items evaluated by external assessors may include, but are not limited to, reviews of the following: analytical capabilities and procedures; COC procedures; document control; quality systems; and QC

procedures. Blind PT samples may be submitted to the laboratory as a form of external audit.

ALS certifications are maintained on the internal network folders and are available by request. Should ALS drop or lose an accreditation, the PMs must notify all clients that may be affected in a timely manner.

13. PERSONNEL TRAINING

The selection of well-qualified personnel is a factor that contributes to ALS's success. Therefore, qualifications of personnel are based upon education and experience. In order to maintain qualified staff, provide personnel advancement within the laboratory, and to provide for personnel's ongoing awareness of potential hazards and protective measures, ALS follows a formal documented program of orientation and training. Records of Health & Safety and waste training are maintained by the Health & Safety Manager/RSO and Facilities/Waste Compliance Manager. Technical training records are forwarded to the Quality Assurance Department for retention.

13.1 ORIENTATION

Before working in the laboratory, new employees receive a four-part orientation as described below:

- Human resources -- involves matters of immediate personal concern, such as benefits and company policies

- Quality assurance -- addresses topics related to ethical conduct, good laboratory practices and ongoing documentation of employee capability demonstrations. Required readings (SOPs, LQAP) are assigned at this time. See ALS SOP 143.

- Health & safety -- provides for a review of ALS's various safety program documents (Chemical Hygiene Plan, CHP; Radiation Protection Plan, RPP; Emergency and Contingency Plan, ECP; Respiratory Protection Plan, ResPP; Waste Management Plan, WMP); as well as other safety and security training.

- Department functional orientation -- focuses on the new employee's basic understanding of their role within the overall role of Operations within the structure of ALS. The department training expands upon the employee's scientific background and work experience to provide the employee with a level of competence that enables the individual to successfully function within the defined responsibilities of his/her position.

Temporary employees receive the same orientation as regular staff, with the exception of the human resources orientation.

SOP 143 details information regarding quality assurance orientation and training for new employees.

13.2 TECHNICAL TRAINING

Chemists (analysts) and technicians are qualified to perform specific analytical procedures and methods. The qualification process, at a minimum, consists of background/theory training, on-the-job training, and demonstration of proficiency. Additional training may include further individualized instruction, programmed learning, conferences and seminars, and specialized training by instrument manufacturers.

The Operations Manager or designee is responsible for providing documentation of analytical training and proficiency for each employee in their group(s) to the Quality Assurance Department for retention. See ALS SOP 150

13.2.1 INITIAL DEMONSTRATION OF CAPABILITY (IDOC)

New analysts and technicians are trained by Group Leaders according to the following guidelines:

* The new employee reads the SOP(s) pertinent to the analytical method being learned, and receives background/theory instruction, as applicable.

* The new employee observes the procedure in which the analytical method and required process documentation is demonstrated by trained personnel. Job requirements are outlined and quality control measurements are defined. For most methods, the trainee performs an Initial Demonstration of Capability (IDOC) by preparing and/or analyzing four (4) blank spike samples under the supervision .

* The results of the new employee's preparation and/or analysis are evaluated and problems and corrective actions are discussed. If the blank spike recovery and precision data meet quality control criteria for that method, the employee is deemed to have demonstrated proficiency and is allowed to work on client samples. If the values generated are outside acceptance limits, then training continues until the trainee can consistently meet the acceptance criteria for the method.

* After the certification process has been successfully completed, the Operations Manager forwards the documentation to the Quality Assurance Department for retention.

13.2.2 CONTINUING DEMONSTRATION OF CAPABILITY (CDOC)

ALS's personnel are required to demonstrate their proficiency upon hire and with each batch of samples. Results from the laboratory control sample (LCS) spike performed by the chemist (analyst) or technician is evaluated ongoing and significant problems are dealt with immediately through the peer review process, non conformance system, and training. This LCS data is available to review upon request. Alternately, RVS samples and PT sample analysis may also be used to demonstrate an employee's capability.

13.3 TRAINING RECORDS

Technical and quality assurance training records are maintained on network servers by the Quality Assurance Department. Health & Safety training records are also maintained on network servers. Waste management training records are managed and maintained by the Facilities/Waste Compliance Manager. Training records are designated for storage using the ALS SOP 150.

14.1 GLOSSARY, ACRONYMS AND SYMBOLS GLOSSARY

TERM	**DEFINITION**
Acceptance Criteria:	Specified limits placed on characteristics of an item, process, or service defined in requirement documents. (ASQ)
Accreditation:	The process by which an agency or organization evaluates and recognizes a laboratory as meeting certain predetermined qualifications or standards, thereby accrediting the laboratory. In the context of the National Environmental Laboratory Accreditation Program (NELAP), this process is a voluntary one. (TNI)
Accrediting Authority, Primary:	The agency or department designated at the Territory, State, or Federal level as the recognized authority with responsibility and accountability for granting TNI accreditation for a specified field of testing. (TNI)
Accuracy:	The degree of agreement between an observed value and the accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components that are due to sampling and analytical operations. (QAMS)

TERM	**DEFINITION**
Aliquot:	A discrete, measured, representative portion of a sample taken for analysis. (EPA QAD)
Ambient:	Usual or natural surrounding conditions, e.g. ambient temperature – the natural, uninfluenced temperature of the surroundings. (NIRP Glossary)
Analyte:	The specific chemicals or components for which a sample is analyzed; may be a group of chemicals that belong to the same chemical family and that are analyzed together. (DoD QSM)
Audit:	A systematic evaluation to determine the conformance to quantitative and qualitative specifications of some operational function or activity. (EPA-QAD)
Background:	Ambient signal response recorded by measuring instruments that is independent of radioactivity contributed by the radionuclides being measured in the sample. (DOE QSM)
Batch:	Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one to twenty environmental samples of the same TNI-defined matrix, meeting the above-mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates, or concentrates) which are analyzed together as a group. An **analytical batch** can include prepared samples originating from various environmental matrices and can exceed 20 samples. (TNI Quality Systems Committee)
Bias:	The deviation of a single measured value of a random variable from a corresponding expected value, or a fixed mean deviation from the expected value that remains constant over replicated measurements within the statistical precision of the measurement (Synonyms: deterministic error, fixed error, systematic error). (DOE QSM)
Blank:	A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, or analysis. The blank is subjected to the same analytical and measurement process as the associated samples. Blanks include: Equipment blank: a sample of analyte free media which has been

TERM	**DEFINITION**
	used to rinse common sampling equipment to check effectiveness of decontamination procedures. (TNI) Field blank: a blank prepared in the field by filling a clean container with pure deionized water and appropriate preservative, if any, for the specific sampling activity being undertaken. (EPA OSWER) Trip blank: Contaminant free water, or appropriate matrix, which accompanies bottles and samples during shipment to assess the potential for sample contamination during shipment. Trip blanks are not opened in the field, and are required for Volatile Organic Analysis only. (NIRP) Instrument Blank: A clean sample (e.g., distilled water) processed through the instrumental steps of the measurement process; used to determine instrument contamination. (EPA-QAD) Method blank: a sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all the steps of the analytical procedures. (TNI) Reagent blank: a sample consisting of reagent(s), without the target analyte(s) or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps. (QAMS)
Blind Sample:	A sub-sample for analysis with a composition known to the submitter. The analyst/laboratory may know the identity of the sample, but not the composition. It is used to test the analyst's or laboratory's proficiency in the execution of the measurement process. (TNI)
Calibration:	To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter, instrument, or other device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements. See Initial Calibration. (TNI)
Calibration, Continuing:	The process of analyzing standards periodically to verify the maintenance of calibration of the analytical system.
Calibration Curve:	The graphical relationship between the known values, such as

TERM	**DEFINITION**
	concentrations, of a series of calibration standards and their instrument response. (TNI)
Calibration, Initial:	The process of analyzing standards, prepared at specified concentrations, to define the quantitative response, linearity and dynamic range of the instrument to the analytes of interest. Initial calibration is performed whenever the results of a continuing calibration do not conform to the requirements of the method in use or at a frequency specified in the method. See Calibration.
Calibration, Initial Check/Verification (ICV):	Verification of the ratio of instrument response to analyte amount, a calibration check is done by analyzing for analyte standards in an appropriate solvent. Calibration check solutions are made from a stock solution which is different from the stock used to prepare calibration standards. (NIRP Glossary)
Carrier:	Carriers are typically non-radioactive (e.g. natural strontium, barium, yttrium) elements. They follow similar chemical reactions as the analyte during processing and are added to samples to determine the overall chemical yield for the analytical preparation steps. The yield of the carrier is typically determined gravimetrically or by ICP and is used to correct radiochemical results for acceptable losses occurring during the preparation process. (DOE QSM)
Chain-of-Custody (COC) Form:	Record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: the number and types of containers, the mode of collection, preservation, and requested samples. (TNI)
Confidential Business Information (CBI):	Information that an organization designates as having the potential of providing a competitor with inappropriate insight into its management, operation or products. TNI and its representatives agree to safeguard identified CBI and to maintain information identified as such in full confidentiality. (TNI)
Confirmation:	Verification of the identity of a component through the use of an approach with a different scientific principle from the original method. These may include, but are not limited to: second column calibration, alternate wavelength, derivatization, mass spectral interpretation, alternative detectors, or additional cleanup procedures. (TNI)

TERM	**DEFINITION**
Conformance:	An affirmative indication or judgment that a product or service has met the requirements of the relevant specifications, contract, or regulation; also the state of meeting the requirements. (ANSI/ASQC E4-1994)
Control Chart:	A graphical plot of test results with respect to time or sequence of measurement, together with limits within which they are expected to lie when the system is in a state of statistical control.
Control Limit:	A range within which specified measurement results must fall to signify compliance. Control limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that nonconforming data be investigated and flagged.
Corrective Action:	The action taken to eliminate the causes of an existing nonconformity, defect, or other undesirable situation in order to prevent recurrence. (ISO 8402)
Counting Efficiency:	The ratio of the net count rate of a radionuclide standard source to its corresponding known activity. (DOE QSM)
Counting Uncertainty (Poissonian):	A statistical estimate of uncertainty in a radiochemical measurement due to the random nature of decay. Every radiochemical result is reported with an associated counting uncertainty, usually at the 95% confidence interval.
Data Quality Indicators:	The qualitative or quantitative statements that specify the quality of data required to support decision for any process requiring chemical or physical analysis.
Data Reduction:	The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form. (EPA-QAD)
Daughter:	A nuclide formed by radioactive decay of a parent radionuclide.
Deficiency:	An unauthorized deviation from acceptable procedures or practices, or a defect in an item. (ASQC)
Demonstration of Capability (DOC):	A procedure to establish the ability of the analyst to generate acceptable accuracy. (TNI)
Detection Limit,	The lowest concentration or amount of the target analyte that can be identified, measured, and reported with confidence that the analyte

TERM	**DEFINITION**
Analyte:	concentration is not a false positive value. See Method Detection Limit. (TNI)
Detection Limit, Instrument (IDL):	The concentration of an analyte that produces an output signal twice the root mean square of the background noise, or the parameter determined by multiplying by three the standard deviation obtained of three to five times the desired IDL on three nonconsecutive days with seven consecutive measurements per day. IDL is only required for the metals and analysis. (DOE QSM)
Detection Limit, Method (MDL):	The Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. It may be determined using replicate spike samples prepared by the lab and taken through all steps of the method. The detection limit is calculated using the ALS SOP 329
Digestion:	A process in which a sample is treated (usually in conjunction with heat) to convert the sample into a more easily measured form. (DoD QSM)
Dilution Factor:	The factor by which the dilution level of the sample differs from that of a predefined method blank. The method blank is prepared within the prescribed parameters of the method, and has a dilution factor of one. The dilution factor does not include a dryness factor. (DOE QSM)
Document Control:	The act of ensuring that documents (and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly, and controlled to ensure use of the correct version at the location where the prescribed activity is performed. (ASQC)
Dry Weight:	The weight of a sample based on percent solids. The weight after drying in an oven at 105$\pm$5^{o}C.
Duplicate, Replicate Analysis:	The analyses or measurements of the variable of interest performed identically on two sub samples of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation, or storage internal to the laboratory. (EPA-QAD)
	The measurements of the variable of interest performed identically

TERM	**DEFINITION**
	on two or more sub-samples of the same samples within a short time interval. (TNI)
Duplicate (Replicate) Error Ratio (DER/RER):	A measure of precision used to assess agreement between radiochemical duplicates (replicates) that compares the discrepancy between two measurements to the associated uncertainties.
Duplicate, Replicate Sample:	A second aliquot of the same sample that is treated the same as the original sample in order to determine the precision of the method.
	A second, separate sample collected at the same time, from the same place, for the same analysis, as the original sample in order to determine overall precision.
Eluent:	A solvent used to carry the components of a mixture through a stationary phase. (DoD QSM)
Elution:	A process in which solutes are washed through a stationary phase by the movement of a mobile phase. (DoD QSM)
Energy Calibration:	The correlation of the multi-channel analyzer (MCA) channel number to decay energy, obtained from the location of peaks from known radioactive standards. (DOE QSM)
False Negative:	An analyte incorrectly reported as absent from the sample, resulting in potential risks from their presence. (DoD QSM)
False Positive:	An item incorrectly identified as present in the sample, resulting in a high reporting value for the analyte of concern. (DoD QSM)
Finding:	An assessment conclusion that identifies a condition having a significant effect on an item or activity. An assessment finding is normally a deficiency and is normally accompanied by specific examples of the observed condition. (TNI)
Half Life ($T_{½}$):	The time required for 50% of a radioactive isotope to decay. (DOE QSM)
Holding Time (Maximum Allowable):	The maximum times that samples may be held prior to analysis and still be considered valid or not compromised. (40 CFR Part 136)
Homogeneity:	The degree to which a property or substance is evenly distributed throughout a material.

TERM	**DEFINITION**
Interference, Spectral:	Occurs when particulate matter from the atomization scatters the incident radiation from the source or when the absorption or emission of an interfering species either overlaps or is so close to the analyte wavelength that resolution becomes impossible. (DoD QSM)
Interference, Chemical:	Results from the various chemical processes that occur during atomization and later the absorption characteristics of the analyte. (DoD QSM)
Internal Standards:	A known amount of standard added to a test portion of a sample as a reference for evaluating and controlling the precision and bias of the applied analytical method. (TNI)
Isomer:	Generally, any two chemicals with the same chemical formula but with a different structure. (DoD QSM)
Isotope:	A variation of an element that has the same atomic number of protons but a different weight because of the number of neutrons. Various isotopes of the same elements may have different radioactive behaviors, some are highly unstable. (NIRP Glossary)
Lot:	A quantity of bulk material of similar composition processed or manufactured at the same time.
Matrix:	The substrate of a test sample. **Field of Accreditation Matrix:** these matrix definitions shall be used when accrediting a laboratory: Drinking Water: any aqueous sample that has been designated a potable or potential potable water source. Non-Potable Water: any aqueous sample excluded from the definition of Drinking Water matrix. Includes surface water, groundwater, effluents, water treatment chemicals, and TCLP or other extracts. Solid and Chemical Materials: includes soils, sediments, sludges, products, and by-products of an industrial process that results in a matrix not previously defined. Biological Tissue: any sample of a biological origin such as fish tissue, shellfish, or plant material. Such samples shall be grouped according to origin. Air and Emissions: whole gas or vapor samples including those contained in flexible or rigid wall containers and the extracted

TERM	DEFINITION
	concentrated analytes of interest from a gas or vapor that are collected with a sorbent tube, impinger solution, filter, or other device. (TNI) Non-aqueous Liquid: any organic liquid with <15% settleable solids.
Minimum Detectable Activity (MDA, Lower Limit of Detection):	The minimum detectable activity is the smallest amount (activity or mass) of an analyte in a sample that will be detected with a probability beta of nondetection (Type II error) while accepting the probability alpha of erroneously deciding that a positive (non-zero) quantity of analyte is present in an appropriate blank sample (Type I error). For the purposes of this standard, the alpha and beta probabilities are both set at 0.05 unless otherwise specified. (ANSI N 13.30 and ANSI N42.23)
Minimum Detectable Concentration (MDC):	The Minimum Detectable Activity expressed in concentration units.
National Voluntary Laboratory Accreditation Program (NVLAP):	A program administered by NIST that is used by providers of proficiency testing to gain accreditation for all compounds/matrices for which NVLAP accreditation is available, and for which the provider intends to provide NELAP PT samples. (TNI)
Negative Control:	Measures taken to ensure that a test, its components, or the environment do not cause undesired effects, or produce incorrect test results. (TNI)
Nonconformance:	An indication or judgment that a product or service has not met the requirements of the relevant specifications, contract or regulation, also the state of failing to meet the requirements. (DoD QSM)
Performance Based Measurement System (PBMS):	A set of processes wherein the data quality needs, mandates, or limitations of a program or project are specified and serve as criteria for selecting measurement processes which will meet those needs in a cost effective manner. (TNI)
Positive Control:	Measures taken to ensure that a test and/or its components are working properly and producing correct or expected results from positive test subjects. (TNI)
Precision:	The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance, or range, in either absolute or relative

TERM	**DEFINITION**
	terms. (TNI)
Proficiency Test Sample:	A sample, the composition of which is unknown to the analyst and is provided to test whether the analyst/laboratory can produce analytical results within specified acceptance criteria. (QAMS)
Qualitative:	Analysis without regard to quantity or specific numeric values. (NIRP Glossary)
Quality Assurance:	An integrated system of activities involving planning, quality control, quality assessment, reporting, and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence. (QAMS)
Quality Control (QC):	The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of the users. (QAMS)
Quality Control Sample:	An uncontaminated matrix spiked with known amounts of analytes. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system. (EPA-QAD) Laboratory Control Sample (LCS): (However named, also Laboratory Fortified Blank, Blank Spike, or QC Check Sample): A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst specific precision and bias, or to assess the performance of all or a portion of the measurement system. (TNI) Laboratory Duplicate (DUP): Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently. (TNI) Matrix Spike (spiked sample or fortified sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency. (QAMS)
Quantitation Limits,	Levels, concentrations, or quantities of a target variable (e.g. target

TERM	**DEFINITION**
Practical (PQL):	analyte) that can be reported at a specified degree of confidence. (TNI) The value at which an instrument can accurately measure an analyte at a specific concentration (i.e. a specific numeric concentration can be quantified). These points are established by the upper and lower limits of the calibration range. (DoD clarification) The lowest concentration where the 95% confidence interval is within 20% of the true concentration of the sample. The percent uncertainty at the 95% confidence level shall not exceed 20% of the results for concentrations greater than the practical quantitation limit. (DOE QSM)
Quantitative:	Analysis with regard to quantities or specific numeric values. (NIRP Glossary)
Radioactive Decay:	The process by which a spontaneous change in nuclear state takes place. This process is accompanied by the emission of energy and subatomic particles. (DOE QSM)
Radiation Yield:	The amount of radiation of the type being measured that is produced per each disintegration which occurs. For gamma spectrometry, this is commonly called gamma abundance. (DOE QSM)
Raw Data:	Any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets records, memoranda, notes, or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm, or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g. tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted. (EPA-QAD)
Reagent Water:	Shall be water (defined by national or international standard) in which no target analytes or interferences are detected as required by the analytical method. (TNI)
Region of Interest (ROI):	In radiochemical analysis, the Multi-channel Analyzer region defining the isotope of interest displayed in terms of energy or channels. (DOE QSM)

TERM	**DEFINITION**
Relative Percent Difference (RPD):	A measure of precision between two duplicate (replicate) results expressed as the percent difference between the results relative to the average of the results.
Reliability Check (Daily):	A periodic check of the Continuing Calibration of an instrument used for radiochemical measurements.
Reporting Limit:	The level at which method, permit, regulatory and client specific objectives are met. The reporting limit may never be lower than the statistically determined MDL, but may be higher based on any of the above considerations. Reporting limits are corrected for sample amounts, including the dry weight of solids, unless otherwise specified.
Retention Time:	The time between sample injection and the appearance of a solute peak at the detector. (DoD QSM)
Rounding Rules:	If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. As an example, 11.443 is rounded to 11.44. If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by 1. As an example, 11.446 is rounded to 11.45. If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number. As an example, 11.435 is rounded to 11.44, while 11.425 is rounded to 11.42. If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures.
Sample:	A single container or series of containers identified by a unique number comprised of material drawn from a single location or a composite of locations during a fixed period representative of that location (s) and time period(s) for the purpose of analytical testing or physical evaluation. (DOE QSM)
Selectivity:	(Analytical chemistry) The capability of a test method or instrument to respond to a target substance in the presence of non-target substances. (EPA-QAD)
Sensitivity:	Capability of method or instrument to discriminate between measurement responses representing different levels (e.g.

TERM	**DEFINITION**
	concentrations) of a variable of interest. (TNI)
Signal-to-Noise Ratio:	The signal carries information about the analyte, while noise is made up of extraneous information that is unwanted because it degrades the accuracy and precision of an analysis and also places a lower limit on the amount of analyte that can be detected. In most measurements, the average strength of the noise is constant and independent of the magnitude of the signal. Thus, the effect of noise on the relative error of a measurement becomes greater and greater as the quantity being measured (producing the signal) decreases in amplitude. (DoD QSM)
Split Sample:	A portion or subsample of a total sample obtained in such a manner that is not believed to differ significantly from other portions of the same sample.
Standard Operating Procedure (SOP):	A written document which details the method of an operation, analysis, or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing routine and repetitive tasks. (QAMS)
Reference Material:	A certified reference material produced by the U.S. National Institute of Standards and Technology or other equivalent organization and characterized for absolute content, independent of analytical method. (EPA-QAD) A reference material one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body. (ISO Guide 30 – 2.2)
Standard (Spike) Addition:	In radiochemistry, the addition of a known quantity of a radiotracer to a sample and to a split or splits of a sample. Both the sample and split(s) are then processed through the method and the difference in response between the samples used to correct for overall bias resulting measurement bias and from losses during preparation. This method of internal calibration is used in radiochemical determinations where isotopic differentiation between target analyte and tracer is not possible.
Statistical Minimum Significant Difference (SMSD):	The minimum difference between the control and a test concentration that is statistically significant, a measure of test sensitivity or power. The power of a test depends in part on the number of replicates per concentration, the significance level selected, and the type of

TERM	**DEFINITION**
	statistical analysis. If the viability remains constant, the sensitivity of the test increases as the number of replicates is increased. (TNI)
Surrogate:	A substance with properties that mimic the analyte of interest. It is unlikely to be found in environmental samples and is added to them for quality control purposes. (QAMS)
Target Analytes:	Identified on a list of project-specific analytes for which laboratory analysis is required.
Tolerance Chart:	A chart in which the plotted quality control data is assessed via a tolerance level (e.g. +/-10% of a mean) based on the precision level judged to be acceptable to meet overall quality/data use requirements instead of a statistical acceptance criteria (e.g. +/- 3 sigma) (applies to radio bioassay laboratories). (ANSI)
Total Propagated Uncertainty (TPU):	An estimate or approximation of the total error associated with a measured value by propagation of individual (preparation, determination) uncertainties.
Traceability:	The property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons. (VIM-6.12)
Tracer:	A traceable internal standard, usually a unique isotope of the element being determined, added to each sample in known amount which enables quantitation of analytes of interest independent of external means of calibration.
Tracer Chemical Recovery:	The percent yield of the recovered radioisotope after the sample/tracer aliquot has undergone preparation and instrument analysis. (DOE QSM)
Tune:	An injected standard required by the method as a check on instrument performance for mass spectrometry. (DoD QSM)
Validation:	Confirmation by examination and provision of evidence that specified requirements have been met. (EPA-QAD)
Verification:	Confirmation by examination and provision of evidence that specified requirements have been met. (TNI)
	NOTE: In connection with the management of measuring equipment, verification provides a means for checking that the deviations between

TERM	DEFINITION
	values indicated by a measuring instrument and corresponding known values of a measured quantity are consistently smaller than the maximum allowable error defined in a standard, regulation or specification peculiar to the management of the measuring equipment. The result of verification leads to a decision either to restore in service, to perform adjustment, to repair or downgrade, or declare obsolete. In all cases, it is required that a written trace of the verification performed shall be kept on the measuring instrument's individual record.
Warning Limits:	The limits (typically 2 standard deviations either side of the mean) shown on a control chart within which most results are expected to lie (within a 95% probability) while the system remains in a state of statistical control.

14.2 ACRONYMS

TERM	DEFINITION
AA	Atomic Absorption
AFCEE	Air Force Center for Environmental Excellence
ANSI/ASQ	American National Standards Institute/American Society for Quality
APHIS	USDA Animal and Plant Health Inspection Service
API	American Petroleum Institute
ARAR	Applicable or Relevant and Appropriate Requirement
ASCII	American Standard Code Information Interchange
ASTM	American Society for Testing and Materials
BFB	Bromofluorobenzene
BNA	Base-Neutral and Acid Extractable Organic Compounds
BS	Blank Spike
BTEX	Benzene, Toluene, Ethylbenzene, Xylene

TERM	**DEFINITION**
°C	Degrees Celsius
CAS	Chemical Abstract Service
CCC	Calibration Check Compound
CCB	Continuing Calibration Blank
CCV	Continuing Calibration Verification
CDPHE	Colorado State Department of Public Health and the Environment
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CF	Calibration Factor
CFR	Code of Federal Regulation
CLLE, CLE	Continuous Liquid-Liquid Extractor
CLP	Contract Laboratory Program
COC	Chain of Custody
CVAA	Cold Vapor Atomic Absorption Spectroscopy.
CWA	Clean Water Act
D	Drift or Difference
DBCP	1,2-Dibromo-3-chloropropane
DCM	Dichloromethane
DENIX	Defense Environmental Management Information Exchange
DER	Duplicate Error Ratio
DFTPP	Decafluorotriphenylphosphine
DI	Deionized
DOC	Demonstration of Capability
DoD	Department of Defense
DOE	Department of Energy

TERM	**DEFINITION**
DOT	Department of Transportation
DPM	Disintegrations per Minute
DQI	Data Quality Indicator
DRO	Diesel Range Organics
ECD	Electron Capture Detector
EDB	Ethylene Dibromide
EDD	Electronic Data Deliverable
EERF	Eastern Environmental Radiation Facility
EMSL	Environmental Monitoring Systems Laboratory
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
FPD	Flame Photometric Detector
GALP	Good Automated Lab Practice
GC	Gas Chromatography
GC/MS	Gas Chromatography/Mass Spectrometry
GFAA	Graphite Furnace Atomic Absorption
GFPC	Gas Flow Proportional Counting
GPC	Gel Permeation Chromatography
GRO	Gasoline range organics
HECD	(Hall) Electrolytic Conductivity Detector
HEM	Hexane Extractable Material
HDPE	High-Density Polyethylene
HPGe	High Purity Germanium Gamma Spectrometer
HPLC	High-Performance Liquid Chromatography

TERM	**DEFINITION**
IC	Ion Chromatography
ICAP-AES	Inductively Coupled Argon Plasma -Atomic Emission Spectroscopy
ICB	Initial Calibration Blank
ICP	Inductively Coupled Plasma
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICS	Interference Check Standard
ICV	Initial Calibration Verification
IDL	Instrument Detection Limit
IPC	Instrument Performance Check
IPN	Incoming Project Notice
IRPIMS	Installation Restoration Program Information Management System
IS	Internal Standard
ISO/IEC	International Standards Organization/International Electrotechnical Commission
KD	Kuderna Danish
LCS	Laboratory Control Sample
LD	Laboratory Duplicate
LFB	Laboratory Fortified Blank
LFM	Laboratory Fortified Matrix
LIMS	Laboratory Information Management System
LLRW	Low Level Radioactive Waste
LQAP	Laboratory Quality Assurance Plan
LRB	Laboratory Reagent Blank
LSC	Liquid Scintillation Counting
LUFT	Leaking Underground Fuel Tank

TERM	**DEFINITION**
LUST	Leaking Underground Storage Tank
MAPEP	Mixed Analyte Performance Evaluation Program
MCAWW	Methods for Chemical Analysis of Waters and Wastes
MDA	Minimum Detectable Activity
MDC	Minimum Detectable Concentration
MDL	Method Detection Limit
MEK	Methyl Ethyl Ketone (2-Butanone)
MIBK	Methyl Isobutyl Ketone
MSA	Method of Standard Additions
MSD	Matrix Spike Duplicate
MSDS	Material Safety Data Sheet
MTBE	Methyl tert-butyl ether
N/A	Not applicable
NIST	National Institute of Standards
NCR	Nonconformance Report
ND	Non Detect
NEIC	National Enforcement and Investigations Center
NELAC	National Environmental Laboratory Accreditation Conference
NELAP	National Environmental Laboratory Accreditation Program
NEPA	National Environmental Policy Act
NFESC	Naval Facilities Engineering Service Center
NIRP	Navy Installation Restoration Program
NIST	National Institute of Standards and Technology
NPDES	National Pollutant Discharge Elimination System

TERM	**DEFINITION**
NVLAP	National Voluntary Laboratory Accreditation Program
OSHA	Occupational Safety and Health Administration
PAH	Polynuclear Aromatic Hydrocarbon
PARCC	Precision, Accuracy, Representativeness, Completeness, Comparability
PBMS	Performance Based Measurement System
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzofuran
PEG	Polyethylene Glycol
PEL	Permissible Exposure Limit
PETN	Pentaerthrite tetranitrate
PID	Photoionization Detector
PM	Project Manager
PNA	Polynuclear Aromatic Hydrocarbon
PQL	Practical Quantitation Limit
psi	pounds per square inch
PT	Proficiency Testing
PTFE	Polytetrafluoroethylene
QA	Quality Assurance
QAPjP	Quality assurance project plan
QASS	Quality Assurance Summary Sheet
QC	Quality Control
QIP	Quench Indicating Parameter
r^2	Correlation Coefficient

TERM	**DEFINITION**
RCRA	Resource Conservation and Recovery Act
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
RFP	Request for Proposal
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
RL	Reporting Limit
ROI	Region of Interest
RPD	Relative Percent Difference
RPM	Revolutions Per Minute
RRT	Relative Retention Time
RSD	Relative Standard Deviation
RSO	Radiation Safety Officer
RT	Retention Time
RTW	Retention Time Window
TNI	The NELAC Institute
SARA	Superfund Amendments and Reauthorization Act
SDWA	Safe Drinking Water Act
SMSD	Statistical Minimum Significant Difference
SOP	Standard Operating Procedure
SOW	Statement of Work
SPCC	System Performance Check Compound
SPLP, SLP	Synthetic Precipitation Leaching Procedure
SVOC	Semivolatile Organic Compound
TAL	Target Analyte List

TERM	**DEFINITION**
TCLP	Toxicity Characteristic Leaching Procedure
TCMX	Tetrachlorometaxylene
TCL	Target Compound List
TDS	Total Dissolved Solids
TIC	Tentatively Identified Compound
TLV	Threshold Limit Value
TNI	The NELAC Institute
TOC	Total Organic Carbon
TPH	Total petroleum hydrocarbon
TPU	Total Propagated Uncertainty
TRPH	Total Recoverable Petroleum Hydrocarbons
TSCA	Toxic Substances Control Act
TSDF	Treatment, Storage, and Disposal Facility
TSS	Total Suspended Solids
TVPH	Total Volatile Petroleum Hydrocarbons
USACE	United Stated Army Corp of Engineers
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UST	Underground Storage Tank
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound
WET	Waste Extraction Test
ZHE	Zero Headspace Extraction

14.3 SYMBOLS

LENGTH	DEFINITION	SYNOMYM
um	micrometer	10^{-6} meter
mm	millimeter	10^{-3} meter
cm	centimeter	0.01 meter
dm	decimeter	0.1 meter
m	meter	

WEIGHT	DEFINITION	SYNOMYM
pg	picogram	10^{-12} gram
ng	nanogram	10^{-9} gram
ug	microgram	10^{-6} gram
mg	milligram	10^{-3} gram
g	gram	
kg	kilogram	10^{3} gram

VOLUME	DEFINITION	SYNOMYM
uL	microliter	10^{-6} Liter
mL	milliliter	10^{-3} Liter
dL	deciliter	0.1 Liter
L	Liter	

CONCENTRATION	DEFINITION
ng/uL	nanograms per microliter
ug/L	micrograms per liter
ug/kg	microgram per kilogram
ug/g	microgram per gram
ug/mL	microgram per milliliter
mg/kg	milligram per kilogram
mg/L	milligram per liter
ug/m^3	microgram per cubic meter
ppb	part per billion
ppm	part per million

TIME	**DEFINITION**	**SYNOMYM**
s or sec	second	1/60 minute
m or min	minute	60 seconds, 1/60 h
h	hour	60 minutes

TEMPERATURE	**DEFINITION**
^{o}C	Degrees Celsius
^{o}F	Degrees Fahrenheit
^{o} K	Degrees Kelvin

ACTIVITY	**DEFINITION**	**SYNOMYM**
Bq	Bequerels	Disintegration/s
Ci	Curie	3.7 x 10^{10} Bq
dpm	Disintegrations per minute	

ELECTRICAL	**DEFINITION**
V	Volt
A	Ampere
EV	Electron Volt
F	Farad
Ω	Ohm
S or mho	Siemens
W	Watt

PREFIXES	**NUMERIC AMOUNT**
tera	10^{12}
giga	10^{9}
mega	10^{6}
kilo	10^{3}
hecto	10^{2}
deca	10
deci	0.1
centi	10^{-2}
milli	10^{-3}
micro	10^{-6}

nano	10^{-9}
pico	10^{-12}
femto	10^{-15}

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and chapters of SW-846 and release these revisions as an update (Update IIIB) to the Third Edition of SW-846. To date, EPA has finalized Updates I, II, IIA, IIB, III, and IIIA to the Third Edition of the SW-846 manual. On May 8, 1998 (see 63 FR 25430) and on November 27, 2000 (see 65 FR 70678). EPA also respectively announced the availability of Draft Update IVA and Draft Update IVB methods and chapters, which were published for guidance purposes only.

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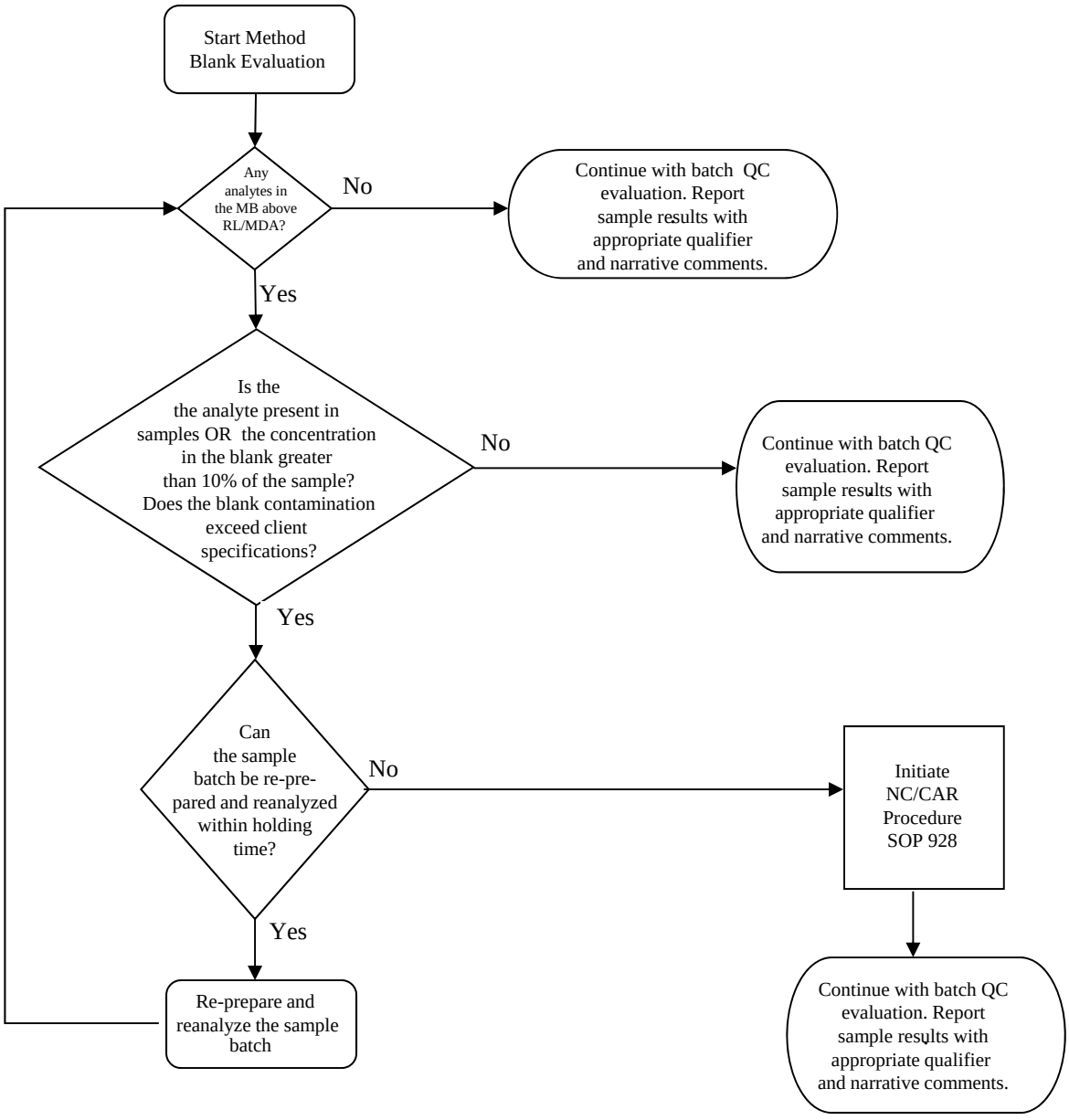
Method Blank Acceptability



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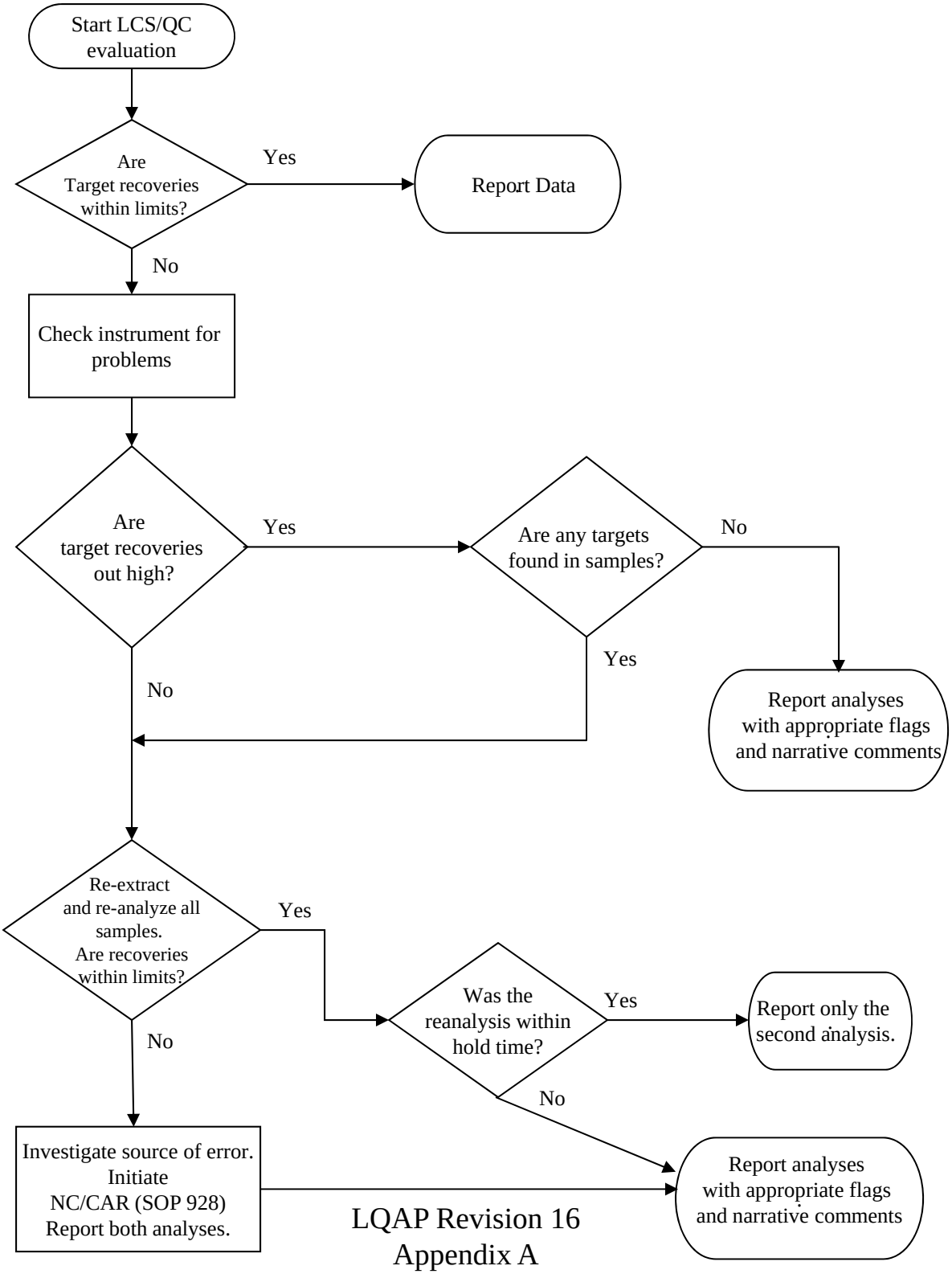
Appendix A

LCS/LCSD Acceptability



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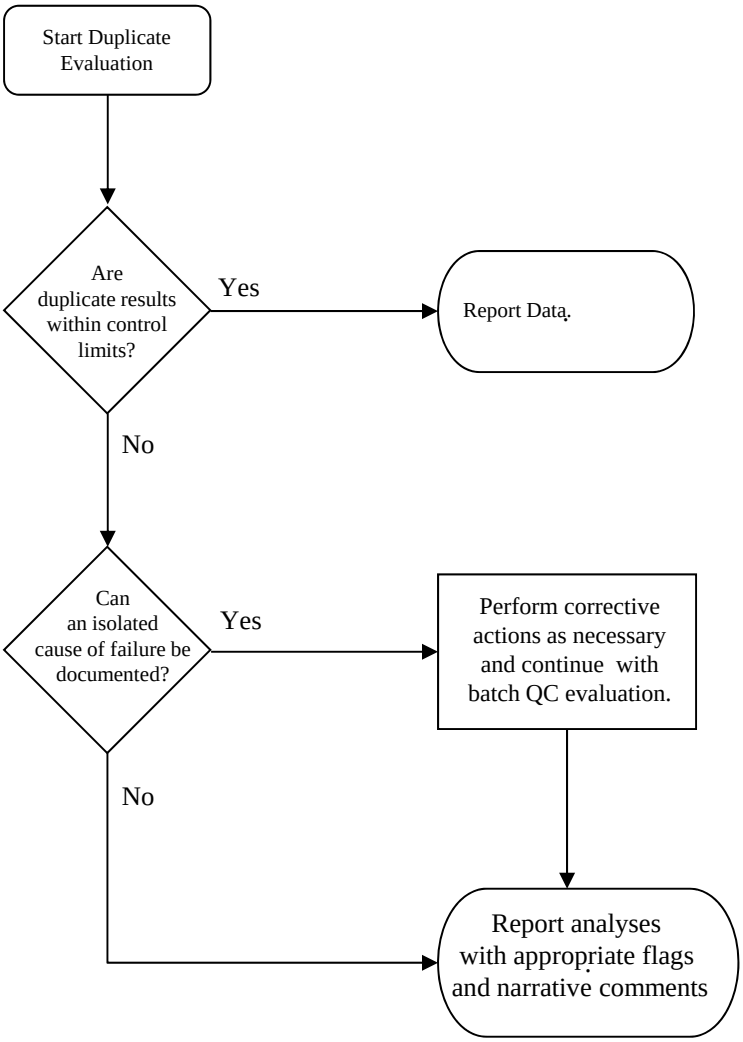
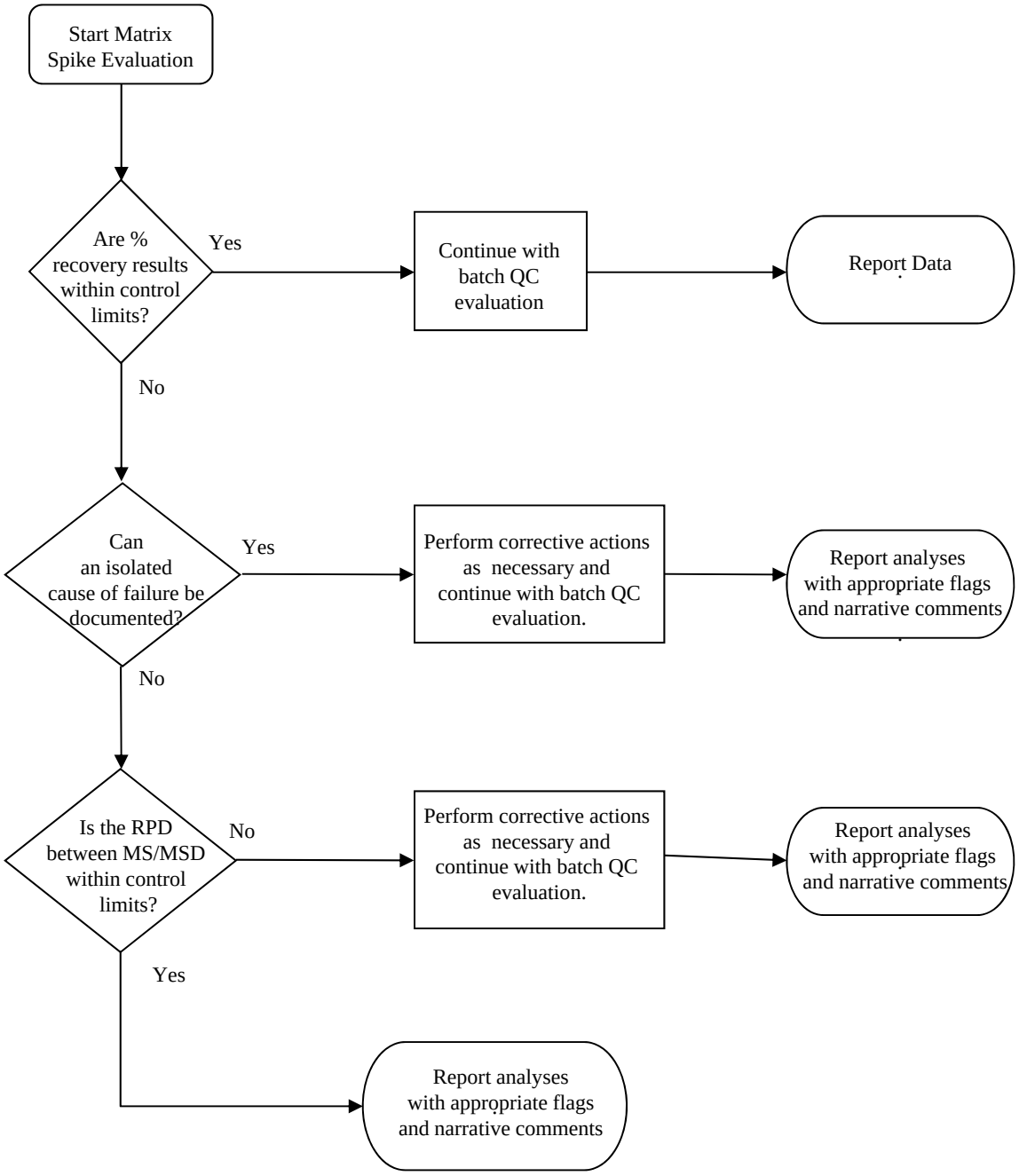
Matrix Duplicate Acceptability



Matrix Spike/Matrix Spike Duplicate Acceptability



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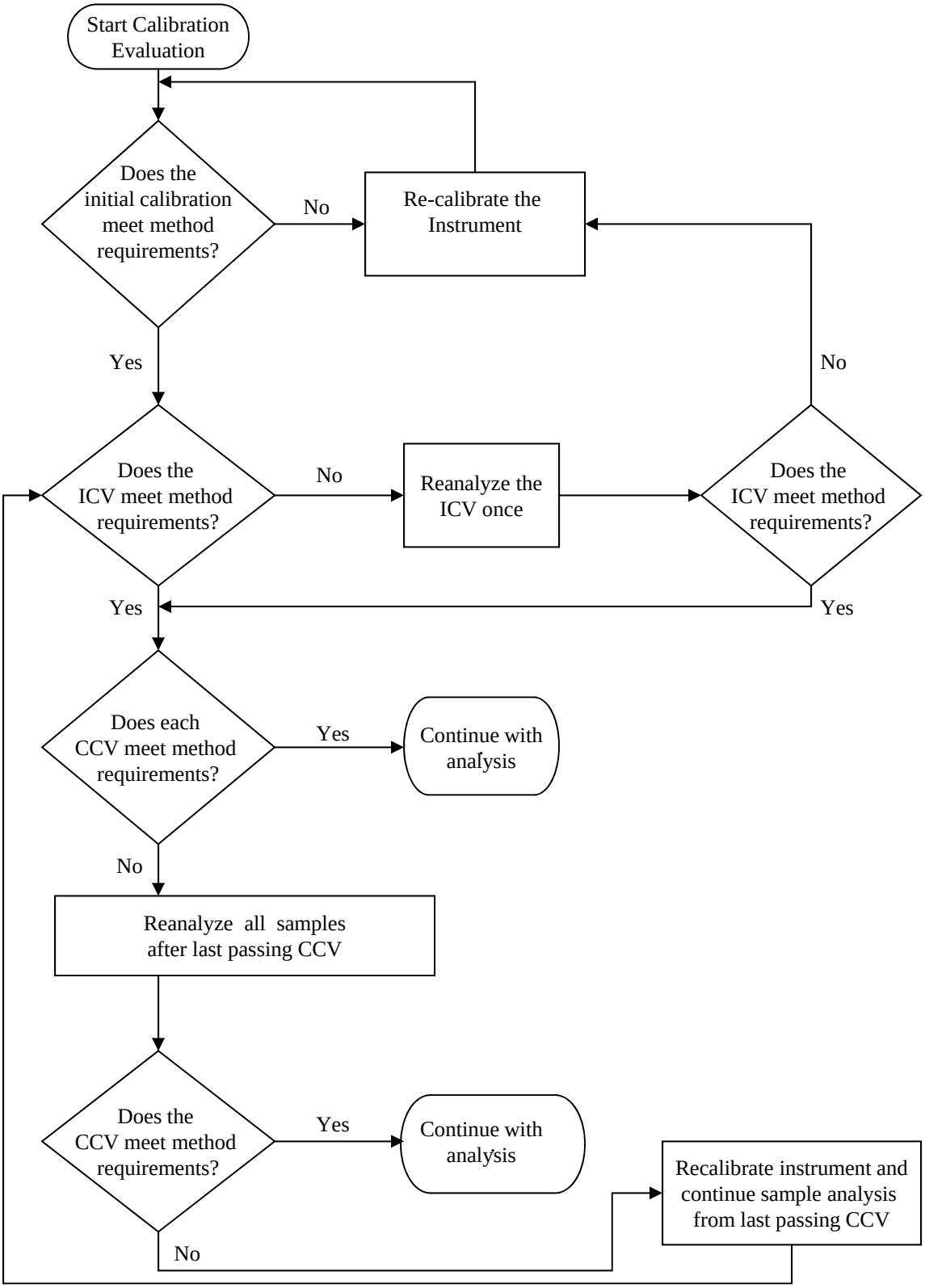
Calibration Acceptablity (Chemistry Only)



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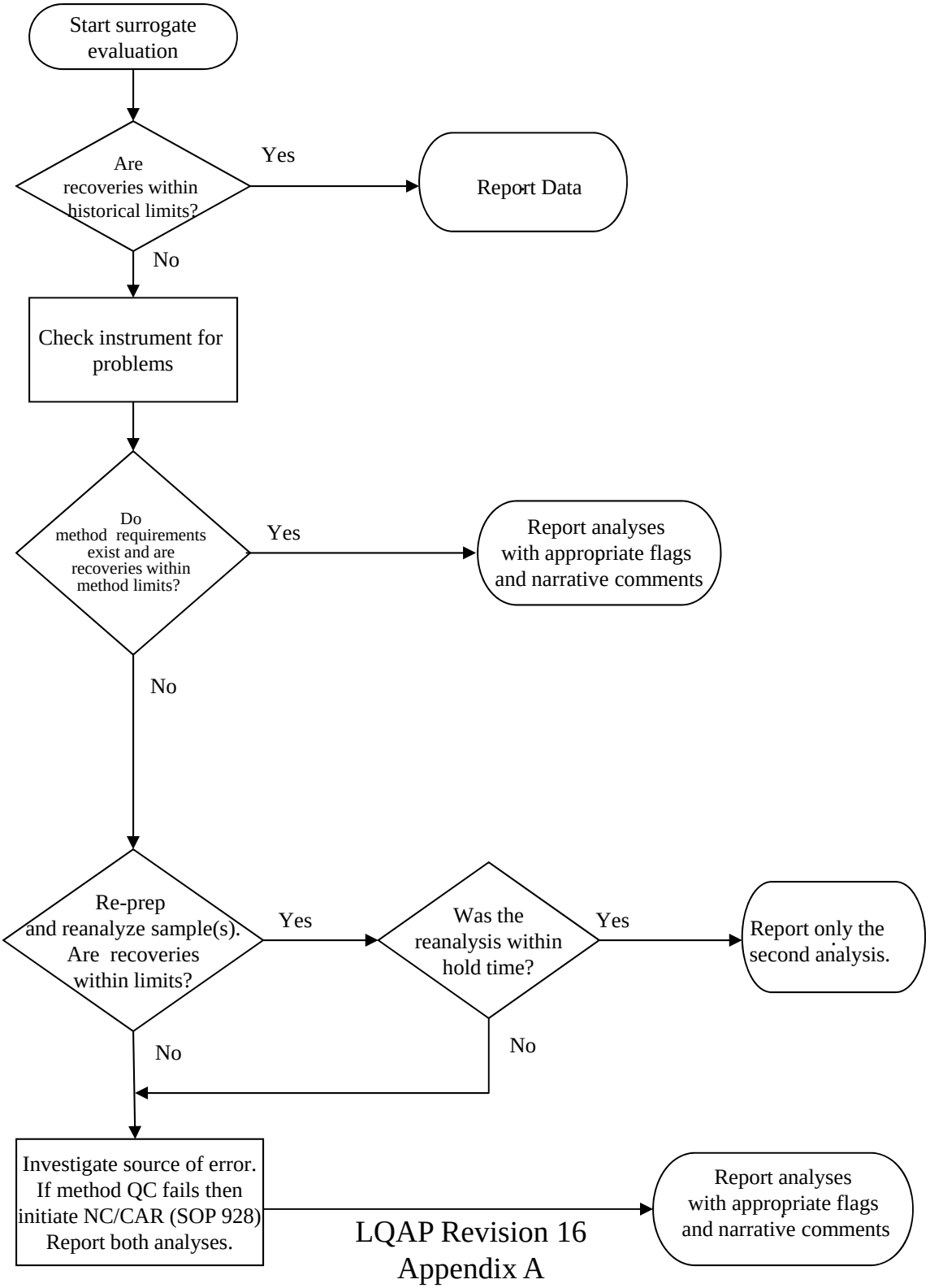
Surrogate – Chemical Yield - Tracer Acceptability



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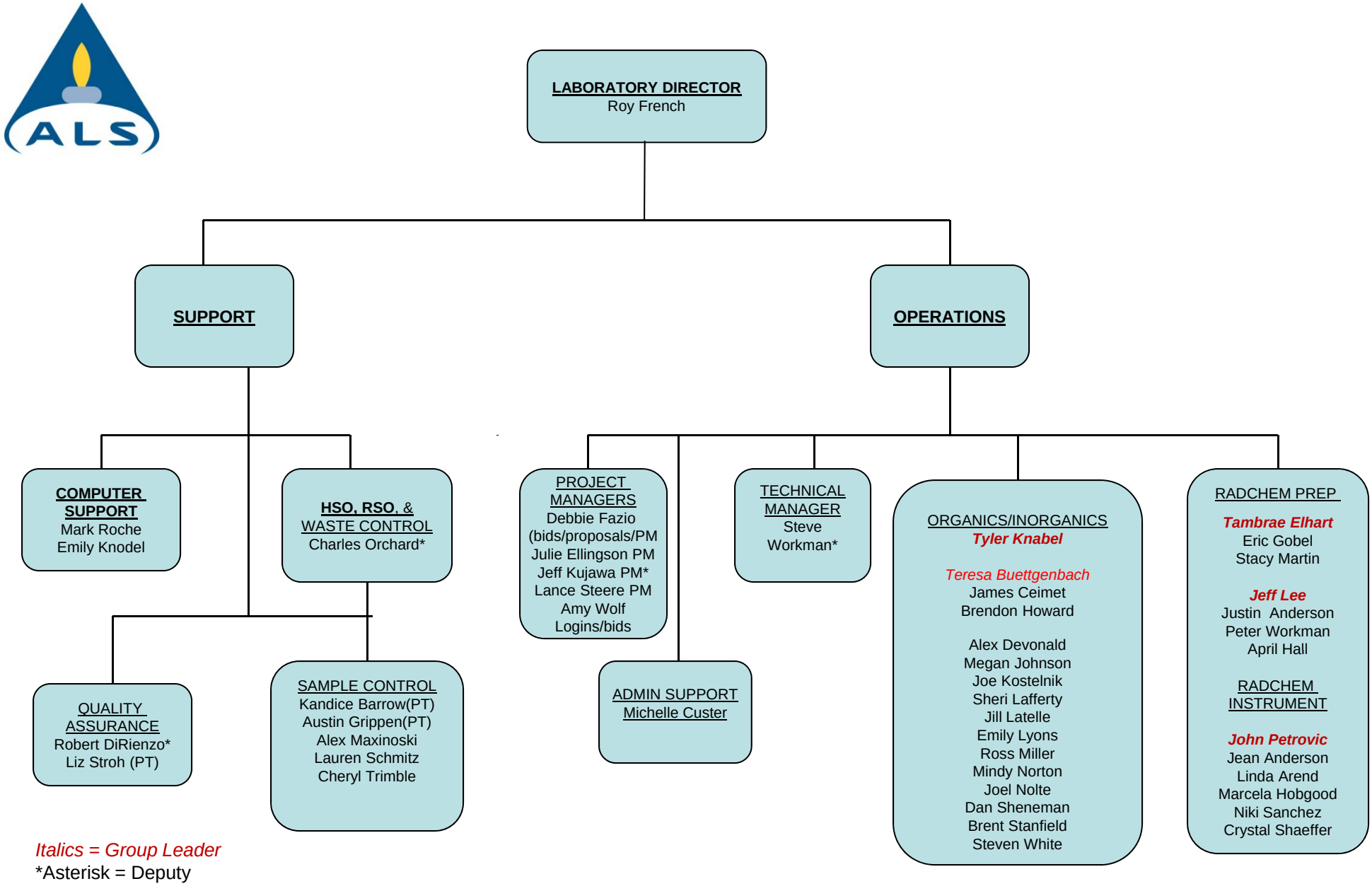
Appendix A



Italics = Group Leader
*Asterisk = Deputy

ALS – Fort Collins
May 9, 2013

ALS Laboratory Group
ANALYTICAL CHEMISTRY & TESTING SERVICES

Sample Handling Guidelines

Fort Collins, CO

General Inorganic Parameters

		Water			Soil/Sludge		
Parameters	**Method**	**Preservative**	**Container**	**Holding Time**	**Preservative**	**Container**	**Holding Time**
Acidity	E305.1	4°C	250 mL / P	14 Days	Matrix Not Applicable		
Alkalinity (Total, Carbonate, Bicarbonate, Hydroxide)	E310.1, SM2320B	4°C	250 mL / P	14 Days	Matrix Not Applicable		
Ammonia	E350.1, SM4500	4°C, H_2SO_4 to pH <2	125 mL / P	28 Days	4°C	4oz WMG	28 Days
Anions: Br, Cl, F, SO4 / NO2, NO3, o-PO4	E300.0, SW9056	4°C	125 mL / P	28 Days / 48 Hours	4°C	4oz WMG	28 D / 48 H from Prep
Chloride	E325.3	4°C	125 mL / P	28 Days	4°C	4oz WMG	28 Days from Prep
Fluoride	E340.2, SM4500, SW9214	4°C	125 mL / P	28 Days	4°C	4oz WMG	28 Days from Prep
Nitrite	E354.1	4°C	125 mL / P	48 Hours	4°C	4oz WMG	48 Hours from Prep
Chromium VI (Hexavalent Cr)	SW7196A(aq, so), SW7196A/3060A (so)	4°C	125 mL / P	24 Hours	4°C	4oz WMG	24 Hours from Prep
Cyanide (Total)	E335.2, SW9010B, SW9013B, SW9014	4°C, NaOH to pH >12	125 mL / P	14 Days	4°C	4oz WMG	14 Days
Cyanide (Amenable to Chlorination)	E335.2, SW9010B, SW9013B, SW9014	4°C, NaOH to pH >12	125 mL / P	14 Days	Matrix Not Applicable		
Cyanide (Weak and Dissociable)	SM4500	4°C, NaOH to pH >12	125 mL / P	14 Days	4°C	4oz WMG	14 Days
Nitrate + Nitrite as N	E353.2	4°C, H_2SO_4 to pH <2	125 mL / P	28 Days	4°C	4oz WMG	28 Days
Oxyanions (bromate, chlorate, chlorite, iodate)	SW8321	4°C, 1 µL 5% EDA/1 mL sample	40 mL / TLC-Amb G	14 Days	Matrix Not Applicable		
Perchlorate	E314.0, SW9058, SW6850, E331.0, DoD Handbook	4°C, 1/3 headspace	250 mL / P	28 Days	4°C	4oz WMG	28 Days
Phosphorous, Total	E365.2, SM4500	4°C, H_2SO_4 to pH <2	125 mL / P	28 Days	4°C	4oz WMG	28 Days
Phosphate, Ortho	E365.2, SM4500	4°C	125 mL / P	48 Hours	4°C	4oz WMG	48 Hours from Prep
pH	E150.1, SW9040, SW9045	4°C	125 mL / P	4 Days from Receipt	4°C	4oz WMG	4 Days from Receipt
Solids, Dissolved (TDS)	E160.1	4°C	250 mL / P	7 Days	Matrix Not Applicable		
Solids, Suspended (TSS)	E160.2	4°C	250 mL / P	7 Days	Matrix Not Applicable		
Solids, Total (TS)	E160.3	4°C	250 mL / P	7 Days	Matrix Not Applicable		
Solids, Volatile (TVS)	E160.4	4°C	250 mL / P	7 Days	Matrix Not Applicable		
Specific Conductance	E120.1, SW9050, SM2510B	4°C	125 mL / P	4 Days from Receipt	Matrix Not Applicable		
Sulfide	E376.1 (aq)	4°C, ZnAc, NaOH to pH >9	250 mL / P	7 Days	Matrix Not Applicable		
Total Organic Carbon (TOC)	E415.1 (aq), 9060 (aq), Walkley Black (so)	4°C, H_2SO_4 to pH<2	125 mL / Amb G	28 Days	4°C	4oz WMG	28 Days
Turbidity	E180.1	4°C	125 mL / P	48 Hours	Matrix Not Applicable		

Metals Parameters

		Water			Soil/Sludge		
Parameters	**Method**	**Preservative**	**Container**	**Holding Time**	**Preservative**	**Container**	**Holding Time**
Metals	E200.7, SW6010B, E200.8, SW6020A	4°C, HNO_3 to pH<2	250 mL / P	6 Months	4°C	4oz WMG	6 Months
Mercury	E245.1, SW7470 (aq), SW7471 (so)	4°C, HNO_3 to pH<2	250 mL / P	28 Days	4°C	4oz WMG	28 Days
Hardness	Calculation from Ca & Mg Results	4°C, HNO_3 to pH<2	250 mL / P	6 Months	Matrix Not Applicable		
Sodium Adsorption Ratio (SAR)	Calculation from Ca, Mg, & Na Results	4°C, HNO_3 to pH<2	250 mL / P	6 Months	Matrix Not Applicable		

Organic Parameters

		Water			Soil/Sludge		
Parameters	**Method**	**Preservative**	**Container**	**Holding Time***	**Preservative**	**Container**	**Holding Time***
Chlorinated Herbicides	SW8151A	4°C	1000 mL / TLC-Amb G	7 / 40 Days	4°C	4oz WMG / TLC	14 / 40 Days
EDB and/or DBCP	8260	4°C, HCl to pH<2, ZH	3 x 40 mL / V-TLS	14 Days	Matrix Not Applicable		
Explosives	SW8330A, SW8330B, SW8332, SW8321	4°C	1000 mL / TLC-Amb G	7 / 40 Days	4°C	4oz WMG / TLC	14 / 40 Days
Glycols (ethylene and propylene)	SW8015D	4°C	3 x 40 mL / V-TLS	7 / 14 Days	4°C	4oz WMG / TLC	14 Days
Lipids	SOP 672	Matrix Not Applicable			Frozen	8oz WMG / TLC	28 Days
Methane, Ethane, Ethene	RSK175	4°C, HCl to pH<2, ZH	3 x 40 mL / V-TLS	14 Days	Matrix Not Applicable		
Moisture	ASTM 2216	Matrix Not Applicable			4°C	4oz WMG / TLC	14 Days
Organochlorine Pesticides	E608, SW8081A	4°C	1000 mL / TLC-Amb G	7 / 40 Days	4°C	4oz WMG / TLC	14 / 40 Days
Organophosphorous Pesticides	SW8141	4°C	1000 mL / TLC-Amb G	7 / 40 Days	4°C	4oz WMG / TLC	14 / 40 Days
PCBs	E608, SW8082	4°C	1000 mL / TLC-Amb G	None	4°C	4oz WMG / TLC	None
Polynuclear Aromatic Hydrocarbons	SW8270D, SW8270D-SIM	4°C	1000 mL / TLC-Amb G	7 / 40 Days	4°C	4oz WMG / TLC	14 / 40 Days
Semivolatile Organics (Base/Neutrals/Acids)	E625, SW8270D , SW8270D-SIM	4°C	1000 mL / TLC-Amb G	7 / 40 Days	4°C	4oz WMG / TLC	14 / 40 Days
Total Petroleum Hydrocarbons							
TRPH (C8-C40)	FL-PRO	4°C, H_2SO_4/HCl to pH<2	1000 mL / TLC-Amb G	7 / 40 Days	4°C	4oz WMG	14 / 40 Days
DRO and/or MO	SW8015M, CAL-LUFT	4°C, H_2SO_4/HCl to pH<2	1000 mL / TLC-Amb G	7 / 40 Days	4°C	4oz WMG / TLC	14 / 40 Days
GRO	SW8015, CAL-LUFT	4°C, H_2SO_4/HCl to pH<2, ZH	3 x 40 mL / V-TLS	14 Days	4°C	4oz WMG / TLC	14 Days
Oil and Grease	E1664 (aq), SW9071 (so)	4°C, H_2SO_4/HCl to pH<2	1000 mL / TLC-Amb G	28 Days	4°C	4oz WMG	28 Days
Volatile Organics	E524.2, E624, SW8260B	4°C, HCl to pH <2, ZH	3 x 40 mL / V-TLS	14 Days	4°C	4oz WMG / TLC	14 Days
BTEX and/or MTBE	E524.2, E624, SE8260B	4°C, HCl to pH <2, ZH	3 x 40 mL / V-TLS	14 Days	4°C	4oz WMG / TLC	14 Days
Volatile Organics	5035A/SW8260B	Matrix Not Applicable			4°C	3 ENCORE Samplers	48 H to Analysis or Freezing
Volatile Organics	5035A/SW8260B	Matrix Not Applicable			4°C / sodium bisulfate	1 Tetra Core Sampler	14 Days

*Where two holding times are provided, the first value indicates holding time to extraction, the second value indicates holding time between extraction and analysis.

ALS Laboratory Group
ANALYTICAL CHEMISTRY & TESTING SERVICES

Sample Handling Guidelines

Fort Collins, CO

RCRA Characterization

		Water			Soil/Sludge		
Parameters	**Method**	**Preservative**	**Container**	**Holding Time***	**Preservative**	**Container**	**Holding Time***
Corrosivity (pH)	SW9040B, SW9045C	4°C	125 mL / P,G	4 Days from Receipt	4°C	4oz WMG	4 Days from Receipt
Ignitability	E1010, ASTM 93-80	4°C	1000 mL / TLC-Amb G	7 Days	4°C	4oz WMG / TLC	14 Days
Paint Filter Liquids	SW9095A	N/A	1000 mL / P, G	N/A	N/A	8oz WMG, P	N/A
Reactivity - Cyanide & Sulfide	SW846 7.3	4°C	125 mL / P, G	14 Days	4°C	4oz WMG	14 Days
TCLP / SPLP Parameters	**Method**	**Preservative**	**Container**	**Holding Time** Collection to Leaching / Leaching to Prep / Prep to Analysis	**Preservative**	**Container**	**Holding Time** Collection to Leaching / Leaching to Prep / Prep to Analysis
Metals	SW1311 / SW1312 / SW6010B	4°C	1000 mL / P	180D / NA / 180D	4°C	4oz WMG	180D / NA / 180D
Mercury	SW1311 / SW1312 / SW7470	4°C	1000 mL / P	28D / NA / 28D	4°C	4oz WMG	28D / NA / 28D
Chlorinated Herbicides	SW1311 / SW1312 / SW8151A	4°C	1000 mL / TLC-Amb G	14D / 7D / 40D	4°C	8oz WMG	14D / 7D / 40D
Organochlorine Pesticides	SW1311 / SW1312 / SW8081A	4°C	1000 mL / TLC-Amb G	14D / 7D / 40D	4°C	8oz WMG	14D / 7D / 40D
Organophosphorous Pesticides	SW1311 / SW1312 / SW8141A	4°C	1000 mL / TLC-Amb G	14D / 7D / 40D	4°C	8oz WMG	14D / 7D / 40D
Semivolatiles	SW1311 / SW1312 / SW8270D	4°C	1000 mL / TLC-Amb G	14D / 7D / 40D	4°C	8oz WMG	14D / 7D / 40D
Volatiles	SW1311 / SW1312 / SW8260B	4°C	1000 mL / TLC-Amb G	14D / NA / 14D	4°C	4oz WMG	14D / NA / 14D

*Where two holding times are provided, the first value indicates holding time to extraction, the second value indicates holding time between extraction and analysis.

Radiochemistry

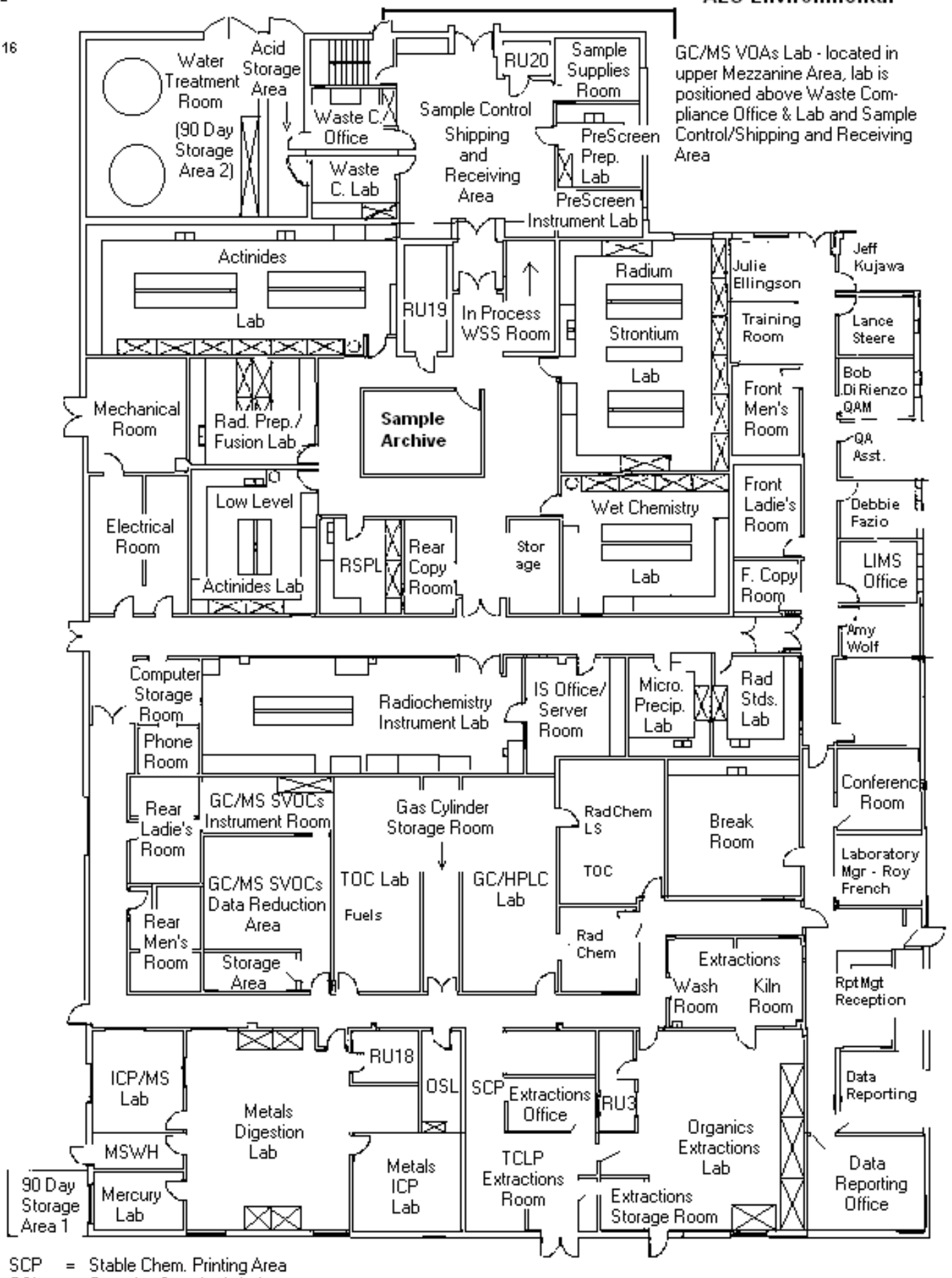
		Water			Soil/Sludge		
Parameters	**Method**	**Preservative**	**Container**	**Holding Time**	**Preservative**	**Container**	**Holding Time**
Americium-241	ASTM D3972	HNO_3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Carbon-14	EERF C-01M	N/A	250 mL / Amb G	N/A	N/A	4oz WMG, WMP	N/A
Chlorine-36	ALS SOP 753	N/A	2000 mL / Amb G	N/A	N/A	4oz WMG, WMP	N/A
Curium-244	ASTM D3972	HNO_3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Gamma Emitters (Stock FANP Library*)	E901.1	HNO3 to pH <2	1000 mL / P	N/A	N/A	16oz WMG, WMP	N/A
Gross Alpha/Beta	E900.0, SW9310	HNO3 to pH <2	500 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Iodine-129	E902.0	N/A	2000 mL / Amb G	N/A	N/A	4oz WMG, WMP	N/A
Iron-55	RESL Fe-01M	HNO3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Lead-210	ALS SOP 704	HNO3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Neptunium-237	ASTM D3972	HNO_3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Nickel-59	ASTM D3972	HNO3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Nickel-63	RESL Ni-01M	HNO3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Plutonium-238, 239	ASTM D3972	HNO_3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Plutonium-241	ASTM D3972	HNO3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Plutonium-242	ASTM D3972	HNO3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Polonium-210	ASTM D3972	HNO_3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Promethium-147	ALS SOP 758	HNO3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Radium, Total Alpha Emitting	E903.0, SW9315	HNO3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Radium-226	E903.0	HNO_3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Radium-226	E903.1, Alpha Spec ALS SOP 701	HNO3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Radium-228	E904.0, SW9320	HNO_3 to pH <2	2000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Radon-222 (Water)	SM 7500-Rn B	N/A, ZH	3 x 40 mL / V-TLS	4 Days	Matrix Not Applicable		
Radon-222 (Air)	E903.1M	N/A	500 mL Tedlar Bag	4 Days	Matrix Not Applicable		
Strontium-89	ASTM D5811	HNO3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Strontium-90 (Total Radiostrontium)	ASTM D5811	HNO_3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Technetium-99	EICHROM	HNO3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Thorium-228, 230, 232	ASTM D3972	HNO3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A
Tritium (H-3)	E906.0	4°C	250 mL / Amb G	6 Months	4°C	8oz WMG	N/A
Uranium-234, 235, 238	ASTM D3972	HNO3 to pH <2	1000 mL / P	N/A	N/A	4oz WMG, WMP	N/A

*Fission Activation and Natural Products Library

Acronym Definitions			Preservative
G - Glass	H - Hours	ALS Laboratory Group	H_2SO_4 - Sulfuric acid
P - Polyethylene	D - Days	225 Commerce Drive	HNO_3 - Nitric acid
Amb - Amber	M - Months	Fort Collins, CO 80524	HCl - Hydrochloric acid
WMG; WMP - Wide Mouth Glass or Poly Jar	E - EPA		NaOH - Sodium hydroxide
V-TLC - Glass Vial Teflon-lined Cap	SW - EPA SW846		ZnAc - Zinc acetate
V-TLS - Glass Vial Teflon-lined Septum	SM - Standard Methods		$NaHSO_4$ - Sodium bisulfate
ZH - Zero Headspace	ASTM - ASTM International	PH: 970.490.1522 FX: 970.490.1522 www.alsenviro.com	EDA - Ethylene diamine

Appendix E
Facilities
Diagram
LQAP Rev 16

ALS Environmental



SCP = Stable Chem. Printing Area
OSL = Organics Standards Laboratory
RSPL = Rad. Sample Prep. Lab
WSS = Warm Sample Storage
MSWH = Metals Satellite Waste Hall

Rev 6/2012

ALS Laboratory Group -- FC

SOP Table of Contents

SOP	Active Date	Schedule Date	Title	Notes	Author
001-049 SAFETY/WASTE					
001 R8	5/3/2013	5/3/2014	Treatment of Quarantined Soils, Aqueous Extracts, and Solid Residues and Cleaning Containers Used To Store Quarantined Sample Materials	Reviewed by C. Orchard 5/3/13 - no changes	CRO
002 R9	3/11/2013	3/11/2014	Laboratory Fume Hood Velocity Monitoring		CRO
003 R7	8/13/2012	8/13/2013	Management of Nonradioactive Hazardous Waste	No Change from Version 6	CRO
008 R10	4/9/2013	4/9/2014	Initial Receipt of Radioactive Samples and External Radiation Exposure Rate and Removeable Radioactive Material Contamination Survey of Incoming Radioactive Material Packages	Reviewed 4/9/2013 by C. Orchard - no changes	CRO
009 R8	3/26/2013	3/26/2014	Incoming Radioactive Material Packages That Exceed Removable Radioactive Material Contamination Limits	Reviewed 3/25/13 by C. Orchard - no revisions needed	CRO
010 R6	7/26/2012	7/26/2014	Survey of Laboratory Areas for Radioactive Contamination		CRO
012 R6	9/21/2012	9/21/2013	Contamination Surveys using Portable Survey Meters (Electra, Micro Roentgen)	Reviewed by C. Orchard 9/20/12 no revisions	CRO
015 R8	8/13/2012	8/13/2013	Disposal of Radioactive Waste	No Change from Version 7	CRO
016 R7	12/8/2010	10/22/2013	Electron Capture Detector Leak Tests		RTF
017 R6	3/26/2013	3/26/2014	Effluent Monitoring and Release	Reviewed 3/25/13 - no revision needed	CRO
024 R4	2/20/2013	2/20/2014	Disposal of Short Lived Radionuclides by Decay in Storage		CRO
026 R3	3/26/2013	3/26/2014	Radioactive Materials Inventory Control Using LIMS	Reviewed 3/25/13 - no revision needed	CRO
027 R2	12/8/2010	11/15/2013	Packaging Samples for Return to Client		CRO
029 R4	8/13/2012	8/13/2013	Calibration and Use of the Berthold LB 1043 AS Hand and Foot Monitors	No Change from version 3	CRO
030 R2	3/26/2013	3/26/2014	Operation of the Rampactor Compactor	Reviewed 3/25/13 by C Orchard - no revision needed	CRO
050-099 DATA REPORTING					
052 R10	10/12/2012	10/12/2013	Data Package Review Procedures for Stable Chemistry Methods	Reviewed 10/12/2012 M. Johnson	EXK
100-199 ADMINISTRATION					
103 R9	6/11/2010	6/11/2014	Qualification and Use of Subcontract Laboratories	Reviewed by Bob on 5-15-12 - No Changes	RPD
127 R11	12/10/2010	12/10/2013	Procurement and Control of Supplies and Services		RPD
132 R7	3/10/2011	3/9/2014	Building Security		CRO

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143 R7	5/26/2011	7/27/2014	Quality Assurance Training: Management Systems, Training, Ethics and Data Integrity	Deletion were made on 7/27/11 by Bob D.	RPD
150 R1	6/9/2011	6/8/2014	Employee Training Records		RPD
200-299 SAMPLE CONTROL					
202 R12	4/11/2011	6/4/2014	Login and Distribution of Samples and Workorders	Added ref to Nederman Moveable Fume Extraction arms (Bob D)	CRO
205 R10	12/15/2011	12/14/2014	Preparation of Bottle Orders, Shipping Sample Kits, and Maintaining Inventory of Bottles, Preservatives, and Labels		CRO
210 R7	3/9/2011	12/14/2014	Use and Calibration Verification of Infrared Temperature Guns	Reviewed by Bob D on 12-15-11	CRO
300-399 GENERAL CHEMISTRY					
300 R16	5/3/2013	5/3/2014	Standards, Solvents, Acids, Bases and Reagents Management in the Laboratory		RPD
303 R12	1/13/2012	1/12/2015	Control, Format and Review of Laboratory Logbooks		RPD
305 R11	5/6/2010	4/9/2014	Balance Calibration, Verification and Utilization	Reviewed by Bob and Liz 4-9-12	RPD
306 R5	4/11/2011	4/10/2014	The Use of Significant Figures and Rules For Rounding Numbers	Reviewed by Bob Di Rienzo 3/7/11	RPD
317 R11	4/11/2011	4/10/2014	Removing and Returning Equipment From Service	Reviewed by Bob Di Rienzo 3/7/11	RPD
318 R7	11/2/2012	11/2/2013	Chain-of-Custody	Reviewed 11/2/12 by L. Stroh	RPD
319 R10	12/12/2012	12/12/2015	Generation and Monitoring of Deionized (DI) Water		RPD
320 R10	3/8/2011	2/25/2015	Monitoring and Recording Oven Temperatures	Reviewed 2/25/13 by B. DiRienzo - no revision needed	RPD
321 R8	6/15/2011	6/14/2014	Calibration Verification of Pipettes and Dispensers		RPD
326 R11	10/16/2012	10/16/2015	Monitoring and Recording Refrigerator and Freezer Temperatures		RPD
329 R11	10/16/2012	10/16/2015	Method Demonstration Procedures: Instrument Detection Limit (IDL), Method Detection Limit (MDL), Detection Limit (DL), and Method and Analyst Demonstration of Capability (DOC)		RPD
334 R7	1/8/2013	1/8/2014	Glassware Cleaning Procedures and Maintenance of Glassware Used in The Organics and Inorganics Departments	Reviwed by T. Buettgenbach 1/8/2013	TLB
336 R0	12/26/2007	6/11/2014	Representative Laboratory Subsampling - Stable Chemistry	Reviewed on 5-15-12 by Bob - No Changes	RPD
337 R1	8/27/2012	8/27/2013	Organics Calibration Procedures -- Method 8000C	Reviewed 8/2012 by T Knaebel-no revision required	RPD
400-499 GC/HPLC and FUELS					
402 R14	4/10/2013	4/10/2014	Determination of Organochlorine Pesticides by Gas Chromatography - Methods SW8081A or B, and EPA 608	Reviewed by D Sheneman 4/10/2013	TWK

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406 R17	10/29/2012	10/29/2013	Extractable Petroleum Hydrocarbons Analysis by Gas Chromatography (TEPH, DRO)	Reviewed and Revised 10/29/12 J. Nolte	TWK
407 R10	8/27/2012	8/27/2013	ORGANOPHOSPHOROUS COMPOUNDS BY GAS CHROMATOGRAPHY -- METHODS SW8141A or B, AND EPA 614	Reviewed by D Sheneman 8/24-no revisions needed	TWK
409 R7	4/10/2013	4/10/2014	Analysis of Polychlorinated Biphenyls (PCBs) by Gas Chromatography -- Methods SW8082 and EPA 608	Reviewed by D Sheneman 4/10/2013	TWK
425 R16	5/3/2013	5/3/2014	Analysis of Total Volatile Petroleum Hydrocarbon (TVPH) Gasoline Range Organics (GRO) by Gas Chromatography -- Methods SW8015B, D and CAL-LUFT	Reviewed by J. Nolte 5/3/13 - no changes	TWK
434 R10	8/27/2012	8/27/2013	Analysis of Chlorinated Herbicides by Gas Chromatography - Methods SW 8151A, EPA 615 and EPA 515.1	Reviewed by D Sheneman 8/2012-no revisions required	TWK
444 R2	10/26/2012	10/26/2013	Extraction and Determination of Glycols by Gas Chromatography -- Method SW8015D	Reviewed by J. Nolte 10/25/12	TWK
449 R3	7/31/2012	7/31/2013	Determination of Dissolved Gases in Water Samples Using Gas Chromatography with Flame Ionization Detection	Change to calibration table 7/30/12	TWK
500-599 GCMS					
506 R19	1/10/2013	1/10/2014	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry - Method SW8270D	Reviewed by T. Knaebel 1/10/2013	TWK
511 R10	11/26/2012	11/26/2013	Volatiles Reagent Water Preparation and Blank Analysis	Reviewed by and revised T. Knaebel 11/8/12	TWK
512 R11	11/2/2012	11/2/2013	Refrigerator Blank Preparation and Analysis	Reviewed by T. Knaebel 11_08_12	TWK
525 R16	5/3/2013	5/3/2014	Determination of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry -- Methods SW8260 C and EPA 624		TWK
526 R8	4/2/2013	4/2/2014	Determination of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) -- Method 524.2	reviewed by T Knaebel 4/2/13	TWK
600-699 EXTRACTIONS					
603 R13	5/6/2013	5/6/2014	Extraction of Hydrocarbons From Soil and Water Samples		TLB
604 R9	11/2/2012	11/2/2013	Silica Gel Cleanup -- Method SW3630C	Reviewed 11/2/12 by P. Schleuter	TLB
607 R10	10/10/2012	10/10/2013	Extract Concentration Using Kuderna-Danish Apparatus	Reviewed by P. Schlueter 10/6/2012	TLB
608 R14	11/6/2012	11/6/2013	Method for Toxicity Characteristic Leaching Procedure (TCLP) Extraction of Wastes for the Analysis of Volatile Organic Compounds by Zero Headspace Extraction (ZHE) - Method SW1311		TLB
609 R14	1/14/2013	1/14/2014	Method for Toxicity Characteristic Leaching Procedure (TCLP) of Wastes and Soils For The Analysis of Metals and Semivolatile Organics - Method SW1311	Reviewed by B. Howard 1/14/2013	TLB
617 R14	5/3/2013	5/3/2014	Continuous Liquid/Liquid Extraction (CLE) -- Method SW3520C	Reviewed by T. Buettgenbach 5/3/13	TLB
620 R0	6/20/2012	6/20/2013	Microwave Extraction - Method SW3546		TLB
622 R8	11/2/2012	11/2/2013	Waste Dilution Extraction -- Method SW3580A	Reviewed and Revised 11/6/12 B. Howard	TLB

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625 R12	5/3/2013	5/3/2014	Soxhlet Extraction -- Method SW3540C	Reviewed by T. Buettgenbach 5/3/13	TLB
626 R11	5/6/2013	5/6/2014	Separatory Funnel Liquid-Liquid Extraction -- Method SW3510C	Edits on 5-6-13 by Bob Di Rienzo	TLB
629 R11	10/10/2012	10/10/2013	Determination of Ignitability by The Pensky-Martens Closed-Cup Tester -- Method SW1010A and ASTM93-80	Reviewed by P. Schlueter 10/6/12	TLB
634 R7	3/27/2013	3/27/2014	Sulfur Cleanup -- Method SW3660B	Reviewed by D. Sheneman 3/26/13	DMS
637 R10	11/9/2011	2/25/2014	Concentration and Solvent Exchange by The Nitrogen Blowdown Technique	Reviewed by T Buettgenbach 2-25-2013	TLB
640 R9	11/2/2012	11/2/2013	Extraction and Gravimetric Determination of Hexane Extractable Material in Solids -- Method SW9071B	Reviwed 11/2/12 by P. Schleuter - no changes	TLB
641 R9	9/10/2012	9/10/2013	Gel Permeation Chromatography (GPC) Cleanup -- Method SW3640A	Reviewed by T. Buettgenbach 9/2012	TLB
642 R9	9/10/2012	9/10/2013	Gravimetric Determination of Percent Moisture For Solid Matrices	Reviewed by T. Buettgenbach 9/2012	TLB
648 R8	11/2/2012	11/2/2013	Florisil Cleanup -- Method SW3620C	Reviewed 11/2/2012 B. Howard- no changes	TLB
651 R10	5/6/2013	5/6/2014	Sulfuric Acid Cleanup -- Method SW3665A	Reviewed by T. Buettgenbach 4/6/13	TLB
658 R9	10/10/2012	10/10/2013	Paint Filter Liquids Test -- Method SW9095B	Reviewed by B. Howard 10/8/12	TLB
663 R8	5/6/2013	5/6/2014	Monitoring TCLP Tumbler Revolutions and Room Temperature	Reviewed by B. Howard 4/5/13	TLB
664 R10	5/3/2013	5/3/2014	Extraction and Derivatization of Samples For Herbicide Analysis by Gas Chromatography -- Methods SW8151A, EPA 615 and EPA 515.1		TLB
666 R8	5/6/2013	5/6/2014	Waste Extraction Test (Cal-WET) For The Analysis of Metals and Semivolatile Organic Compounds	Reviewed by B Howard 4/5/2013	TLB
668 R5	11/9/2012	11/9/2013	Synthetic Precipitation Leaching Procedure (SPLP) For The Analysis of Metals and Semivolatile Organics -- Method SW1312	Reviewed11/2/2012 B. Howard	TLB
669 R6	11/9/2012	11/9/2013	Method for Synthetic Precipitation Leaching Procedure (SPLP) Extraction of Samples For The Analysis of Volatile Organic Compounds by Zero Headspace Extraction (ZHE) -- Method SW1312	Reviewed and revised 11/9/12 - B. Howard	TLB
670 R14	9/21/2012	9/21/2013	Analysis of Total Organic Carbon By Methods EPA 415.1, SW9060A, and SM5310 C	Reviewed by T. Buettgenbach 9/21/12 no revisions	TLB
671 R10	11/2/2012	11/2/2013	Determination of n-Hexane Extractable Material (HEM) and Silica Gel Treated Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry For Aqueous Samples -- Methods EPA 1664A and SW9070A	Reviewed 11/2/12 by P. Schleuter	TLB
672 R5	11/2/2012	11/2/2013	Extraction and Gravimetric Determination of Lipids in Tissues	Reviewed 11/2/12 by P. Schleuter	TLB
673 R3	10/10/2012	10/10/2013	Extraction of Polychlorinated Biphenyl Wipes Using Ultrasonic Bath Agitation	Reviwed by B. Howard 10/8/12	TLB
674 R1	4/10/2013	4/10/2014	Gravimetric Determination of Magnesium Oxide Reactivity	Reviewed 4/10/2013 by B. DiRienzo	EAL

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700-799 RADIOCHEMISTRY					
700 R13	10/15/2012	10/15/2013	Preparation of Environmental And Drinking Water Samples For Tritium Analysis -- Method EPA 906.0		JTL
701 R1	4/10/2013	4/10/2014	Determination of Ra-226 in Aqueous Matrix by Alpha Spectrometry	This SOP is not online for offering this analysis to clients as on 3-12-12	JTL
702 R20	10/16/2012	10/16/2013	Preparation of Gross Alpha and Gross Beta in Environmental Matrices -- EPA Method 900.0 and SW-846 Method 9310	Reviewed 10/15/12 J. Lee	JTL
703 R9	11/28/2012	11/28/2013	Sample Prescreening	Reviewed 11/27/12 by M. Clemmer	MBC
704 R10	5/6/2013	5/6/2014	Analysis of Tritium and Other Beta-Emitting Nuclides by Liquid Scintillation Counting -- Method EPA 906.0	Reviewed by J. Petrovic 4/3/12 - no changes	JTL
707 R12	5/6/2013	5/6/2014	Radiostrontium in Water, Soil, Filters, Vegetation and Hazardous Waste Samples		JTL
708 R9	4/19/2013	4/19/2014	Calculation of Radioanalytical Results	Reviewed by J Petrovic 4/18/13 - no changes	MBC
709 R7	11/28/2012	11/28/2013	Verification and Validation of Radioanalytical Software	Reviewed 11/27/12 by M. Clemmer	MBC
710 R1	10/12/2012	10/12/2013	Reagent and Standard Preparation for ReadioChemistry		TDE
711 R9	9/24/2012	9/24/2013	Preparation of Water and Solid Samples for the Analysis of Polonium-210 -- EML Procedure Po-01		TDE
712 R16	5/6/2013	5/6/2014	Determination of Total Alpha-Emitting Radium Isotopes in Drinking Water -- EPA Method 903.0 and SW9315		JTL
713 R12	9/10/2012	9/10/2013	Analysis of Gamma Emitting Radionuclides by Gamma Spectrometry -- Method EPA 901.1	Reviewed by M. Clemmer 9/2012	JCP
714 R12	4/5/2013	4/5/2014	Analysis of Alpha Emitting Radionuclides by Alpha Spectrometry	Reviewed 4/5/2013 by J. Petrovic	JCP
715 R16	10/15/2012	10/15/2013	Review of Radioanalytical Data	Reviewed 10/15/12 J. Petrovic no changes needed	JCP
724 R11	10/15/2012	10/15/2013	Analysis of Alpha and Beta Emitting Radionuclides by Gas Flow Proportional Counter -- EPA Method 900.0	Reviwed 10/15/12 J. Petrovic	JCP
726 R8	5/6/2013	5/6/2014	Determination of Lead -210 in Soils, Sediments, and Waters		JTL
733 R9	9/25/2012	9/25/2013	Checking the pH of Aqueous Samples in the Radiochemistry Department	Re-released with minor revisions - no rev # change	TDE
736 R1	10/12/2012	10/12/2013	Representative Laboratory Subsampling - Radiochemistry	Reviewed 6/10/2011 - no revision necessary	TDE
739 R11	11/26/2012	11/26/2013	Preparation of Samples for Analysis by Gamma Spectroscopy	Reviewed and Revised 11/2012 T. Elhart	TDE
748 R6	1/8/2013	1/8/2014	Preparation of Liquid and Solid Samples For The Analysis of Fe-55	Reviewed by T. Elhart 1/8/2013	TDE
749 R1	5/6/2013	5/6/2014	DETERMINATION OF RADIUM-228 VIA CHEMICAL SEPARATION OF RADIUM AND ACTINIUM.	Reviewed by J. Lee 4/5/13	JTL
751 R5	3/28/2013	3/28/2014	Actinides -- Americium/Curium Separation -- Purification by TRU and TEVA Spec Column		TDE
753 R5	4/22/2013	4/22/2014	Determination of Radioactive Iodine in Environmental Samples -- EPA Method 902.0		JTL

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754 R7	9/7/2012	9/7/2013	Preparation of Solid Samples For Tritium Analysis by Microwave Oven	Reviewed by J. Lee 9/7/12	JTL
755 R11	4/22/2013	4/22/2014	Determination of Technetium-99 in Solid and Water/Aqueous Samples		TDE
758 R4	8/2/2012	8/2/2013	Determination of Promethium-147 in Water	Reviewed by T. Elhart 8/12 - no changes	TDE
760 R8	1/8/2013	1/8/2014	Preparation of Solid Samples by Potassium Pyrosulfate Fusion	Reviewed by T. Elhart 1/8/2013	TDE
765 R6	1/8/2013	1/8/2014	Separation and Analysis of Neptunium-237 in Environmental Matrices	Reviewed by T. Elhart 1/8/2013	TDE
766 R8	3/27/2013	3/27/2014	Witnessing the Addition of Carriers, Tracers and Standards in Radiochemistry Samples	Reviewed by T. Elhart 3/26/13. No revision needed	TDE
767 R8	1/8/2013	1/8/2014	Sample Preparation: Filter Leaching	Reviewed by T. Elhart 1/8/2013	TDE
772 R6	10/16/2012	10/16/2013	Preparation of Water and Soil Samples for the Analysis of Carbon-14 Using Potassium Permanganate -- EPA EERF Method C-01	Reviewed J. Lee 10/15/12 no changes	JTL
773 R12	1/8/2013	1/8/2014	Total Dissolution of Solids for the Radiochemical Determination of Actinides and Other Non-Volatile Radionuclides	Reviewed by T. Elhart 1/8/2013	TDE
774 R3	5/6/2013	5/6/2014	Nickel 59, 63 in Water and Soil Samples Using Eichrom Nickel Resin	Reviewed by J. Lee 4/5/13	JTL
776 R14	3/29/2013	3/29/2014	Preparation of Water Samples for Actinides		TDE
777 R11	4/9/2012	5/30/2013	Actinides - Thorium, Americium and Plutonium Sequential Separation by Anion Exchange		TDE
778 R14	1/8/2013	1/8/2014	Actinides - Uranium, Plutonium, and Americium/Curium (Partial) Sequential Separation by Ion Exchange	Reviewed by T. Elhart 1/8/2013	TDE
783 R10	9/7/2012	9/7/2013	Radium-226 in Aqueous and Soil Matrices -- Radon Emanation Technique--Method EPA 903.1		JTL
785 R5	5/2/2013	5/2/2014	Total Activity in Environmental Matrices	Reviewed by J. Lee 5/2/13 - no changes	JTL
786 R6	5/2/2013	5/2/2014	Gross Alpha in Water by Coprecipitation Method -- SM7110C	reviewed by J. Lee 5/2/13 - no changes	JTL
791 R6	4/10/2013	4/10/2014	Preparation of Silica Gel Samples For Tritium Analysis	Reviewed 4/10/2013 by J. Lee	JTL
799 R4	10/15/2012	10/15/2013	Determination of Radon-222 in Water Samples by Liquid Scintillation Counting - SM 7500-Rn B and ASTM D5072-92	Reviwed 10/15/12 by J. Lee	JTL
800-899 METALS					
806 R15	4/22/2013	4/22/2014	Digestion of Waters, Soils and Wastes for Metals Analysis -- Methods SW3005A, SW3010A, SW3050B, EPA 200.2 and CLP SOW ILMO3.0 and ILMO4.0	Reviwed 4/22/13 by R. French - no changes	MTL
807 R13	9/7/2012	9/7/2013	Determination of Metals by Inductively Coupled Plasma Emission Spectroscopy - Method EPA 200.7 (Trace ICAP)	Reviewed by M. Lundgreen r 9/7/12	MTL
812 R15	10/10/2012	10/10/2013	Preparation and Determination of Mercury by Cold Vapor Atomic Absorption Spectroscopy -- Methods SW7470A, SW7471A, EPA 245.1	Reviewed by M. Lundgreen 10/2/12	MTL
827 R9	4/22/2013	4/22/2014	Determination of Elements by Inductively Coupled Plasma Mass Spectrometry -- Methods EPA 200.8 AND SW6020A	Reviewed 4/22/13 by R. French - no changes	MTL

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834 R8	9/7/2012	9/7/2013	Determination of Metals by Inductively Coupled Plasma Emission Spectroscopy -- Method SW6010B (Trace ICAP)	Reviewed by M. Lundgreen 9/7/2012	MTL
900-999 QUALITY ASSURANCE					
901 R10	3/13/2012	3/13/2015	Verification of Laboratory Weights		RPD
923 R12	12/11/2012	12/11/2014	Verification of Thermometers		RPD
926 R13	9/20/2012	9/20/2013	Controlled Document Management		RPD
927 R2	8/17/2012	8/17/2013	Preparation and Review of Standard Operating Procedures		RPD
928 R10	7/27/2012	7/27/2015	Non-Conformance and Corrective Action Procedures		RPD
937 R11	12/30/2011	12/29/2014	Internal Audits	See CE-QA001	RPD
939 R4	1/24/2010	12/13/2013	Manual Re-Integration Policy and Procedures	Reviewed bvy Bob 12/13/11	RPD
997 R0	6/10/2011	6/9/2014	Client Communication		RPD
998 R0	6/9/2011	6/8/2014	Estimation of Uncertainty of Analytical Measurements for Stable Chemistry		RPD
999 R0	6/7/2011	6/6/2014	Minimum Validation Protocol and Documentation Requirements for New and Modified Methods and Documentation Requirements for Project Specific Modified Testing Activities		RPD
1100-1199 WET CHEMISTRY					
1100 R11	8/31/2012	8/31/2013	Determination of Total Suspended Solids (TSS or Total Non-Filterable Residue) -- Methods EPA 160.2 and SM2540D	Reviewed by E. Lintner 8/12 no changes	EAL
1101 R11	8/31/2012	8/31/2013	Total Solids, Total Dissolved Solids (TDS or Total Filterable Residue), and Total Fixed and Volatile Solids -- Methods EPA 160.3, EPA 160.1, and EPA 160.4 and Methods SM2540B, SM2540C and SM2540E	Reviewed by E. Linter 8/2012 no changes	EAL
1104 R7	11/7/2012	11/7/2013	Potentiometric Determnation of (Simple) Fluoride in Water and Soil Using an Ion Selective Electrode -- Methods EPA 340.2, SW9214 and SM4500-F~C	Reviewed by E. Linter 11/6/12	EAL
1106 R10	8/31/2012	8/31/2013	Bicarbonate, Carbonate, Hydroxide, and Total Alkalinity by Titration -- Methods EPA 310.1 and SM2320B	Reviewed by E. Linter 8/2012 no changes	EAL
1110 R15	8/31/2012	8/31/2013	Determination of Total and Amenable Cyanide (Distillation) - - Methods SW9010C, SW9013, SW9014, EPA 335.1, EPA 335.2 and CLP Inorganic SOW (ILMO4.0); Determination of Weak and Dissociable Cyanide -- Method SM4500-CN I	Reviewed by E. Lintner 8/2012 - no changes	EAL
1112 R8	1/8/2013	1/8/2014	Determination of Reactive Cyanide and Sulfide -- EPA Method SW-846, Chapter 7	Reviewed and revised by E. Lintner 1/8/2013	EAL
1113 R12	8/31/2012	8/31/2013	Determination of Inorganic Anions by Ion Chromatography -- Methods EPA 300.0 and SW9056	Reviewed by E. Lintner 8/2012 - no changes	EAL
1117 R5	3/1/2013	3/1/2014	Total Organic Carbon in Soil by Rapid Dicromate Oxidation -- MSA Walkley-Black Method	Reviewed 3/1/13 by E. Lintner - no revision	EAL
1119 R7	11/7/2012	11/7/2013	Determination of Total Phosphorus and Ortho-Phosphate in Water -- Methods EPA 365.2 and SM4500-P B(5) and E	Reviewed by E. Lintner 11/6/12	EAL
1120 R7	8/31/2012	8/31/2013	Determination of Total Sulfides in Water -- Methods EPA 376.1 and SM4500-S2F	Reviewed by E. Lintner 8/2012 - no changes	EAL
1121 R8	8/31/2012	8/31/2013	Determination of Hexavalent Chromium in Solid Matrices Using Alkaline Digestion (Method SW3060A) and Analysis by Method SW7196A	Reviewed by E. Lintner 8/2012 - no changes	EAL

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1122 R7	12/5/2012	12/5/2013	Determination of Hexavalent Chromium by Methods SW7196A and SM3500-Cr-B	Reviewed 12/5/12 by E Lintner	EAL
1125 R5	3/18/2013	3/18/2014	Determination of Perchlorate in Water Using Ion Chromatography -- Methods EPA 314.0 and SW9058	Reviewed 3/4/2013 by E Lintner; no revision	EAL
1126 R18	8/31/2012	8/31/2013	Determination of pH by Electrometric Meaurement -- Methods EPA 150.1, SW9040C, SW9045D and SM4500-H+ B	Reviewed by E. Lintner 8/2012 - no changes	EAL
1127 R9	4/11/2013	4/11/2014	Determination of Nitrogen as Nitrate Plus Nitrite, Nitrite, and Nitrate in Environmental Water and Soil Samples Using a Colorimetric, Automated, Cadmium Reduction Procedure -- Methods EPA 353.2, SM4500-NO3-I, and Quikchem Method 10-107-04-1-C		EAL
1128 R10	8/31/2012	8/31/2013	Determination of Specific Conductance -- EPA Methods 120.1, SW9050A, and SM2510B	Reviewed by E Lintner 8/2012 - no changes	EAL
1129 R7	12/5/2012	12/5/2013	Determination of Ammonia Using An Automated Phenolate Procedure -- Methods EPA 350.1, SM4500 NH3-NH, and Quikchem Method 10-107-06-1-C	Reviewed 12/5/12 by E. Lintner	EAL
1130 R7	1/8/2013	1/8/2014	Determination of Nitrogen, Nitrite (as NO2-N) in Water And Soil by Colorimetric Spectrophotometric Determination -- EPA Method 354.1 and SM4500-NO2 -B	Reviewed by E. Lintner 1/8/2013	EAL
1132 R4	12/5/2012	12/5/2013	Sediment Load	Reviewed 12/5/12 by T. Elhart	EAL
1133 R5	8/31/2012	8/31/2013	Acidity by Titration - Methods EPA 305.1 and SM2310B	Reviewed by E. Lintner 8/2012 - no changes	EAL
1400-1499 INFORMATIONS SYSTEMS MANAGEMENT					
1400 R7	3/18/2010	3/29/2014	Process Software Validation	Reviewed with Marl/Kurt on 3-29-12	MSR
1401 R6	4/12/2011	4/11/2014	Computer and LIMS Backup and Restoration Protocols		MSR
1402 R7	3/18/2010	3/29/2014	Laboratory Information Management System (LIMS) Version Control	Reviewed with Mark/Kurt during internal audit 3-29-12	MSR
1403 R0	4/12/2011	3/29/2014	Change Control	Reviewed with Mark/Kurt during Internal Audit 3-29-12	MSR
MISC- ANNUAL DOCUMENTS/REFRESHERS					
2001 R1	9/28/2012	9/28/2014	ALS Safety Module 1 - Introduction	Contact Charles for Location of this training	CRO
2002 R1	10/31/2012	10/31/2014	ALS Safety Module 2 - General Health and Safety		CRO
2003 R1	12/31/2012	12/31/2014	ALS Safety Module 3 - Incident Management		CRO
2004 R1	2/28/2013	2/28/2015	ALS Safety Module 4 - Emergency Response		CRO
2005 R2	5/1/2013	5/1/2015	ALS Safety Module 5E - Exposure Control		CRO
2006 R0	3/26/2013	3/26/2014	ALS Safety Module 6 - Manual Handling		CRO
2007 R0	3/26/2013	3/26/2014	ALS Safety Module 7 - Vehicle Safety		CRO
2010 R0	3/26/2013	3/26/2014	ALS Safety Module 10 - Violence in the Workplace		CRO
2013 R0	3/26/2013	3/26/2014	ALS Safety Module 13 - Environmental Management		CRO
2014 R0	3/26/2013	3/26/2014	ALS Safety Module 14 - Hazardous Samples		CRO

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CE-GEN0	6/25/2012	6/25/2013	RECORDS MANAGEMENT POLICY	Corporate SOP - Idelis Williams	RPD
CEGEN00	7/27/2011	7/26/2014	Laboratory Ethics and Data Integrity	Corporate SOP - Idelis Williams	RPD
CEQA001	12/30/2011	12/29/2014	Internal Audits	Corporate Internal Audit Guidance	RPD
CHP R13	3/26/2013	3/26/2014	Chemical Hygiene Plan (CHP)	Reviewed by C. Orchard 3/25/13 - no revision needed	CRO
ECP R10	8/13/2012	8/13/2013	Emergency and Contingency Plan (ECP)	No Change from version 9	CRO
EX1 R0	12/29/2011	1/1/2015	ISO 17025:2005 General requirements for the competence of testing and calibration laboratories		RPD
EX2 R3	12/29/2011	12/1/2013	DOE QSAS Revision 2.6		RPD
EX3 R4	12/29/2011	12/1/2013	DoD QSM Version 4.2		RPD
EX4 R0	12/29/2011	12/1/2013	TNI Volume 1 Modules 1, 2, 4, 6		RPD
EX5 R0	12/29/2011	12/1/2013	Work Order Review Folders	QA Info Folder contains Reference Methods documents, Management Systems documents, and Safety & Health documents.	RPD
IQA R0	6/21/2011	5/15/2014	Initial Quality Assurance Orientation & Ethics and Data Integrity Training	SOP 143 Training No Chenges 5-15-12	RPD
LQAP R16	8/15/2012	8/15/2013	Laboratory Quality Assurance Plan (LQAP)		RPD
RESPP R	3/26/2013	3/26/2014	Respiratory Protection Plan (RESPP)	Reviewed by C. Orchard 4/25/13 - no revision needed	CRO
RPP R7	8/13/2012	8/13/2013	Radiation Protection Plan (RPP)	No Changes for Version 6	CRO
Vid1 R0	6/8/2011	6/7/2025	Video Safety Training - Planning For Safety in Laboratory Operations	Blue	CRO
Vid10 R0	6/8/2011	6/7/2025	Video Safety Training - Getting Organized - Laboratory Housekeeping	Blue	CRO
Vid11 R0	6/8/2011	6/7/2025	Video Safety Training - Fundamentals of Radiation Safety	Brown	CRO
Vid12 R0	6/8/2011	6/7/2025	Video Safety Training - Radiation Safety and Common Sense	Green	CRO
Vid13 R0	6/8/2011	6/7/2025	Video Safety Training - Using MSDS	Gray	CRO
Vid14 R0	6/8/2011	6/7/2025	Video Safety Training - Radiation Safety: I. Key to Contamination Control	White	CRO
Vid2 R0	6/8/2011	6/7/2025	Video Safety Training - Protecting the Air You Breathe: Hoods and Glove Boxes	Blue	CRO
Vid3 R0	6/8/2011	6/7/2025	Video Safety Training - Handle with care: Glassware in the Laboratory	Blue	CRO
Vid4 R0	6/8/2011	6/7/2025	Video Safety Training - Keep Your Eyes on Safety: Eye Protection in the Laboratory	Blue	CRO
Vid5 R0	6/8/2011	6/7/2025	Video Safety Training - A Place for Everything: Chemical Storage in the Laboratory	Blue	CRO
Vid6 R0	6/8/2011	6/7/2025	Video Safety Training - Safety: It's Your Responsibility - Basic Chemical Hygiene Practices	Blue	CRO
Vid7 R0	6/8/2011	6/7/2025	Video Safety Training - How Do You Feel? - Symptoms of Chemical Exposure	Blue	CRO
Vid8 R0	6/8/2011	6/7/2025	Video Safety Training - When Accidents Happen: Spills in the Laboratory	Blue	CRO

SOP	Active Date	Schedule Date	Title	Notes	Author
Vid9 R0	6/8/2011	6/7/2025	Video Safety Training - Think Twice! Hazardous Waste Disposal	Blue	CRO
WMP R9	8/13/2012	8/13/2013	Waste Management Plan (WMP)	No change from version 8	CRO

ALS Environmental Analytical Intruments List

Technology	ALS Instrument ID	Instrument Description	Manufacturer	Model	Serial Number
Location	Condition	Year Purchased	Methods	Software	Version
Alpha Spec					
Tower 1		Alpha Spectrometer (tower)	Ortec	Tower	N/A
RAD - Room 151	Good	1996	908,ASTM 3972,U-02,RESL/ID, EMSL/LV, 903,7500RaC	Alpha Vision	5.32.02
MCB#1		Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector
RAD - Room 151	Good	1996	908,ASTM 3972,U-02,RESL/ID, EMSL/LV, 903,7500RaC	Alpha Vision	5.32.02
MCB#2		Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector
RAD - Room 151	Good	1996	908,ASTM 3972,U-02,RESL/ID, EMSL/LV, 903,7500RaC	Alpha Vision	5.32.02
MCB#7		Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector
RAD - Room 151	Good	1996	908,ASTM 3972,U-02,RESL/ID, EMSL/LV, 903,7500RaC	Alpha Vision	5.32.02
MCB#4		Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector
RAD - Room 151	Good	1996	908,ASTM 3972,U-02,RESL/ID, EMSL/LV, 903,7500RaC	Alpha Vision	5.32.02
MCB#5		Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector
RAD - Room 151	Good	1996	908,ASTM 3972,U-02,RESL/ID, EMSL/LV, 903,7500RaC	Alpha Vision	5.32.02

ALS Environmental Analytical Intruments List

Technology

ALS Instrument ID	Instrument Description	Manufacturer	Model	Serial Number
Location	Condition	Year Purchased	Methods	Software	Version
MCB#6	Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector
RAD - Room 151	Good	1996	908,ASTM 3972,U-02,RESL/ID, EMSL/LV, 903,7500RaC	Alpha Vision	5.32.02
MCB#8	Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector
RAD - Room 151	Good	1996	908,ASTM 3972,U-02,RESL/ID, EMSL/LV, 903,7500RaC	Alpha Vision	5.32.02
Tower 2	Alpha Spectrometer (tower)	Ortec	Tower	N/A
RAD - Room 151	Good	1996	908,ASTM 3972,U-02,RESL/ID, EMSL/LV, 903,7500RaC	Alpha Vision	5.32.02
MCB#3	Alpha Spectrometer (octete)	Ortec	Ultra 600mm2	per detector
RAD - Room 151	Good	1996	908,ASTM 3972,U-02,RESL/ID, EMSL/LV, 903,7500RaC	Alpha Vision	5.32.02

Cleanup

GPC	GPC (Gel Permeation Cleanup) Apparatus	J2 Scientific	Accuvap	GPC-1017-1-DI
EXT - Room 134	Good	2009	3640	PrepLink	0.99.66.59

ALS Environmental Analytical Intruments List

Technology	ALS Instrument ID	Instrument Description	Manufacturer	Model	Serial Number
	Location	Condition	Year Purchased	Methods	Software	Version
CVAA						
	CETAC7500	Mercury Analyzer (Cold Vapor Atomic Absorption) w autosampler	CETAC	M7500	031001QTA
	Metals	Good	2010	7470,7471,EPA 245.1	Quicktrace	version 1.6.5
	CETAC	Mercury Analyzer (Cold Vapor Atomic Absorption) w autosampler	CETAC Technologies	M-6000A	079730AST
	Metals - Room 139	Good	2002	7470,7471,EPA 245.1	Cetac Hg Analyzer	Version 1.5.2

ALS Environmental Analytical Intruments List

ALS Instrument ID	Instrument Description	Manufacturer	Model	Serial Number
Location	Condition	Year Purchased	Methods	Software	Version

Technology

Gamma Spec

14	Gamma Spectrometer-14	Gamma Vision	6.09	05034922	
RAD - Room 151	Good	2004	901.1, Gamma Emitters	Seeker	version 2.2.2.3
13	Gamma Spectrometer-13	Gamma Vision	6.09	32-TP10869A	
RAD - Room 151	Good	2004	901.1, Gamma Emitters	Seeker	version 2.2.2.3
12	Gamma Spectrometer-12	Gamma Vision	6.09	32-TP40384A	
RAD - Room 151	Good	2004	901.1, Gamma Emitters	Seeker	version 2.2.2.3
15	Gamma Spectrometer-15	Gamma Vision	6.09	51-TP32763A	
RAD - Room 151	Good	2004	901.1, Gamma Emitters	Seeker	version 2.2.2.3
16	Gamma Spectrometer-16	Gamma Vision	6.09	51-TP12858A	
RAD - Room 173	Good	2004	901.1, Gamma Emitters	Seeker	version 2.2.2.3
#3	Gamma Spectrometer-6	EG&G Ortec	LS - 1116	26-P-396A	
RAD - Room 151	Good	1996	901.1, Gamma Emitters	Seeker	version 2.2.2.3
#9	Gamma Spectrometer-2	EG&G Ortec	LS - 1116	34-TP40551A	
RAD - Room 151	Good	1996	901.1, Gamma Emitters	Seeker	version 2.2.2.3
#7	Gamma Spectrometer-4	EG&G Ortec	LS - 1116	32-TP20722B	
RAD - Room 151	Good	1996	901.1, Gamma Emitters	Seeker	version 2.2.2.3

ALS Environmental Analytical Intruments List

ALS Instrument ID	Instrument Description	Manufacturer	Model	Serial Number
Technology				
Location	Condition	Year Purchased	Methods	Software	Version
#6	Gamma Spectrometer-3	EG&G Ortec	LS - 1116	32-TP20757A
RAD - Room 151	Good	1996	901.1, Gamma Emitters	Seeker	version 2.2.2.3
#4	Gamma Spectrometer-10	EG&G Ortec	LS - 1116	32-TP20736A
RAD - Room 151	Good	1996	901.1, Gamma Emitters	Seeker	version 2.2.2.3
#10	Gamma Spectrometer-9	EG&G Ortec	LS - 1116	32-TP10850A
RAD - Room 151	Good	1996	901.1, Gamma Emitters	Seeker	version 2.2.2.3
#2	Gamma Spectrometer-7	EG&G Ortec	LS - 1116	32-TN10858B
RAD - Room 151	Good	1996	901.1, Gamma Emitters	Seeker	version 2.2.2.3
#1	Gamma Spectrometer-8	EG&G Ortec	LS - 1116	32-TN10861B
RAD - Room 151	Good	1996	901.1, Gamma Emitters	Seeker	version 2.2.2.3
#5	Gamma Spectrometer-5	EG&G Ortec	LS - 1116	34-TP40551A
RAD - Room 151	Good	1996	901.1, Gamma Emitters	Seeker	version 2.2.2.3
#8	Gamma Spectrometer-1	EG&G Ortec	LS - 1116	26-PJ96A
RAD - Room 151	Good	1996	901.1, Gamma Emitters	Seeker	version 2.2.2.3
	Gamma Spectrometer-11	EG&G Ortec	LS - 1116	32-TP20875A
RAD - Room 173	Good	1996	901.1, Gamma Emitters	Seeker	version 2.2.2.3

ALS Environmental Analytical Intruments List

Technology / ALS Instrument ID	Instrument Description	Manufacturer	Model	Serial Number
Location	Condition	Year Purchased	Methods	Software	Version
GC					
GC#5	Gas Chromatograph (Dual FPD)	Hewlett Packard	5890 Series II	3033A32550
GC - Room 132	Good	unk	8141, EPA 614	EZ Chrom Elite	version 3.3.2
GC#10	Gas Chromatograph (Dual ECD)	Agilent	7890A(G3440A)	11171045
GC Room 132	Good	2011	8081, 608	EZ Chrom Elite	version 3.2.1
GC#11	Gas Chromatograph (Dual ECD)	Agilent	7890A (G3440A)	11171043
GC-Room 132	Good	2011	8082, EPA 608	EZ Chrom Elite	version 3.3.2
GC#9	Gas Chromatograph (FID)	Hewlett Packard	5890A	2750A19027
GC - Room 135	Good	1996	RSK-175, 8015 methanol	EZ Chrom Elite	version 3.2.1
Fuels 3	Gas Chromatograph (FID)	Hewlett Packard	5890A	3121A35609
Fuels - Room 135	Good	1996	8015-DRO	Enviroquant G1045	Version A.00.00
ECD4	Gas Chromatograph (Dual ECD)	Hewlett Packard	5890 Series II	3310A47805
GC - Room 132	Good	1996	8151, EPA 615	EZ Chrom Elite	version 3.3.2
GC6	Gas Chromatograph (PID/FID)	Hewlett Packard	5890	2443A03716
Fuels - Room 135	Good	1996	8015 GRO	EZ Chrom Elite	version 3.3.2
GC7	Gas Chromatograph (FID)	Hewlett Packard	5890	2750A18840
Fuels - Room 135	Good	1996	8015 Glycols, 8015 DRO	ChemStation	B.02.04

ALS Environmental Analytical Intruments List

Technology					
ALS Instrument ID	**Instrument Description**		**Manufacturer**	**Model**	**Serial Number**
Location	**Condition**	**Year Purchased**	**Methods**	**Software**	**Version**
ECD1	Gas Chromatograph (Dual ECD)		Hewlett Packard	5890 Series II	3310A49739
GC - Room 132	Good	1996	8082, screening instrument	EZ Chrom Elite	version 3.3.2

ALS Environmental Analytical Intruments List

Technology	ALS Instrument ID	Instrument Description	Manufacturer	Model	Serial Number
Location	Condition	Year Purchased	Methods	Software	Version
GC/MS					
HPSV4		Gas Chromatograph (MS)	Agilent	7890A/5975C	CN11541177 and US11423931
Semi Volatiles Laboratory	Good	2012	8270D	Chemstation	E02.02.1431
HPV 2		OI Purge and Trap - Agilent GC/MS	OI/Agilent	Archon, 5971	13833, 3188A03493
VOAs - Room 201	Good	2003, 1996	8260C, 524.2.624	EnviroQuant ChemStation	B01.00
HPV 4		Teckmar P&T and Gas Chromatograph (MS)	Hewlett Packard	6890/5973	US10226006
VOAs - Room 201	Good	2003	8260, 524.2, 624	MSD Chem Station	Version D.03.00.611
TOC1		Total Organic Carbon (TOC) Analyzer & Autosampler	Tekmar - Dohrmann	14 - 7045 - 000	01011007
TOC - Room 131	Good	2002	415.1	NA	
#1		Gas Chromatograph (MS)	Hewlett Packard	6890	US00040094
SVOCs - Room 144	Good	2001	8270	HPChemStation	B.01.00
#3		Gas Chromatograph (MS)	Hewlett Packard	6890	US00031554
SVOCs - Room 144	Good	1996	8270	HPChemStation	B.02.05
#2		Detector, Gas Chromatograph (MS)	Hewlett Packard	5973	US91911895
SVOCs - Room 144	Good	1996	8270	EnviroQuant Chem Station	B.01.00

ALS Environmental Analytical Intruments List

Technology

ALS Instrument ID	Instrument Description	Manufacturer	Model	Serial Number
Location	Condition	Year Purchased	Methods	Software	Version
HPV 4	Teckmar P&T and Gas Chromatograph (MS)	Hewlett Packard	5890 Series II	3019A28661
VOAs - Room 201	Good	1996	8260, EPA 524.2, EPA 624	MSD Chem Station	Version D.03.00.611

GPC

WPC1050	Gas Flow Proportional Counter	Protean	WPC 1050	12152125
Rad Chem - Prescreen Lab	Good	2012		Oxford	1.01,1.10,1.11
C	Gas Flow Proportional Counter	Canberra	LB - 4110	2268
RAD - Room 151	Good	2008	Sr-01/02/04,ASTMD5811-00, 900, 903,903.1,9310,9315	Oxford	1.01,1.10,1.11
A	Gas Flow Proportional Counter	Canberra	LB - 4110	CR (13923)
RAD - Room 151	Good	1996	Sr-01/02/04,ASTMD5811-00, 900, 903,903.1,9310,9315	Oxford	1.01,1.10,1.11
B	Gas Flow Proportional Counter	Canberra	LB - 4110	43727
RAD - Room 151	Good	1996	Sr-01/02/04,ASTMD5811-00, 900, 903,903.1,9310,9315	Oxford	1.01,1.10,1.11
LB5100A	Gas Flow Proportional Counter	Tennelec	LB - 5100	13923 (A)
RAD - Room 173	Good	1996	Sr-01/02/04,ASTMD5811-00, 900, 903,903.1,9310,9315	Oxford	1.01,1.10,1.11

ALS Environmental Analytical Intruments List

Technology / ALS Instrument ID	Instrument Description	Manufacturer	Model	Serial Number
Location	Condition	Year Purchased	Methods	Software / Version
HPLC				
HPLC 4	High Performance Liquid Chromatograph UV	HP	1050	33172802213
HPLC - Room 135	Good	2004	8330	
IC				
IC2	Ion Chromatograph (IC) - Perchlorate Analysis	Dionex	DX - 120	98070245
Wet Chem	Good	2000	314.0, 9058	Dionex Peaknet version 5.1
IC	Ion Chromatograph (IC) - Anions Analysis	Dionex	DX - 120	99060762
Wet Chem	Good	1999	300.0, 9056	Dionex Peaknet version 5.1
ICP				
ICP6500	Fully Automated, Computer Controlled, Dual View, ICP-AES	Thermo-Electron	ICP 6500 Duo	20101507
Metals - Room 138	Good	2013	6010, 200.7	iTeva 9.8
ICPTrace2	Inductively Coupled Plasma (ICP) - axial (trace)	Thermo Jarrell Ash	1342900	338590
Metals - Room 138	Good	2006	6010, 200.7	ICP Manager Version 2.0.0.800
ICPMS				
ICPMS2	Inductively Coupled Plasma (ICP)/MS	Agilent	7700 Series	JP09400112
Metals-Room 138	Good	2010	6020, 200.8	Masshunter B.01.01

ALS Environmental Analytical Intruments List

Technology / ALS Instrument ID	Instrument Description	Manufacturer	Model	Serial Number
Location	Condition	Year Purchased	Methods	Software / Version
LSC				
TRICARB	Liquid Scintillation Counter	Packard	2700TR	406415
RAD - Room 132	Good	2004	906.0, ASTM D5072,ASTM C1387-98, SM 7500 Rn-B	TriCarb 2700 TR
Q1220	Liquid Scintillation Counter	Wallac	1220	2200205
RAD - Room 151	Good	2003	906.0, ASTM D5072,ASTM C1387-98, SM 7500 Rn-B	WinQ version 1.2
6500	Liquid Scintillation Counter	Beckman	LS 6500	7068426
RAD - Room 131	Good	1997	906.0, ASTM D5072,ASTM C1387-98, SM 7500 Rn-B	LS6000 Data Ca version 2.11
6000	Liquid Scintillation Counter	Beckman	LS 6000TA	598860
RAD - Room 131	Good	1996	906.0, ASTM D5072,ASTM C1387-98, SM 7500 Rn-B	LS6000 Data Capture version 2.11
Physical				
	Ignitability Apparatus	Pensky Martens	K16200	R07002896B
Organics - Extractions	Good	2012		

ALS Environmental Analytical Intruments List

Technology / ALS Instrument ID	Instrument Description	Manufacturer	Model	Serial Number
Location	Condition	Year Purchased	Methods	Software	Version
UV/VIS					
Lachat	Flow Injection Analyzer (Automated NO2/NO3, NH3)	Lachat	QuickChem 8000	A83000 - 642
Wet Chem	Good	2000	350.1,353.2	Omnion FIA	version 1.3
Spec	UV Spectrophotometer	Sequoia - Turner	Model 340	905970923742
Wet Chem	Good	1997	7196	NA	
Wet Chem					
	Meter, Conductivity	VWR Scientific	23226 - 523	A22036
Wet Chem	Good	1997		NA	
	Meter, pH	Fischer Scientific	50	C0000643
Wet Chem	Good	1996		NA	
	Meter, pH	Corning	320	C5961
Wet Chem	Good	1996		NA	

Quality Manual

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Effective Date: 02/20/2014

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Laboratory Director John R. Kern	Date
Quality Manager Michael Desmarais	Date
Technical Director Kirby L. Gray	Date
Technical Director Nan S. Wilson	Date
Systems Manager Brandan Borgias	Date
Supervisor Inorganic Instrument Department Danny Sevy	Date
Supervisor Classical Chemistry Department Dianne Gardner	Date
Supervisor ABA Department Heather Green	Date

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1.0 QUALITY POLICY STATEMENT

SVL Analytical, Inc. (SVL) recognizes that an effective quality system is paramount to providing analytical data that is scientifically meaningful, legally defensible, technically accurate, and based upon the highest ethical standards. To reinforce the above objectives, SVL has committed itself to follow and be in compliance with the 2009 TNI Standards.

The emphasis of SVL's Quality Manual (QM) is to define control procedures for receipt, handling, and storage of samples; preparation and storage of standards; calibration and maintenance of analytical equipment; performance of analytical methods; customer service; and the generation, review, and reporting of analytical data.

At SVL, quality assurance begins with the definition of Data Quality Objectives (DQO) and continues on through data reporting. Control procedures are defined for every step of the program as detailed in SVL's Standard Operating Procedures (SOPs). SVL realizes that without these controls in all phases of the analytical process, data may become suspect and hence of less value to our clients. Therefore, SVL is committed to providing data of the highest quality, usability, and defensibility for every project undertaken. SVL personnel concerned with any aspect of environmental testing are required to familiarize themselves with all quality documentation (including this manual) used at SVL and they are required to comply with all policies and procedures outlined therein.

SVL's Technical Management and Quality Manager ensure that this QM complies with all applicable TNI Quality System Standards and sees that it is reviewed annually and revised as needed. Evidence of signatory approval by senior management of this QM and SVL SOPs are available in PDF format by request.

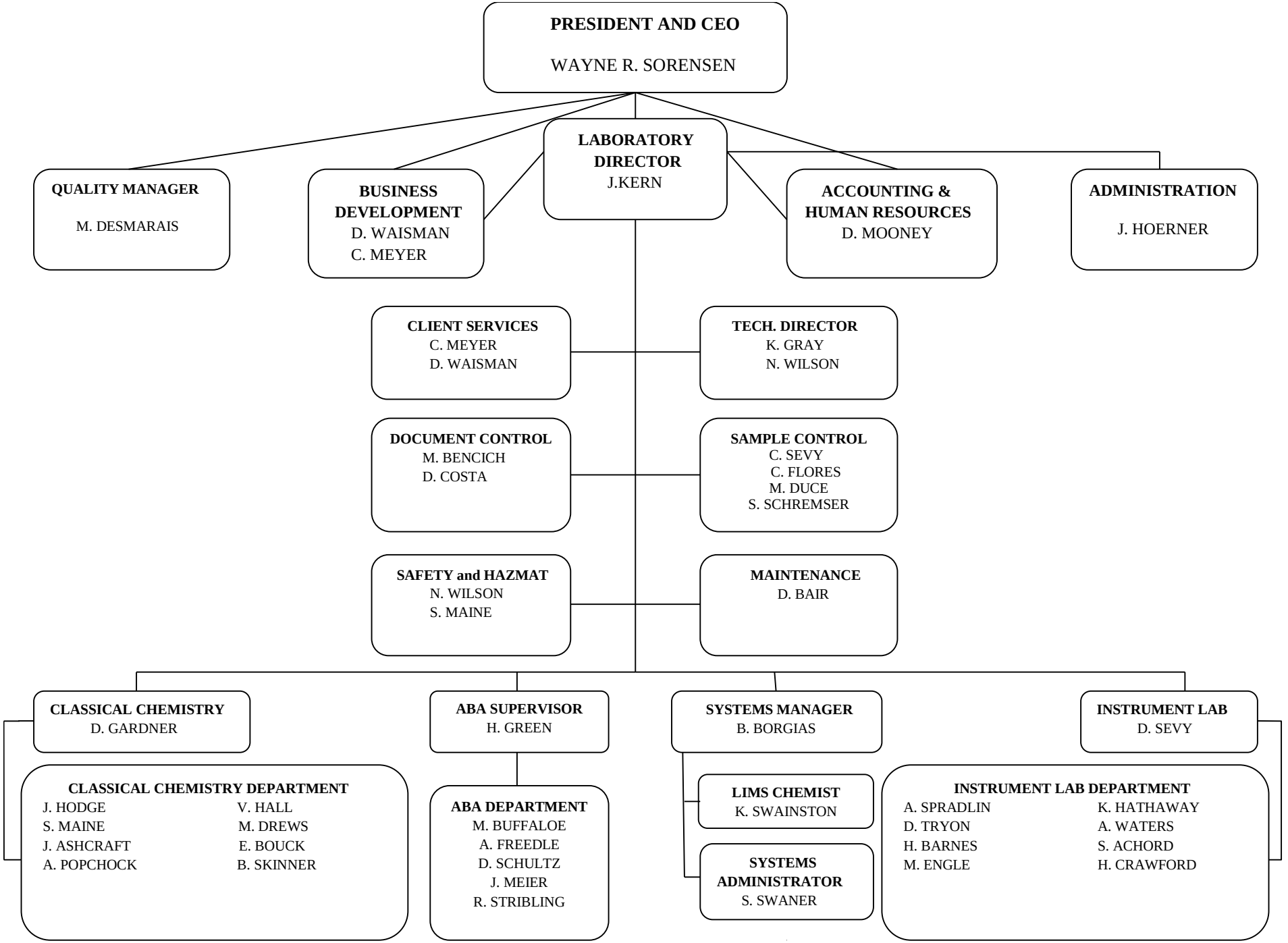
SVL's commitment to client confidentiality (including national security concerns) and their proprietary rights is paramount to all operations conducted within its quality system; as such, a signed confidentiality statement is maintained in each employees personnel file.

After reading this document employees are required to sign a signature page. By signing, the employee confirms that they have read, understood, and will comply with the Quality Manual and the TNI Standards it is based upon.

2.0 ORGANIZATION AND STRUCTURE

The organizational structure of SVL follows a traditional scheme of management with a few modifications. The President/CEO is at the top of the chain of command followed immediately by the Laboratory Director, Quality Manager, Business Development and Accounting/Human Resources. The following supervisors/departments are managed under the Laboratory Director: Business Development, Accounting/Human Resources, Administration, Maintenance, Technical Directors, Document Control Office, Client Services, Safety and HAZMAT, Classical Chemistry, ABA, Instrument Lab and Systems Manager. The Systems Administrator and LIMS Chemist report to the Systems Manager. The Classical Department reports to the Classical Department Supervisor. The Instrument Lab Department reports to the Instrument Lab Department Supervisor. The ABA, Alkalinity and TDS labs report to the ABA Department Supervisor.

2.1 Organization Chart


PRESIDENT AND CEO
WAYNE R. SORENSEN
QUALITY MANAGER
M. DESMARAIS
BUSINESS DEVELOPMENT
D. WAISMAN
C. MEYER
LABORATORY DIRECTOR
J.KERN
ACCOUNTING & HUMAN RESOURCES
D. MOONEY
ADMINISTRATION
J. HOERNER
CLIENT SERVICES
C. MEYER
D. WAISMAN
TECH. DIRECTOR
K. GRAY
N. WILSON
DOCUMENT CONTROL
M. BENCICH
D. COSTA
SAMPLE CONTROL
C. SEVY
C. FLORES
M. DUCE
S. SCHREMSER
SAFETY and HAZMAT
N. WILSON
S. MAINE
MAINTENANCE
D. BAIR
CLASSICAL CHEMISTRY
D. GARDNER
ABA SUPERVISOR
H. GREEN
SYSTEMS MANAGER
B. BORGIAS
INSTRUMENT LAB
D. SEVY
CLASSICAL CHEMISTRY DEPARTMENT
J. HODGE
S. MAINE
J. ASHCRAFT
A. POPCHOCK
V. HALL
M. DREWS
E. BOUCK
B. SKINNER
ABA DEPARTMENT
M. BUFFALOE
A. FREEDLE
D. SCHULTZ
J. MEIER
R. STRIBLING
LIMS CHEMIST
K. SWAINSTON
SYSTEMS ADMINISTRATOR
S. SWANER
INSTRUMENT LAB DEPARTMENT
A. SPRADLIN
D. TRYON
H. BARNES
M. ENGLE
K. HATHAWAY
A. WATERS
S. ACHORD
H. CRAWFORD

2.2 Employee List

Position	Employee	Degree	Years of Lab Experience
President and CEO	Wayne Sorensen	BS 1962	46
Laboratory Director	John R. Kern	MS 1982	30
Systems Manager	Brandan A. Borgias	PhD 1985	32
Document Control Officer	Melba Bencich		32
Client Services Manager	Christine Meyer		34
Business Development Manager	Dave Waisman	MS 1985	19
Technical Director	Kirby L. Gray	BS 1972	30
Technical Director/Safety Officer	Nan S. Wilson	BS 1996	17
Supervisor Inorganic Instrument	Danny Sevy		27
Supervisor Classical Chemistry	Dianne Gardner	BA 1987	9
Supervisor ABA	Heather Green	BS 2009	5
Systems Administrator	Scott Swaner		10
LIMS Chemist	Kale Swainston	BS 1998	15
Accounting and Human Resources	Donella Mooney		22
Quality Manager	Michael Desmarais	BS 1995	16
ICP Spectroscopist	Anne Spradlin	BA 1983	27
ICP Chemist	Matt Engle	MS 2012	1
ICP Analyst	David Tryon		9
ICP-MS and GFAA Analyst	Kevin Hathaway		27
IC Chemist	Andrew Waters	BS 2005	9
CVAA Chemist	Sam Achord	BS 2009	2
Analyst	Heather Crawford		4
Analyst	Heidi Barnes		10
Chemist	Jim Hodge		46
Chemist	Victoria Hall	BS 2013	<1
Chemist/HAZMAT Coordinator	Sherry Maine	MS 2004	12
Chemist	Matthew Drews	BS 2011	1
Chemist	Andrew Popchock	BS 2011	3
Chemist	Mikel Buffaloe	BS 2013	1
Analyst	Anita Guzman-Freedle	BS 1979	5
Analyst	Eric Bouck		5
Analyst	Debbie Schultz		11
Analyst	Robin Stribling		7
Analyst	Jerry Meier		3
Analyst	Judy Ashcraft		42
Analyst	Ben Skinner		<1
Sample Control Officer	Crystal Sevy		10
Sample Receiving	Cindy Flores		11
Sample Receiving	Mark Duce		2
Sample Receiving	Shelley Schremser		<1
Document Control	Dianne Costa		6
Maintenance	Dan Bair		6
Receptionist	Jena Hoerner		<1

2.3 Key Employee Resumes

See Appendix 1

3.0 JOB DESCRIPTIONS

3.1 Laboratory Director

The Laboratory Director supervises day-to-day operations of the laboratory. Responsible for monitoring standards of performance in quality control and quality assurance, and for monitoring the validity of the analyses performed and data generated in the laboratory. The Laboratory Director holds a weekly staff meeting to discuss client and technical issues.

3.2 Systems Manager

The Systems Manager supervises operations of the Information Technology groups. The Systems Manager uses Excel, Crystal Reports, and other software to develop and maintain client reports and electronic data deliverables (EDDs). Element is the Laboratory's Information Management System (LIMS) and the Systems Manager works with the LIMS Chemist to make sure that Element meets the needs of SVL.

3.3 Department Supervisor

Department supervisors conduct the day-to-day operations of our analytical departments. They are responsible for department safety and analyst training. They are also responsible for review of out-going analytical data.

3.4 Quality Manager

The Quality Manager is responsible for implementation of the quality system. The Quality Manager manages the performance testing program and conducts laboratory audits. The Quality Manager obtains and maintains laboratory accreditations, reviews and approves SOPs, conducts staff training in integrity and quality systems, and manages the CAR/PAR program. The Quality Manager is a TNI member.

3.5 Document Control Officer (DCO)

DCO is responsible for the generation and the retention of analytical reports and records, including but not limited to Chains-of-Custody and

sample shipping documents. DCO is also responsible for delivering electronic data deliverables.

3.6 Sample Control Officer (SCO)

SCO is responsible for sample receipt, job creation/verification, sample storage, and sample disposal.

3.7 Technical Director

Technical Directors provide technical support to laboratory staff and provide final reviews of analytical data packages. Other responsibilities include Level III reporting.

3.8 Safety

Safety Officer is responsible for revising the Chemical Hygiene Plan annually, conducts safety training and oversees response teams. Other duties include providing accident reports to the state.

3.9 Hazmat Officer

Hazmat Officer is responsible for overseeing SVL's hazardous waste program (including setting up 8-hour refresher courses annually).

4.0 APPROVED LABORATORY SIGNATORIES

The Laboratory Director John Kern, Systems Manager Brandan Borgias, Technical Directors Kirby Gray and Nan Wilson have full authority. Department Supervisors Dianne Gardner, Heather Green and Danny Sevy are approved laboratory signatories for analytical reports. LIMS Chemist Kale Swainston, DCO Melba Bencich and Quality Manager Michael Desmarais have report generation privileges.

5.0 RECORDS AND DOCUMENT CONTROL

All records and documents are kept for 5 years unless otherwise specified by client contract. Electronic instrument data and LIMS data are kept for 10 years.

5.1 Standard Operating Procedures (SOPs)

The Quality Manager retains the master copies of SOPs. Electronic copies are available on the laboratory's computer network. Signed and

dated SOPs are available by request in PDF format. All SOPs are scheduled for review each year. Electronic copies are available on the laboratory network on the date of the Quality Manager's final review. The SOP's effective date is two weeks after the date the Quality Manger signs the controlled copy. When a revision is created, the previous version is removed from the master file and electronic database. The retired controlled copy is retained in the SOP archive file.

5.2 Quality Manual (QM)

The Quality Manager retains the controlled copy of the QM. The QM is scheduled for review annually or when revisions are needed. Management may make hard copies available to accrediting authorities, laboratory staff and clients as needed; otherwise, the QM is available in electronic format. A signed and dated QM is available by request in PDF format. When a revision is created, copies are sent out to our accrediting bodies and previous versions are removed from use. The retired controlled copy is retained in the QM archive file.

5.3 Analytical Data

The DCO retains analytical data, including calibration records and quality control. Documents are secured in storage containers.

5.4 Training Records

The Quality Manager maintains records of analyst training and proficiency; ref, SOP SVL 1010. Documents are secured in storage containers.

5.5 Performance Testing Samples

The Quality Manager maintains records of analysis of performance testing samples and the reports associated with the analyses. Reports are stored in Quality Managers office.

5.6 External and Internal Audits

The Quality Manager retains records of external and internal audits. Reports are stored in Quality Managers office.

5.7 Corrective Action Reports (CARs)

CARs are kept electronically and filed by hardcopy. CARs are stored in Quality Managers office.

5.8 Laboratory Logbooks

SVL controls the issue, use, and closure of laboratory logbooks. The process is described in SOP SVL 2017. Examples of logbooks may include: the conductivity of laboratory water, preparation of reagents and standards, preparation of samples, calibration of balances, calibration of micropipets, volumetric pipets and repipettors, maintenance of instruments, temperatures of ovens and refrigerators, etc. The Quality Manager assigns and archives logbooks. Documents are secured in storage containers.

5.9 Chain of Custody (COC)

The DCO is in charge of COC retention; they are currently held for five years, unless a longer time is required by contract. Sample log-in and job creation are maintained in SVL's LIMS. COCs and sample receiving check-in sheet are scanned into PDF format, which can be accessed through Element. Documents are secured in storage containers.

5.10 Analytical Reports

The DCO creates and retains both hardcopies and PDFs of analytical reports. Electronic files are backed up and archived for ten years and hardcopy for five years as described in SVL 2021. Both types of analytical reports are stored in secured storage containers to protect them from damage.

5.11 Backup and Storage of Electronic Data

5.11.1 Electronic Data Collection: Currently the backup server is protected with an administrative password, which is changed every 6 months; it is in control of the Systems Administrator; ref, SOPs SVL 2020 and 2021.

5.11.2 Archives of Electronic Data: Data files that reside on the SVL file servers are backed up on a daily basis and kept onsite for 90 days: a full backup of the data files residing on the server is done monthly and sent to an offsite storage facility for 10 years (longer if required by contract). All software used to recover data files is also stored at the offsite facility for the same time frame.

5.11.3 Backup Storage: A secure fire-proof safe is maintained inside SVL to house the electronic data collected via the current backup system.

6.0 TRACEABILITY OF MEASUREMENTS

6.1 Chemicals and Reagents

SVL uses reagent grade or better chemicals. Some equivalent grades are "VWR Omni-Trace", "Fisher Trace Metals", "Baker Instra-Analyzed", "Baker A.C.S.", "Baker Analyzed", "Fisher A.C.S.", and "Fisher Certified". SVL requires a certificate of analysis or purity (certificates are scanned and attached to Element), for stock standards and reagents. Upon receipt, all chemical containers are labeled and entered into SVL's LIMS.

SVL records the preparation of reagents and standards in controlled logbooks or electronically in the LIMS. The initials of the preparer, the date prepared, the lot number and amount of stock materials, the final volume, the matrix, and the expiration date are all recorded. A label is created within the LIMS with unique identifiers attached to all aliquots of the reagent/standard.

Preparation instructions are included in the SOPs for standards and reagents used in the analytical methods. SVL labels containers of prepared reagents and standards with their contents, a unique reference number, date prepared, disposal (expiration) date and a perceived hazard warning. Every aliquot is assigned a unique identifier.

SVL routinely obtains reference standards from commercial sources. These standards are used to check and document the concentration of calibration standards and validate method QC requirements.

SVL stores reagents and standards separately from samples.

6.2 Water

The primary reagent water in the laboratory is furnished by a reverse osmosis system followed by a micropore filter with an ion-exchange resin cartridge. This satisfies the specifications of ASTM Type II water. When Type I (18 MΩ-cm) water is required, SVL inserts a four-cartridge ion-exchange system or a Millipore Synergy UVR into the line. SVL measures and records the resistivity of the laboratory water each weekday.

7.0 TEST METHODS

7.1 Analyses Performed by SVL

SVL routinely performs the following analytical methods.

ANALYTE	METHOD	TECHNIQUE
Aluminum	EPA 200.7, SW846 6010B&C	ICP
Antimony	EPA 200.7, SW846 6010B&C	ICP
Antimony	EPA 200.8, SW846 6020&A	ICPMS
Arsenic	EPA 200.7, SW846 6010B&C	ICP
Arsenic	EPA 200.8, SW846 6020&A	ICPMS
Barium	EPA 200.7, SW846 6010B&C	ICP
Barium	EPA 200.8, SW846 6020&A	ICPMS
Beryllium	EPA 200.7, SW846 6010B&C	ICP
Beryllium	EPA 200.8, SW846 6020&A	ICPMS
Boron	EPA 200.7, SW846 6010B&C	ICP
Boron	EPA 200.8, SW846 6020&A	ICPMS
Cadmium	EPA 200.7, SW846 6010B&C	ICP
Cadmium	EPA 200.8, SW846 6020&A	ICPMS
Calcium	EPA 200.7, SW846 6010B&C	ICP
Chromium	EPA 200.7, SW846 6010B&C	ICP
Chromium	EPA 200.8, SW846 6020&A	ICPMS
Chromium, Hexavalent	SM 3500 CR B&D	Colorimetry
Cobalt	EPA 200.7, SW846 6010B&C	ICP
Cobalt	EPA 200.8, SW846 6020&A	ICPMS
Copper	EPA 200.7, SW846 6010B&C	ICP
Copper	EPA 200.8, SW846 6020&A	ICPMS
Gallium	EPA 200.7, SW846 6010B&C	ICP
Gold	EPA 231.2	GFAA
Iron	EPA 200.7, SW846 6010B&C	ICP
Lanthanum	EPA 200.7, SW846 6010B&C	ICP
Lead	EPA 200.7, SW846 6010B&C	ICP
Lead	EPA 200.8, SW846 6020&A	ICPMS
Lithium	EPA 200.7, SW846 6010B&C	ICP
Magnesium	EPA 200.7, SW846 6010B&C	ICP
Manganese	EPA 200.7, SW846 6010B&C	ICP
Manganese	EPA 200.8, SW846 6020&A	ICPMS
Mercury	EPA 245.1, SW846 7470A, 7471B	CVAA
Molybdenum	EPA 200.7, SW846 6010B&C	ICP
Molybdenum	EPA 200.8, SW846 6020&A	ICPMS
Nickel	EPA 200.7, SW846 6010B&C	ICP
Nickel	EPA 200.8, SW846 6020&A	ICPMS
Potassium	EPA 200.7, SW846 6010B&C	ICP
Scandium	EPA 200.7, SW846 6010B&C	ICP
Selenium	SM 3114C	Hydride AA
Selenium	EPA 200.7, SW846 6010B&C	ICP
Selenium	EPA 200.8, SW846 6020&A	ICPMS
Silica	EPA 200.7	ICP
Silicon	SW846 6010B&C	ICP
Silver	EPA 200.7, SW846 6010B&C	ICP
Silver	EPA 200.8, SW846 6020&A	ICPMS
Sodium	EPA 200.7, SW846 6010B&C	ICP
Strontium	EPA 200.7, SW846 6010B&C	ICP

ANALYTE	METHOD	TECHNIQUE
Thallium	EPA 200.7, SW846 6010B&C	ICP
Thallium	EPA 200.8, SW846 6020&A	ICPMS
Tin	EPA 200.7, SW846 6010B&C	ICP
Titanium	EPA 200.7, SW846 6010B&C	ICP
Uranium	EPA 200.8	ICPMS
Vanadium	EPA 200.7, SW846 6010B&C	ICP
Vanadium	EPA 200.8, SW846 6020&A	ICPMS
Zinc	EPA 200.7, SW846 6010B&C	ICP
Zinc	EPA 200.8, SW846 6020&A	ICPMS
Acidity	SM 2310 B	Automated Titration
Alkalinity	SM 2320 B	Automated Titration
Ammonia	EPA 350.1	Automated Colorimetry
Bromide	EPA 300.0	Ion Chromatography
Chemical Oxygen Demand	EPA 410.4	Colorimetry
Chloride	EPA 300.0	Ion Chromatography
Color	SM 2120 B	Colorimetry
Conductivity	EPA 120.1	Wheatstone Bridge
Corrosivity	SM 2330 B	Langelier Index
Cyanide, Total	EPA 335.4, SW 846 9012 B	Automated Colorimetry
Cyanide, Free	ASTM D-7237-10	Amperometry
Cyanide, WAD	SM 4500 CN I	Automated Colorimetry
Dissolved Organic Carbon	SM 5310 B	Combustion
Fluoride	EPA 300.0	Ion Chromatography
Hardness	SM 2340B, Ca as $CaCO_3$ by 200.7	ICP Sum
Ignitability	SW846 1010A	Pensky-Martin
Nitrate	EPA 300.0	Ion Chromatography
Nitrate + Nitrite	EPA 353.2	Automated Colorimetry
Nitrate + Nitrite	EPA 300.0	Ion Chromatography
Nitrite	EPA 300.0	Ion Chromatography
Odor	SM 2150B	Sniff Panel
ortho-Phosphate	SM 4500 P E	Colorimetry
pH (aqueous)	SM 4500-H^+ B	Electrometric
pH (soil)	EPA 9045C&D	Electrometric
Paste pH	ASA Monograph 9	Electrometric
Phosphate, Total	SM 4500 P E	Persulfate Digestion
Residue, Filterable (TDS)	SM 2540 C	Gravimetric
Residue, Non Filterable (TSS)	SM 2540 D	Gravimetric
Specific Conductance	EPA 120.1, SM 2510 B	Wheatstone Bridge
Sulfate	EPA 300.0	Ion Chromatography
Sulfide	SM 4500 S^{-2} F	Titrimetric
Surfactants (MBAS)	SM 5540 C	Colorimetry
Total Nitrogen	D 5176-91	Combustion
Total Solids	SM 2540 B	Gravimetric
Total Kjeldahl Nitrogen	EPA 351.2	Colorimetry
Total Organic Carbon	SM 5310 B	Combustion
Total Volatile Solids	EPA 160.4, SM 2540 E	Gravimetric
Turbidity	EPA 180.1	Nephelometric
TCLP (Toxicity Characteristic Leaching)	SW846 1311 &NV Extraction Procedure 1311	Extraction

ANALYTE	METHOD	TECHNIQUE
SPLP (Synthetic Precipitation Leaching)	SW846 1312 & NV Extraction Procedure 1312	Extraction
STLC (Soluble Threshold Limit Concentration)		Extraction
MWMP (Meteoric Water Mobility)	ASTM E2242-12	Extraction
CA-WET (California Waste Extraction Test)		Extraction
CEC (Cation Exchange Capacity)	SW846 9081, 9080	Exchange
Textural Analysis (Particle Size)	ASA "Methods of Soil Analysis" Number 9, Part 1	
Specific Gravity	ASA 9	Displacement
TOM/TOC	USDA, HB60(24)	Colorimetry
ANP (Acid Neutralization Potential)	Titration	Combustion
NCV (Net Carbonate Value)	Titration	Combustion
NAG (Net Acid Generation)	Titration	Combustion
ABA (Acid Base Account)	ASTM E1915-05 & EPA 600/2-78-054	Combustion
Total Sulfur + Sulfur Forms		Combustion
Total Carbon		Combustion
Arsenic Speciation	K.S. Subramanian et al.	GFAA
Iron Speciation	HACH-8146	Colorimetry
Gradation		Sieving
Loss on Ignition	Soil & Plant Analysis Council	Gravimetric
Percent Silica	ASTM 2795	Colorimetry
Tot Suspended Particulates	40CFR 50, App B amend 12/6/82	Gravimetric
Flash Point	SW-846 1010, ASTM D93-80	Pensky-Martin

6010B, 6020 and 7471A are maintained for those states that haven't implemented the EPA request to use the current promulgated method.

7.2 References

2009 TNI Standard.

Methods for the Determination of Metals in Environmental Samples Supplement I, EPA/600/R-94/111, May 1994.

Methods for the Determination of Inorganic Substances in Environmental Samples, EPA/600/R-93/100, August 1993.

Field and Laboratory Methods Applicable to Overburden and Minesoils, EPA 600/2-78-054.

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW 846), Third Edition, Update IV, January 2008.

Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.

Standard Methods for the Examination of Water and Wastewater, 19th Edition, 1995.

Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1999.

Standard Methods for the Examination of Water and Wastewater, 21st Edition, 2005.

Standard Methods for the Examination of Water and Wastewater, 22nd Edition, 2012

ASTM Book of Standards, part 31.

Soil Testing and Plant Analysis, 3rd Edition, Soil Sciences Society of America, 1990.

American Society of Agronomy, "Methods of Soil Analysis" Number 9, Parts 1 and 2.

U.S. Department of Agriculture, Handbook #60.

U.S. Department of the Interior, Bureau of Reclamation, Procedure for Determining Moisture, Ash, and Organic Content of Soil, USBR 5430-89.

Manual for the Certification of Laboratories Analyzing Drinking Water, Fifth Edition.

8.0 NEW WORK

The Business Development group discusses new work with clients before the work is received. If the work being requested involves tests not usually performed by SVL, the project is discussed with Department Supervisors to determine if the work can be accepted. Quotes and projects are logged so that there is no confusion about what is expected by the client. If work is received that does not adhere to the guidelines put forth in the quote or project, the client will be contacted for clarification. It is SVL's responsibility to inform the client that appropriate tests and/or calibration methods have been selected

that are capable of meeting the client's requirements. Occasionally SVL receives a work order with no prior notification that requests unusual tests, or tests to be conducted in a time frame not suitable for the work requested. When this occurs, the SCO reviews the job with the Laboratory Director, Client Services and/or Department Supervisors to determine if the work can or should be accepted. Routine work from established clients normally is not reviewed with the clients before jobs are set up, unless there is a problem with sample integrity or information on the COC.

SVL reviews and makes available in LIMS, the parameters associated with a client's project (project or work order memos shall be attached when special instructions are involved). A schedule is accessible for the work that has been received; this allows the staff to plan workloads and to track jobs. A Laboratory/Technical Director or Client Services member shall review all work orders. Adjustments to work schedules and staff deployment are made based upon the workload. Department Supervisors keep equipment and supplies on hand for routine work and for many non-routine tests as well. For further detail regarding the above, see SOP SVL 1027.

8.1 Sample Acceptance Policy

8.1.1 Samples received at SVL will be accepted for testing if the following criteria are all met at the time of sample receipt:

8.1.2 A proper SVL or client COC will accompany the sample shipment and must be completed in full (unless a project number is specified and is on file with SVL), including but not limited to; the client's name, address, phone/fax numbers, contact person, unique sample identification of individual samples, sample locations (if applicable), date and time of collection, collector's name, preservative type, sample matrix, filtered or unfiltered, number of bottles, analytes and/or tests to be performed, method of analysis, and any comments concerning sample specifics or QC requirements.

8.1.3 The use of correct sample containers (with proper preservation) for the sample matrices collected and ensuring that sufficient sample volume is provided for the tests requested (including extra volumes for QC requirements).

8.1.4 Accurate labeling of sample bottles using coded, water resistant labels and permanent ink, with said labels being cross referenced with information contained in the COC.

8.1.5 Adherence to holding time requirements as required by test or method requested.

8.1.6 In the event that a sample is received in non-compliance with this policy, the sample in question will be segregated and the client notified by telephone or email. The client may direct SVL to continue on with analysis of the non-conforming sample(s). Non-conformities will be noted on the sample receipt/chain of custody and within the final report if applicable; ref, SOP SVL 2001.

8.1.7 New clients will be informed of this policy through Client Services or Sample Receiving. They will be provided with a copy of the QM (hard copy or electronically) or a hand out on sample acceptance (located in SVL's waiting room or in Sample Receiving). As a reminder current clients/samplers will receive a copy of the sample acceptance policy if they submit samples that do not meet SVL's requirements.

9.0 CALIBRATION

9.1 Thermometers

Calibrating thermometers is described in SOP SVL 1004.

Quality Control Services calibrates SVL's NIST-certified thermometers.

SVL calibrates in-house liquid-in-glass thermometers against a NIST-certified thermometer annually. Digital thermometers are calibrated against a NIST certified thermometer quarterly. The IR gun is calibrated against a NIST certified thermometer quarterly. The calibrated thermometers are labeled with the appropriate correction factors.

9.2 Balances

Servicing and calibrating balances is described in SOP SVL 1025.

Quality Control Services calibrates SVL's balances.

SVL checks the calibration of a balance before each day of use with at least two weights traceable to a NIST traceable standard. For analytical balances, the measured weight must agree with the certified weight

within 0.1%. Balances that fail the criterion are checked with Class-1 weights. If they fail again, they are removed from service.

9.3 Balance Weights

Calibrating balance weights is described in SOP SVL 1025.

Quality Control Services calibrates SVL's set of Class-1 weights, with Reference Standards Traceable to NIST.

SVL uses certified Class-1 weights to certify the Class-4 weights used for the daily calibration of balances.

9.4 Micropipets

The calibration of micropipets is described in SOP SVL 1026.

SVL checks the calibration of variable-volume micropipets weekly. Fixed-volume micropipets are checked quarterly. If a measurement is out of control the mean of three measured volumes is taken and must agree with the expected value within 3%. Micropipets that fail this criterion are repaired or removed from service.

9.5 Repipettors

The calibration of repipettors is described in SOP SVL 1026.

SVL checks the calibration of repipettors quarterly. The measured volume must agree with the expected value within 3%. Repipettors that fail this criterion are repaired or removed from service.

9.6 Refrigerators

SVL records the temperature of sample, standard, and reagent storage refrigerators each weekday. The process is described in SOP SVL 2004. The temperature must meet the 0-6ºC as described in SOP SVL 2001. If a temperature is outside this criterion, the temperature is recorded again after one hour. If the temperature is still outside the acceptance range, samples, standards, and reagents are transferred to alternate refrigerators or coolers.

9.7 Ovens

SVL records the temperature of ovens every day that the oven is in use. The required temperature of each oven is stated in the applicable SOPs.

9.8 Inductively Coupled Plasma Mass Spectrometer (ICP-MS)

SVL calibrates its ICP-MS in accordance with EPA methods 200.8 and 6020A. A tune standard analysis is performed prior to calibration. Five

calibration standards and a calibration blank are analyzed at the beginning of a sequence. The software creates a linear calibration curve that must have a correlation coefficient of at least 0.995. Calibration points will be verified against the curve (see SVL 1020).
The low calibration standard should be within ± 30% and the remaining calibration standards within ± 10% of the indicated concentration. An Initial Calibration Verification (ICV) from a secondary source follows to verify the calibration. An Initial Calibration Blank (ICB) indicates the system is clean. A Reporting Limit Check Standard (RLCS) indicates that the results derived at the reporting limit can be recovered within our acceptance criteria. Analysis of a Continuing Calibration Verification (CCV) and a Continuing Calibration Blank (CCB) follow after every ten samples and at the end of the analytical sequence. The acceptance criteria are defined in SOPs SVL 4111, 4112 and 4132.

9.9 Inductively Coupled Plasma Spectrometer (ICP)

SVL calibrates ICPs in accordance with EPA methods 200.7 and 6010C. A single calibration standard and a calibration blank are analyzed at the beginning of a sequence. Interference check standards are run to show that interelement correction factors are current. An RLCS indicates that the results derived at the reporting limit can be recovered within our acceptance criteria. An ICV from a secondary source follows to verify the calibration. An ICB indicates the system is clean. Analysis of a CCV and a CCB follow after every ten samples and at the end of the analytical sequence. The acceptance criteria are defined in SOP SVL 4102 & 4135. RLCSs are analyzed at the end of drinking water and 6010C runs.

9.10 Graphite Furnace Atomic Absorption Spectrometer (GFAA)

SVL calibrates it's GFAA in accordance with EPA method 231.2 for gold and K.S. Subramanian et al. for arsenic speciation. Three calibration standards and a calibration blank are analyzed at the beginning of a sequence. Perkin-Elmer instruments create a linear calibration curve that must have a correlation coefficient of at least 0.995. Calibration points will be verified against the curve (see SVL 1020). The low calibration standard should be within ±30% and the remaining calibration standards within ±10% of the indicated concentration. An ICV from a secondary source follows to verify the calibration. An ICB indicates the system is clean. An RLCS indicates that the results derived at the reporting limit can be recovered within our acceptance criteria. Analysis of a CCV and a CCB follow after every

ten samples and at the end of the analytical sequence. The acceptance criteria are defined in SOPs SVL 4115 and 4082.

9.11 Mercury Analyzer (CVAA)

SVL calibrates its CVAA in accordance with EPA methods 245.1, 7470A, and 7471B. Six calibration standards and a calibration blank are analyzed at the beginning of a sequence. The instrument creates a linear calibration curve that must have a correlation coefficient of at least 0.995. Calibration points will be verified against the curve (see SVL 1020). The low calibration standard should be within ±30% and the remaining calibration standards within ±10% of the indicated concentration. An ICV from a secondary source follows to verify the calibration. An Initial Calibration Blank (ICB) indicates the system is clean. An RLCS indicates that the results derived at the reporting limit can be recovered within our acceptance criteria. Analysis of a CCV and a CCB follow after every ten samples and at the end of the analytical sequence. The acceptance criteria are defined in SOP SVL 4010.

9.12 Flame Atomic Absorption Spectrometer (FLAA)

SVL calibrates FLAAs in accordance with analytical method requirements. The acceptance criteria are defined in SOP SVL 4105.

9.13 Ion Chromatograph (IC)

SVL calibrates ICs in accordance with EPA method 300.0. Five calibration standards and a calibration blank are analyzed. The instrument creates a quadratic calibration curve that must have a correlation coefficient of at least 0.995. Calibration points will be verified against the curve (see SVL 1020). The low calibration standard should be within ±30% and the remaining calibration standards within ±10% of the indicated concentration. An ICV from a secondary source follows to verify the calibration. An ICB indicates the system is clean. An RLCS indicates that the results derived at the reporting limit can be recovered within our acceptance criteria. A CCV and a CCB follow after every ten samples and at the end of the analytical sequence. The acceptance criteria are defined in SOPs SVL 4122 and 4133.

9.14 Flow-Injection Auto Analyzer (FIA)

SVL calibrates FIAs in accordance with EPA methods 335.4 (Total Cyanide), 350.1 (Ammonia), 351.2 TKN, 353.2 (Nitrate and Nitrite), 9012 B (Total Cyanide), and Standard Methods 4500-CN-I (WAD Cyanide), and ASTM D-7237-10 (Amperometric Free Cyanide). A minimum of five calibration standards and a calibration blank are

analyzed at the beginning of each analytical sequence. The instrument software creates a linear or quadratic calibration curve that must have a correlation coefficient of at least 0.995. Calibration points will be verified against the curve (see SVL 1020). The low calibration standard should be within ±30% and the remaining calibration standards within ±10% of the indicated concentration. A Laboratory Control Sample (LCS) and an ICV from a secondary source verifies the calibration curve. An ICB indicates the system is clean. An RLCS indicates that the results derived at the reporting limit can be recovered within our acceptance criteria. Analysis of a CCV and a CCB follow after every ten samples and at the end of the analytical sequence. The acceptance criteria are defined in SOPs SVL 4012, SVL 4045, SVL 4099, SVL 4048, SVL 4075, and SVL 4131.

9.15 Total Organic Carbon Analyzer (TOC)

SVL calibrates TOC analyzers in accordance with SM 5310 B. Six calibration standards for total carbon are analyzed and a linear curve is constructed, the curve must have a correlation coefficient of at least 0.995. Calibration points will be verified against the curve (see SVL 1020). The low calibration standard should be within ±30% and the remaining calibration standards within ±10% of the indicated concentration. An ICV from a secondary source verifies the calibration curve. An ICB indicates the system is clean. An RLCS indicates that the results derived at the reporting limit can be recovered within our acceptance criteria. A CCV and CCB are analyzed at the beginning of each analytical sequence, after every ten samples and at the end of the analytical sequence. The acceptance criteria are defined in SOP SVL 4116.

9.16 UV/Visible Spectrophotometers (UV/VIS)

SVL calibrates its UV/Visible spectrophotometer in accordance with the applicable published methods. A minimum of three calibration standards and a calibration blank are analyzed at the beginning of each analytical sequence. The calibration curve must have a correlation coefficient of at least 0.995. Calibration points will be verified against the curve (see SVL 1020). The low calibration standard should be within ±30% and the remaining calibration standards within ±10% of the indicated concentration. An ICV from a secondary source follows to verify the calibration. An ICB indicates the system is clean. A CCV and CCB are analyzed at the beginning of each analytical sequence, after every ten samples and at the end of the analytical sequence. The

acceptance criteria are defined in SOPs 4037, 4040, 4042, 4043, 4044, 4123 and 4125.

9.17 LECO Carbon/Sulfur Analyzer

Total Sulfur and Total Carbon are determined from analysis of a small aliquot of crushed sample using a LECO furnace. In addition, organic and inorganic carbon and pyrolysis loss and residual sulfur may be determined by roasting a sample, analyzing it by LECO, and calculating the difference between the pre and post roast carbon and sulfur values. Three sets of three calibration standards for carbon and sulfur are analyzed to prepare a calibration curve that must have a correlation coefficient of at least 0.995. Calibration points will be verified against the curve (see SVL 1020). The low calibration standard should be within ±30% and the remaining calibration standards within ±10% of the indicated concentration. An ICV from a secondary source follows to verify the calibration. An ICB indicates the system is clean. An RLCS indicates that the results derived at the reporting limit can be recovered within our acceptance criteria. A CCV and CCB are analyzed at the beginning of each analytical sequence, after every ten samples and at the end of the analytical sequence. The acceptance criteria are defined in SOPs SVL 4097, 4061 and 4129.

9.18 pH and Ion Selective Electrode Meters (ISE)

SVL calibrates pH and ISE meters in accordance with the applicable published methods.

9.19 Class A Glassware

Class A glassware is verified, assigned a unique identifier and logged in upon receipt as described in SOP SVL 1026.

10.0 SAMPLING, SAMPLE RECEIVING, AND STORAGE

10.1 Sampling

SVL does not conduct sampling. Sampling procedures that lead to contamination of client's samples in the field are beyond SVL's control. SVL recommends the following procedures to its clients.

Sample preservation is critical for sample integrity. Chemical and biological reactions may occur that begin to change some chemical species upon sample collection. Unfortunately, for most samples,

immediate analysis is neither economically feasible nor logistically possible. Although no chemical preservative exists that is valid for every parameter, SVL strongly recommends the preservation methods, container type, sample size and estimated maximum holding times for collection of water and wastewater samples summarized in Table 1. Solid samples are best preserved by cooling the sample to a range between 0- 6°C.

Table 1

Analysis	Volume Required (mL)	Container	Preservative	Holding Time
Color	50	P,G	Cool to ≤ 6 °C	48 Hours
Conductance	100	P,G	Cool to ≤ 6°C	28 Days
Hardness	100	P,G	HNO_3 to pH<2	6 Months
Odor	300	G only	Cool to ≤ 6°C	24 Hours
pH	25	P,G	None Required	* ASAP
Temperature	1000	P,G	None Required	* ASAP
Turbidity	100	P,G	Cool to ≤ 6 °C	48 Hours
Filterable Residue (TDS)	100	P,G	Cool to ≤ 6 °C	7 Days
Non-Filterable Residue (TSS)	100	P,G	Cool to ≤ 6 °C	7 Days
Total Residue	100	P,G	Cool to ≤ 6 °C	7 Days
Volatile Residue	100	P,G	Cool to ≤ 6 °C	7 Days
Settleable Matter	1000	P,G	Cool to ≤ 6 °C	48 Hours
Dissolved Metals	200	P,G	Filter on site; HNO_3 to pH<2	6 Months
Total Metals	100	P,G	HNO_3 to pH<2	6 Months
Chromium (VI)	200	P,G	Cool to ≤ 6 °C	24 Hours/ 28 days**
Mercury, Dissolved	100	P,G	Filter; HNO_3 to pH<2	28 Days
Mercury, Total	100	P,G	HNO_3 to pH<2	28 Days
Acidity	100	P,G	Cool to ≤ 6 °C	14 Days
Alkalinity	100	P,G	Cool to ≤ 6 °C	14 Days
Bromide	100	P,G	None Required	28 Days
Chloride	50	P,G	None Required	28 Days
Cyanide	500	P,G	Cool to ≤ 6 °C; NaOH to pH>12	14 Days
Fluoride	300	P	None Required	28 Days
Ammonia	400	P,G	Cool to ≤ 6 °C H_2SO_4 to pH<2	28 Days

Analysis	Volume Required (mL)	Container	Preservative	Holding Time
Total Kjeldahl Nitrogen	500	P,G	Cool to ≤ 6 °C H_2SO_4 to pH<2	28 Days
Nitrate plus Nitrite	100	P,G	Cool to ≤ 6 °C H_2SO_4 to pH<2	28 Days
Nitrate	100	P,G	Cool to ≤ 6 °C	48 Hours
Nitrite	50	P,G	Cool to ≤ 6 °C	48 Hours
Ortho-Phosphate Dissolved	50	P,G	Filter on site; Cool to ≤ 6 °C	48 Hours
Total Phosphate	50	P,G	Cool to ≤ 6 °C; H_2SO_4 to pH<2	28 Days
Total Dissolved Phosphate	50	P,G	Filter on site; Cool to ≤ 6 °C; H_2SO_4 to pH<2	28 Days
Silica	50	P only	Cool to ≤ 6 °C	28 Days
Sulfate	50	P,G	Cool to ≤ 6 °C	28 Days
Sulfide	500	P,G	Cool to ≤ 6 °C add 2 mL zinc acetate plus NaOH to pH>9	7 Days
COD	50	P,G	Cool to ≤ 6 °C H_2SO_4 to pH<2	28 Days
Total Organic Carbon	25	40 mL amber vials	Cool to ≤ 6 °C H_2SO_4 to pH<2	28 Days
Phenolics	500	G only	Cool to ≤ 6 °C H_2SO_4 to pH<2	28 Days
MBAS	1200	P,G	Cool to ≤ 6 °C	48 Hours

* pH and temperature should be measured in the field whenever possible. They are subject to rapid change. Measurements of pH and temperature made in the laboratory will almost always be out of holding time.

** If preserved in the following manner add 0.45 mL buffer solution to each vial. Adjust the pH to 9.3 – 9.7 using about 2 drops of 10 N sodium hydroxide and about 3-5 drops of 1N sodium hydroxide.

SVL has formed alliances with other laboratories for the analysis of organic parameters. The recommended containers and preservatives are

Analysis	Amount Required	Container	Preservative	Holding Time Until Extraction	Holding Time After Extraction Until Analysis
Mercury, Low Level***					
524.2 (Volatile Organic Compounds)	3x40mL vials	G,T	Cool to ≤ 6 °C; HCl to pH<2	14 days	NA

Analysis	Amount Required	Container	Preservative	Holding Time Until Extraction	Holding Time After Extraction Until Analysis
Mercury, Low Level***					
608 (Pesticides and/or PCBs)	3 L	amber G,T	Cool to ≤ 6 °C	7 days	40 days
624 (Volatile Organic Compounds)	3x40mL vials	G,T	Cool to ≤ 6 °C; HCl to pH<2	14 days	NA
625 (Semi-volatile Organic Compounds)	3 L	amber G,T	Cool to ≤ 6 °C	7 days	40 days
1664 Hexane Extractable Materials	2L	G only	Cool to ≤ 6 °C H_2SO_4 or HCl to pH<2	28 days	NA
8081A (Pesticides)	8 oz (soil) 1L (aqueous)	amber G,T	Cool to ≤ 6 °C	14 days 7 days	40 days
8082 (PCBs)	8 oz (soil) 1 L (aqueous)	G,T	Cool to ≤ 6 °C	14 days 7 days	40 days
8260B (Volatile Organic Compounds)	4 oz (soil) 3x40mL (aq)	G,T	Cool to ≤ 6 °C; HCl to pH<2	14 days	NA
8270C (Semi-volatile Organic Compounds)	8 oz (soil) 1 L (aqueous)	amber G,T	Cool to ≤ 6 °C	14 days	40 days
8015 (TPH-Gasoline)	4 oz (soil) 3x40 mL (aq)	amber G,T	Cool to ≤ 6 °C; HCl to pH<2	14 days	35 days
8015AZ ****	8 oz (soil)	G,T	Cool to ≤ 6 °C	48 hours	14 days for extraction and analysis
8260BAZ****	4 oz (soil)	G,T	Cool to ≤ 6 °C	48 hours	NA
8015 (TPH-Diesel Motor Oil)	1 L (aq) 8 oz (soil)	amber G,T	Cool to ≤ 6 °C: HCl to pH<2	14 days	40 days

*** Call for sampling and hold time requirements.

**** TPH 8015AZ and 8260AZ (soils) have a 48 hour hold time before extraction.

10.1 Sampling Cont'd

Field blanks allow for identification of systemic and random sample contamination that may result from the sampling equipment, storage containers, sampling agents, or chemicals added to preserve samples. Field blanks consist of a sample container of distilled or deionized water with the appropriate chemical preservative. Preservation, filtration, storage, handling, and analysis are performed as if the field blanks were samples. To achieve accurate and meaningful data, field blank containers should be filled with analyte-free water and the appropriate preservative at the sampling site.

Sources of sample contamination include unclean sample containers and filters; impure solvents and reagents; and use of cleaning products inappropriate for the proposed analysis. Hair, tobacco smoke, and dust also are appreciable sources of contamination, so sampling should be conducted in as careful a manner as possible.

Before filtering samples for dissolved parameters, the filter paper should be rinsed with de-ionized or distilled water and with a small portion of sample. The filtration apparatus should also be rinsed with de-ionized or distilled water between samples. Handle filter paper only on the edge, using appropriate forceps (plastic for trace metals analysis).

Use the proper sample container for the parameter specified. Samples for trace metals analysis must not come into contact with any metallic surface; samples for organic analysis must not come into contact with any plastic surface.

Sampling personnel should complete a COC form that documents sampler, sample identification, sampling date and time, sample location (state of sample origin if applicable), matrix type, number of sample containers, type of preservation, whether samples have been filtered, and the parameters to be analyzed.

10.1.1 Sub-sampling

In the event that SVL must undertake sub-sampling, SVL will use the appropriate container (uniquely identified) and the proper preservation. If SVL undertakes the sub-sampling of matrices that are required to be performed in the field, SVL will identify those samples on the analytical report; ref, SOP SVL 2018.

10.2 Sample Receiving and Storage

SOPs SVL 2001, SVL 2003, and SVL 2004 describe sample receiving, job creation, and sample storage, respectively.

SVL takes a temperature reading from the sample shipping containers (coolers) upon receipt and opening. Each sample is checked for visible damage and the presence of an intact custody seal (if required). SVL gives each group of samples a unique job number (e.g., " W1E0027"). Sample ID’s are automatically assigned a serial number suffix (-01 thru -99) appended to the work order number they belong to. The work order number is auto-generated by the LIMS and follows the format W YAnnnn, where Y is the last digit of the year, A corresponds to the month in which the work order was created (A=Jan., B=Feb.…L=Dec),

and nnnn is a serial number for the work order in a particular month. Individual sample containers are assigned a designator (A, B, C …) and these are tracked in the LIMS so the particular container used for an analysis can be tracked. For an example "W1E0027-03 D" would be the fourth container for the third sample in the 27th work order of May 2011.

Job numbers remain with the samples throughout the analytical process. Each sample is assigned a unique, sequential identification number. Samples are labeled with a bar code (containing both the sample and job numbers) before storing the sample.

Samples that require refrigeration are stored in walk-in coolers (which are kept between 0ºC and 6°C), except during times of sample preparation or analysis. Samples that do not require refrigeration are stored in an ambient temperature storage room. The laboratory does not refrigerate soil samples that were received without refrigeration. Samples are retained by SVL for a minimum of 30 days (or longer if required by the client) after an analytical report has been issued to the client. At the end of the specified period, samples are returned to the client or discarded in an appropriate manner.

Sample custodians, technicians and analysts use the custody log feature of the LIMS to track sample movement during receipt, preparation, and disposal. SVL personnel are responsible for logging the samples into their custody, where they assume accountability for the sample(s). When use of the sample is complete, personnel must scan samples back into the appropriate home location or another employee may assume custody by scanning/logging the sample into their custody via the LIMS.

10.3 Sample Disposal and Hazardous Waste

Procedures for sample disposal are described in SOP SVL 1001. Disposal procedures follow federal and state regulatory requirements. SVL's hazardous waste program is described in SOP SVL 1008.

11.0 EQUIPMENT AND INSTRUMENTS

SVL uses the following instruments to generate analytical data and to calibrate other instruments.

11.1 SVL performs instrument maintenance as recommended by the manufacturer. SVL maintains service contracts with vendors for its

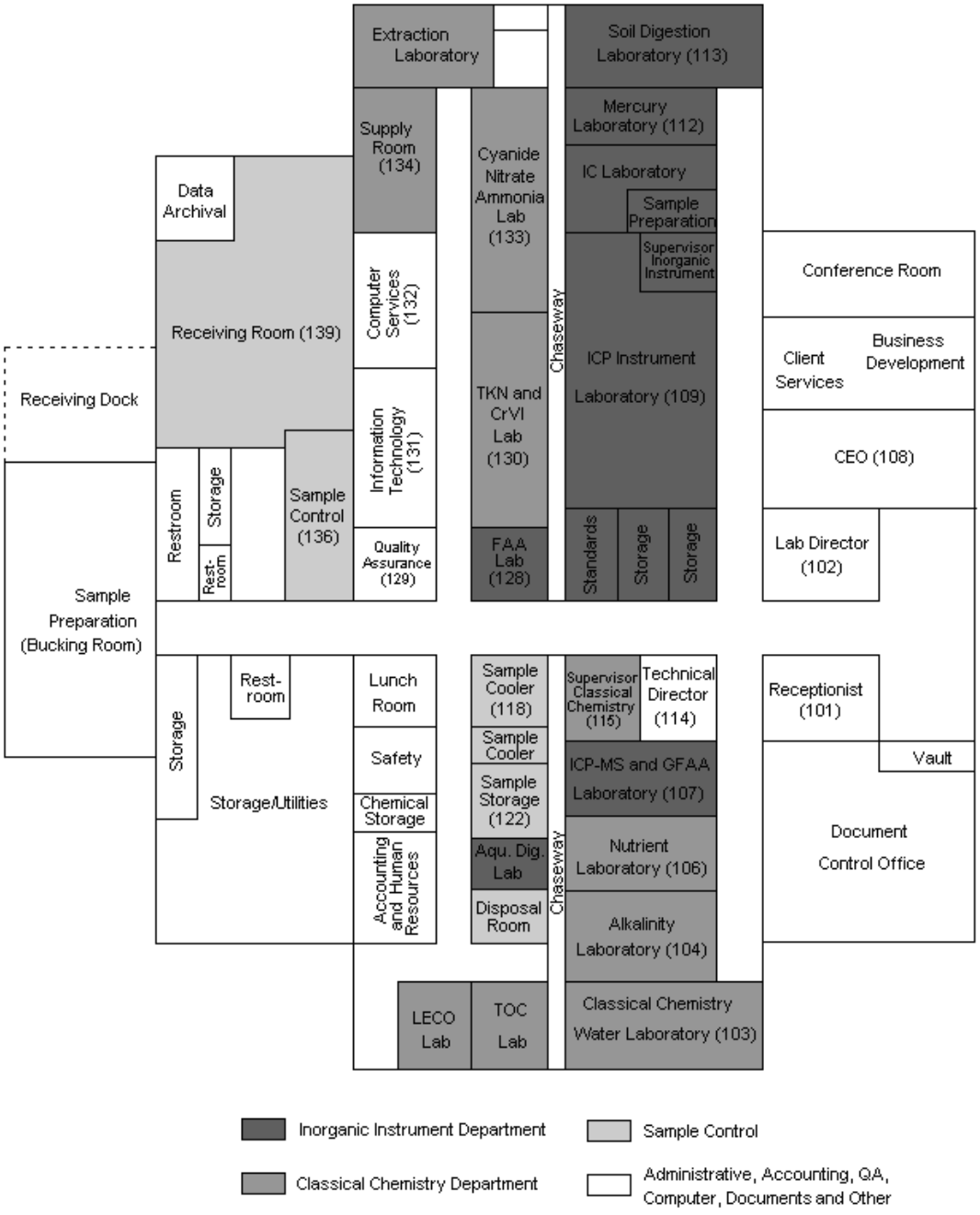
major analytical instrumentation. Maintenance logbooks are kept to provide a record of major and minor repairs; as well as, preventative maintenance.

11.2 The analysts and supervisors will determine if a repair has created a need to update instrument MDLs, linear ranges, calibrations etc.

INSTRUMENT	MANUFACTURER	MODEL	SERIAL NUMBER
Spectrometer (ICP-MS)	Perkin-Elmer	ELAN 5000	W0660402
Spectrometer (ICP-MS)	Agilent	7700 Series	JP10490758
Spectrometer (ICP) Thermo 1	Thermo Electron	ICAP 6500 Duo	IC5D20130703
Spectrometer (ICP) Thermo 2	Thermo Electron	ICAP 6500 Duo	IC65DC133703
Spectrometer (ICP) Optima 5	Perkin-Elmer	Optima 5300	077N5011902
Spectrometer (ICP) Optima 6	Perkin-Elmer	Optima 5300	077N6062101
Spectrometer (ICP) Optima A	Perkin-Elmer	Optima 8300	078N2080202
Atomic Absorption Spectrometer with Graphite Furnace	Perkin-Elmer	Analyst 600	601S3090501
Atomic Absorption Spectrometer with Vapor Generation Assembly	Varian	AA 55B	EL03048142
Mercury Analyzer with Autosampler	CETAC	M-6100	021202QT6
Mercury Analyzer with Autosampler	CETAC	M-7500	110801QTA
11 Digestor Blocks	Environmental Express	Hot Block	
Ion Chromatograph	Dionex	ICS900	08041118
Ion Chromatograph	Dionex	ICS90	04090417
Ion Chromatograph	Dionex	ICS900-C	09040981
Automated Flow Analyzer	O-I-Analytical	FS3100-2	Multi-component
Automated Flow Analyzer	O-I-Analytical	FS3100	Multi-component
2 Micro Distillation Units	Lachat	ID 001	A2000-828 and 081100001017
3 MIDI Distillation Units	BSL		
2 Ammonia Distillation Units	Andrews Glass		
Ammonia/N analyzer	Astoria Pacific	A2	200104
Automated Flow Analyzer	Alpkem	Alpkem TKN	200220
Block Digestor	Westco Scientific	Easy Digest 40/20	As. # INS0030HW
Auto Titrator with Autosampler 4	Metrohm	Titrino 809 Titrando	1809001007108
Auto Titrator with Autosampler 5	Metrohm	Titrino 809 Titrando	1809001013143
UV/Visible Spectrophotometer A	Genesys	20	3SGN243026
UV/Visible Spectrophotometer B	Genesys	20	3SGN341012
Turbidimeter A	Hach	2100N	95041453
Turbidimeter B	Hach	2100N	080906024269
COD Reactor	VELP Scientifica	ECO 25	101448
COD Reactor	VELP Scientifica	ECO 25	171440
pH Meter	Accumet	AB15	AB92325857

INSTRUMENT	MANUFACTURER	MODEL	SERIAL NUMBER
pH Meter	Accumet	AB15	AB92326969
pH Meter	Beckman	11 pH Meter	0224055
pH Meter B	Thermo	Orion A III	J06383
pH Meter	Thermo	Orion 320	019525
pH Meter C	Thermo	Orion A III	J06171
Dissecting Microscope	Nikon	104	
Polarizing Microscope	Nikon	106	
Centrifuge	Beckman	GS-6 Centrifuge	
Centrifuge	MISTRAL	3000i	51149
Centrifuge	IEC	K	70652271
Flashpoint detector	Precision Scientific	74537	108A-2
Conductance Meter	Fisher	AB30	AB 92329154
Conductance Meter	Fisher	AB30	AB 92338713
Elemental Analyzer B	LECO	SC632	3208
Elemental Analyzer A	LECO	SC632	3526
Carbon/Nitrogen Analyzer (TOC)	Shimadzu	TOC-VCSH-N	H51104135009 C5
Carbon/Nitrogen Analyzer (TOC)	Shimadzu	TOC-LCSN/TNM-L	H54105000234
Semi-Micro Balance	Mettler	AE-240	K89952
Semi-Micro Balance	Mettler	AE-240	G43270
Analytical Balance	Mettler	PJ 360	F89531
Analytical Balance	Mettler	PJ 360	G49684
Analytical Balance	Mettler	PB30	A04506
Analytical Balance	Mettler	PJ360	F89533
Analytical Balance	Ohaus	N1D110	1122352966
Analytical Balance	Ohaus	EOF110	F2221120252601
Analytical Balance	Ohaus	AR2140 Adventurer	1203121033
Analytical Balance	Ohaus	AR1530 Adventurer	1203200181P
Analytical Balance	Ohaus	AS 513	8028301193
Analytical Balance	Ohaus	AV-114	8029081142
Analytical Balance	Leco	050	329
Analytical Balance	Leco	CPA1245	26250271
IR Thermometer	Control Company	36934-180	101839552
IR Thermometer	Raytek	Ranger ST	98660090
Thermometer	HBI	145ºC to 205ºC	4B1321
Thermometer	Ertco	-20ºC to 110ºC	5283
Thermometer	HB	-20º C to 150ºC	L94280
Thermometer	HB	-1º C to 201ºC	3846

12.0 FACILITIES



12.1 SVL is an analytical laboratory specializing in the performance of tests and methods used in the characterization of environmental and mining samples. Since 1972, SVL has analyzed water, soil, sediment, sludge, oil, paint, rock, animal tissue, vegetation, air filters, and various other sample types. SVL occupies a 25,000 square foot laboratory facility architecturally designed and specifically organized to ensure efficient operation and meet the needs of a large capacity analytical laboratory. Building access, security and safety features have been carefully considered. Access through the outside laboratory entrance and to internal areas is limited to laboratory staff and other essential personnel. Visitors are logged in/out and made aware of safety protocols during their stay at SVL.

13.0 STANDARD OPERATING PROCEDURES

SVL performs work in accordance with the requirements of its SOPs. SVL's SOPs are listed below and describe all aspects of its work performance including Safety and Quality Assurance (1000 Series), Sample and Document Management (2000 Series) and Inorganic Analysis (4000 Series).

SOP NUMBER	DESCRIPTION
SVL 1001	SAMPLE DISPOSAL
SVL 1002	WRITING AND REVISING STANDARD OPERATING PROCEDURES
SVL 1004	CALIBRATING THERMOMETERS
SVL 1005	INTERNAL QUALITY ASSURANCE AUDITS
SVL 1007	SOIL STERILIZATION
SVL 1008	DISPOSAL OF HAZARDOUS WASTE
SVL 1010	TRAINING
SVL 1011	PERFORMING AN MDL STUDY
SVL 1015	PROCUREMENT, RECEIVING, AND SUBCONTRACTING
SVL 1017	RECORDS RETENTION AND PROTECTION
SVL 1019	CORRECTIVE ACTION
SVL 1020	CALIBRATION FOR ANALYTICAL METHODS
SVL 1021	MANUAL INTEGRATION
SVL 1023	SOFTWARE VERIFICATION
SVL 1025	CALIBRATING BALANCES
SVL 1026	CALIBRATING MICROPIPETS, REPIPETTORS, AND GLASSWARE
SVL 1027	CLIENT SERVICES
SVL 1028	CALCULATIONS FOR ANALYTICAL METHODS
SVL 1029	PERFORMANCE TESTING SAMPLES
SVL 1030	INITIAL, PERIODIC AND AFTER-MAINTENANCE CHECKS

SOP NUMBER	DESCRIPTION
SVL 1031	COMPUTER AND INFORMATION SECURITY POLICY
SVL 1032	CHEMICAL REAGENTS, PREPARED STANDARDS, AND QC SOLUTIONS
SVL 1033	ACCEPTANCE LIMITS AND TRENDING
SVL 2001	SAMPLE RECEIVING
SVL 2003	SVL JOB CREATION
SVL 2004	SAMPLE STORAGE AND SECURITY
SVL 2006	DATA CORRECTIONS
SVL 2007	CASE FILE ASSEMBLY
SVL 2009	DATA REVIEW
SVL 2013	DATA PACKAGE PRODUCTION
SVL 2015	LEVEL 3 – CLP DATA PACKAGE
SVL 2017	LOGBOOK CONTROL
SVL 2018	PREPARATION AND SUBSAMPLING OF EARTH, ROCK, AND TISSUE SAMPLES
SVL 2019	REANALYSIS PROCEDURES
SVL 2020	COMPUTER-RESIDENT SAMPLE DATA CONTROL
SVL 2021	DATA BACKUP AND RESTORE
SVL 2022	SAMPLE RECEIVING – FOREIGN SOILS
SVL 4010	EPA 245.1, SW-846 7470A and 7471A; DETERMINATION OF MERCURY (CVAA)
SVL 4012	EPA 335.4, SM 4500 CN E and SW-846 9012B; TOTAL CYANIDE BY MICRODIST™ and MIDI DISTILLATION FOLLOWED BY AUTOMATED COLORIMETRY
SVL 4013	GLASSWARE WASHING FOR CLASSICAL CHEMISTRY
SVL 4021	FILTER DIGESTION
SVL 4022	PERCENT SOLIDS/ PERCENT MOISTURE
SVL 4024	SM 2120 B; COLOR
SVL 4025	EPA 120.1 and SM 2510 B; CONDUCTIVITY
SVL 4026	EPA 180.1; TURBIDITY
SVL 4028	SM 4500 H^+ B; pH
SVL 4029	SPECIFIC GRAVITY
SVL 4031	SM 2310 B; ACIDITY
SVL 4032	SM 4500 S^{2-} F; SULFIDES BY TITRATION
SVL 4034	SM 2540 C and SM 2540 D; TOTAL DISSOLVED SOLIDS AND SUSPENDED SOLIDS
SVL 4035	SM 2540 B and EPA 160.4; TOTAL AND VOLATILE SOLIDS
SVL 4037	SM 5540 C; METHYLENE BLUE ACTIVE SUBSTANCES
SVL 4040	SM 4500 P E; TOTAL PHOSPHORUS (AQUEOUS SAMPLES)
SVL 4042	SM 4500 P E; ORTHO-PHOSPHATE (AS P)
SVL 4043	EPA 410.4; CHEMICAL OXYGEN DEMAND
SVL 4044	TOTAL ORGANIC MATTER
SVL 4045	EPA 351.2; TOTAL KJELDAHL NITROGEN
SVL 4048	EPA 353.2; NITRATE/NITRITE AS N: AUTOMATED CADMIUM RE REDUCTION
SVL 4049	SW-846 9081; CATION EXCHANGE CAPACITY

SOP NUMBER	DESCRIPTION
SVL 4060	LOSS ON IGNITION (SVL METHOD)
SVL 4061	DETERMINATION OF ACID GENERATION POTENTIAL (AGP), ACID NEUTRALIZATION POTENTIAL (ANP), AND ACID-BASE ACCOUNT (ABA)
SVL 4065	METEORIC WATER MOBILITY EXTRACTION
SVL 4068	SW-846 1312; SYNTHETIC PRECIPITATION LEACHING PROCEDURE (SPLP)
SVL 4070	TOTAL SUSPENDED PARTICULATES
SVL 4075	SM 4500 CN I; WAD CYANIDE BY MIDI DISTILLATION FOLLOWED BY SEMI-AUTOMATED COLORIMETRY
SVL 4078	EPA METHOD 3020A; SAMPLE DIGESTION FOR TOTAL METALS IN AQUEOUS SAMPLES FOR ICP-MS
SVL 4079	EPA METHOD 3010A; SAMPLE DIGESTION FOR TOTAL METALS IN AQUEOUS SAMPLES FOR ICP
SVL 4080	EPA METHOD 3005A; SAMPLE DIGESTION FOR TOTAL RECOVERABLE METALS IN AQUEOUS SAMPLES FOR ICP
SVL 4082	ARSENIC SPECIATION As(III) AND As(V)
SVL 4084	SM 2320 B; DETERMINATION OF ALKALINITY AND pH USING THE AUTOTITRATOR
SVL 4093	CASSETTE FILTER DIGESTION
SVL 4094	EPA METHOD 3050B; SAMPLE DIGESTION FOR METALS IN SOILS
SVL 4095	SW-846 1010; FLASHPOINT DETERMINATION (PENSKY-MARTENS CLOSED TESTER)
SVL 4096	SW-846 9045 C and 90045 D; pH DETERMINATION FOR SOILS
SVL 4097	ASTM 1915-05; TOTAL SULFUR, TOTAL CARBON
SVL 4099	EPA 350.1; AMMONIA BY SEMI-AUTOMATED COLORIMETRY
SVL 4102	EPA 200.7 and SW-846 6010C; ANALYSIS OF METALS BY METHODS 6010C AND 200.7 USING THE PERKIN-ELM OPTIMA ICP
SVL 4105	SM 3114 B; SELENIUM BY HYDRIDE
SVL 4106	METHOD 200.2; SAMPLE DIGESTION FOR TOTAL RECOVERABLE METALS IN AQUEOUS SAMPLES BY ICP AND ICP-MS
SVL 4108	SAMPLE PREPARATION FOR DISSOLVED AND POTENTIALLY DISSOLVED METALS IN AQUEOUS SAMPLES
SVL 4111	EPA METHOD 200.8; ANALYSIS OF METALS BY ICP-MS
SVL 4112	SW-846 6020A; ANALYSIS OF METALS BY ICP-MS
SVL 4114	SW-846 1311; TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP)
SVL 4116	SM 5310 B; TOTAL ORGANIC CARBON
SVL 4118	CALIFORNIA WASTE EXTRACTION TEST (CA-WET)
SVL 4119	PREPARATION OF QC SOLUTIONS FOR METALS ANALYSIS
SVL 4120	ASTM D-5176; TOTAL NITROGEN
SVL 4121	SM 2150 B; DETERMINATION OF THRESHOLD ODOR NUMBER (TON)
SVL 4122	EPA 300.0; INORGANIC ANIONS BY ION CHROMATOGRAPHY USING THE DIONEX DX100 AND ICS-90
SVL 4123	ASTM D-2795 and D-3682-78 SOLID SILICA
SVL 4124	EPA 231.2; OPERATIONOF PERKIN/ELMER GFAA: ANALYSIS OF GOLD BY GRAPHITE FURNACE
SVL 4125	SM 3500 Cr B; HEXAVALENT CHROMIUM
SVL 4127	pH DETERMINATION FOR PASTE

SOP NUMBER	DESCRIPTION
SVL 4128	SOIL ELECTRICAL CONDUCTIVITY BY ASA-9
SVL 4129	NET CARBONATE VALUE (NCV)
SVL 4130	NET ACID GENERATION (NAG)
SVL 4132	ANANLYSIS OF METALS BY THE AGILENT ICP-MS (EPA METHOD 200.8)
SVL 4133	DETERMINATION OF THIOCYANATE BY ION CHROMOTOGRAPHY USING DIONEX ICS-90 AND ICS-900
SVL 4134	ANALYSIS OF METALS BY AGILENT ICP-MS (SW-846 METHOD 6020A)
SVL 4135	ANALYSIS OF METALS BY METHODS 6010C AND 200.7 USING THE THERMO iCAP 6000 SERIES ICP SPECTROMETER
SVL 4136	TEXTURAL CLASS BY EPA-600/2-78-054
SVL 4137	EXTRACTIONS COMPENDIUM
SVL 4138	ASTM D-7275 – RECOVERY of AQUEOUS CYANIDES by EXTRACTION from MINE ROCK and SOIL after REMEDIATION of PROCESS RELEASES

13.1 Deviations

Occasionally, a deviation from an SOP is required to generate an accurate result for a given test or client. This may occur when a client specifically requires a modification, or when the sample matrix interferes with the analysis. The Laboratory Director or a Department Supervisor may authorize a deviation. The analyst documents details of the deviation from the SOP on the instrument raw data printout or the job bench sheet with a notation in the work order memo in Element. The deviation will be indicated on the report.

13.1.1 In the event that an SOP needs to be immediately amended an email will be sent to the Quality Manager outlining the necessary change. The change can go into effect immediately prior to the SOP being amended.

14.0 QUALITY CONTROL

14.1 Quality Control Parameters

SVL uses a number of quality control parameters to validate calibration, and to measure contamination, accuracy, and precision. Each SVL SOP indicates the parameters required for the method being used.

14.1.1 Blanks

Method Blank Is an aliquot of analyte-free water that is put through all the steps of a specific method along with the samples. It is sometimes called a Laboratory Reagent Blank.

Calibration Blank The zero-concentration standard analyzed as part of a calibration curve.

Field Blank Randomly selected sample container that is filled with analyte-free water and the appropriate chemical preservative in the field.

Trip Blank Is a specific type of field blank. A trip blank is not opened in the field. It is a check on sample contamination from the time the container is sealed at the lab or supplier. It is used to verify the container's integrity during sample transport and the container's time on site (it should always be with sampling group).

The acceptance criterion for a blank may be set by the published method, by client DQOs, or by historical statistics. In the absence of these directives, the acceptance criterion may default to less than the reporting limit.

14.1.2 Matrix Spike

Is an aliquot of sample to which a known amount of analyte has been added prior to sample preparation or digestion. It is a measure of the effect of the sample matrix on the analytical method. It is sometimes called the "Laboratory Fortified Matrix".

The recovery is calculated by:

% Recovery = 100 x (MS – S) / SA

Where the MS = Spiked Sample Result
S = Sample Result
SA = Spike Added

Acceptance criteria for the matrix spike recovery may be determined by the published method, by client DQOs, or set between 70-80% to 120-130%. For those methods without guidelines the QA Manager will set default limits for the acceptance range. Individual SOPs will have the recovery range acceptance requirements. There are no requirements if the concentration of the analyte in the original sample is greater than five times the concentration of the spike.

14.1.3 Analytical Spike or Post-Digestion Spike

Is an aliquot of sample to which a known amount of analyte has been added after sample preparation. It is a measure of the effect of the matrix on a digestate or extract.

14.1.4 Laboratory Control Sample (LCS)

Is a solution or material of known concentration that is added to an analyte-free matrix and then analyzed to evaluate the recovery and accuracy of a method. It is sometimes called a Laboratory Fortified Blank.

Acceptance criteria for the LCS recovery may be determined by the published method, by the manufacturer of the standard, by client DQOs or the QA Manager will set default limits.

14.1.5 Sample Duplicate

A second similar aliquot of a sample treated exactly the same through preparation and analysis. The Relative Percent Difference (RPD) between the values of the duplicates is a measure of the precision of the analytical method.

$$RPD = 100 \times | S - D | / [(S + D)/2]$$

The acceptance criterion for the RPD is usually set at 20.

14.1.6 Matrix Spike Duplicate (MSD)

A second similar aliquot that is spiked, it is treated exactly the same as the first matrix spike (MS) through preparation and analysis. The RPD between the recovery values is a measure of the precision of the analytical method.

$$RPD = 100 \times | MSD - MS | / [(MSD + MS) / 2]$$

14.1.7 Interference Check Sample (ICS)

A sample with known concentrations of elements used to determine if the inter-element correction factors are valid.

14.1.8 Initial Calibration Verification (ICV)

A standard made from a second source from the calibration standards. It is analyzed immediately after the calibration to determine the validity of the calibration standards.

14.1.9 Continuing Calibration Verification (CCV)

A calibration standard (primary or secondary source) analyzed after every ten samples, and at the end of an analytical sequence to verify that the calibration is still valid.

14.1.10 Reporting Limit Check Standard (RLCS)

A check standard that is constructed out of either a primary or secondary source made up at same concentration as the reporting limit. An acceptance range of ±30% for single analyte methods and ±50% for multi-analyte methods was made the default. RLCS results are batched as a Standard Reference Material (SRM) which can be pulled into Element for control charting purposes.

14.1.11 Initial Calibration Blank (ICB)

A matrix matched deionized water sample ran to prove the system is clean with no carry-over.

14.1.12 Continuing Calibration Blank (CCB)

A matrix matched deionized water sample ran to prove the system is clean with no carry-over.

14.1.13 Serial Dilution

Dilute a sample by a minimum of five fold (1+4). Agreement within 10% between the concentration for the undiluted sample and five times the concentration for the diluted sample indicates the absence of interferences.

14.1.14 Quality Control Sample (QCS)

A solution of method analytes of known concentrations which is used to fortify an aliquot of blank solution or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards.

14.1.15 Instrument Performance Check (IPC)

A solution of method analytes, used to evaluate the performance of an instrument system with respect to a defined set of method criteria.

14.2 Control Charts

SVL utilizes Element to provide personnel with the up to the minute ability to trend inputted QC results. It is recommended that analysts and technicians regularly consult trending charts to provide themselves with real time information. By trending an analysis, the analyst or technician can look at a current or past snapshot of QC recoveries and possibly determine when prep procedures or QC samples were done incorrectly or when they may have used contaminated or expired components. Trending can also be used to show when an instrument's components begin to degrade or fail.

The process is defined in SOP SVL 1033. RLCSs, prep blanks, LCSs, duplicates and matrix spikes are tracked. A standard X bar control chart is used to plot results. Upper and lower warning limits of ±2s (where s equals standard deviation) and upper and lower control limits of ±3s are calculated using at least 20 measurements (if possible) during a 6 month period.

14.3 Acceptance Limits

Acceptance limits for quality control parameter recoveries may be set by published analytical methods, DQOs or be default limits set by the QA Manager. Individual SOPs will provide the accepted recoveries for each method. Acceptance limits are also outlined in SOP SVL 1033.

14.4 General Frequency of Quality Control Checks

For those methods that do not have published QC requirements, SVL will use the following QC and frequency if applicable per batch of 20 samples:

Initial Calibration Verification once per calibration.

Initial Calibration Blank once per calibration.

Reporting Limit Check Standards at a minimum of 1 per analytical run.

Method or Instrument Blanks at a frequency of 5%.

Laboratory Fortified Blank or LCS at a frequency of 5%.

Matrix Spiked Samples at a frequency of 10%.

Matrix Spike Duplicates at a frequency of 5%.

Continuing Calibration Verification every ten samples.

Continuing Calibration Blank every ten samples.

14.5 Maintenance

SVL breaks maintenance down into the following categories: initial maintenance, periodic maintenance, and after-maintenance performance checks. The requirements for performing maintenance or filling out maintenance logbooks can be found in SOP SVL 1030. Initial checks can be either checks performed during instrument setup or daily checks performed before the start of operations. Periodic checks are those checks that are performed on set time intervals (i.e. weekly, monthly, biannually, etc). After-maintenance checks are done after repairs have been completed or when an instrument has been moved to a new location. This is done in order to document acceptable ongoing instrument performance.

14.6 Uncertainty of Measurement

SVL uses control charting as a means of determining when selected parameters (batch QC) are out of control. Warning and unacceptable control limits are defined at 2 and 3 sigma, respectively. See QM 14.2 and SOP SVL 1033.

Almost all approved methods used at SVL contain a section related to precision and bias. Random uncertainties cannot be determined statistically and can only be estimated by a trained analyst. Uncertainty represents a bias associated with analytical measurements. The presence and magnitude of bias can be determined by assessment of SVL's QC sample results on our analytical reports.

SVL reports data to 2 or 3 significant figures, dependent upon the sensitivity required by our clients, with the number of decimal places reported determined by the sensitivity of the method.

14.6.1 Rounding

Rounding of analytical results is dependent upon the number of significant figures used by a method. Rounding for percent recovery on QC samples is also dependent upon the number of significant figures. Element is setup and our analysts are directed

to round up to the significant figure assigned to that method. SVL uses the following rounding rule: A result of 5 or greater rounds the results up to the significant figure assigned in Element.

15.0 CORRECTIVE ACTION

The SVL Corrective Action Program is defined in SOP SVL 1019.

Any employee may initiate a Corrective Action Report (CAR) to support the quality system. Some examples are: The need for an SOP revision, incorrect results released to clients, an overdue MDL study, overdue or improper training, incorrect data reduction or review, improper instrument setup or calibration, or use of an incorrect analytical method.

If there is a non-acceptable result on a Performance Test Sample, the Quality Manager documents the failure as a CAR and works with the analysts and supervisors to discover the root cause of the failure. If there are findings from an internal or external audit, the Quality Manager issues a CAR to appropriate staff members so they can prepare a corrective action plan to rectify the issues.

Root cause analysis is the goal of corrective action and as such a cause will be identified, and a process outlined, so that a failure will not re-occur or its re-occurrence will be minimized.

15.1 Preventative Action

A “preventative action” is a pro-active process for dealing with a problem before it happens. It is taken to eliminate the cause of an undesirable situation in order to prevent its occurrence rather than a reaction to the identification of a problem or nonconformity. These actions are taken to reduce the probability that a potential problem will occur. They may also include contingencies to reduce the “seriousness” should a future problem occur. Subjects for “preventative action” may be implemented to address a weakness in the quality system that is not yet causing nonconformities and can be initiated internally or externally (client complaints). The focus for preventative actions should be to avoid creating nonconformities, but may also lead to improved laboratory efficiencies.

SVL uses the CAR template to document ideas, plans or actions whether developed internally or externally. These reports are audited at

a future date to ensure that the changes sought have been implemented and are effective.

16.0 TRAINING

SVL conducts annual training in legal and ethical responsibilities for all staff members. SVL provides training sessions that are developed in order to provide staff members with the analytical tools necessary for ever changing environmental regulatory requirements. New employees will be given various types of introductory training as soon as possible after their hire date.

SVL management and supervisors train staff members in laboratory safety. At a minimum this consists of an annual review of the Chemical Hygiene Plan. It also includes seminars on important safety issues throughout the year.

Staff members also receive training in the quality system and QM. At a minimum this consists of an annual review of the QM.

Department supervisors ensure that staff is adequately trained to perform the analyses assigned to them. The process is defined in SOP SVL 1010. Training includes, as appropriate, quality control requirements, instrument operation, instrument maintenance, software operation, reading the published method, reading the applicable SVL SOPs, and completion of an Initial Demonstration of Capability (IDOC). When an IDOC is not defined by the analytical method, the Quality Manager will create default criteria and outline them in the training summary forms which will be included in their personnel files. Upon completion of training, a Demonstration of Capabilities Certificate is placed within their personal file.

SVL Management defines the required elements for training for analytical methods. A Supervisor or a fully trained analyst provides training, when possible. If no fully trained analyst exists, an analyst may learn a new analysis by reading the appropriate method and instrument manual, then performing an IDOC.

During the training period, an analyst may produce data for clients under the supervision of a fully trained analyst; if there is not a trained analyst the Department Supervisor will review and sign off on all aspects of the work performed. A Department Supervisor or a fully trained analyst must review and sign all trainee work produced.

16.1 To document continued proficiency, an analyst must perform one of the following tasks annually:

16.1.1 Successfully analyze a blind performance sample.

16.1.2 Complete another IDOC.

16.1.3 Successfully analyze a blank and four separately prepared LCSs or duplicates (for those methods where a LCS is not commercially available).

16.2 Analysts and technicians who do not successfully complete a DOC within a year must complete an IDOC before being re-certified for a method.

17.0 ETHICS AND CONFIDENTIALITY

17.1 SVL is committed to providing its clients with accurate and defensible data and meeting all client requirements for data quality and integrity. To achieve our commitment, and as a condition for employment with SVL, all employees agree to follow SVL's policy regarding ethics and data integrity characterized but not limited to the items listed below.

17.1.1 All reported data, including dates and times, shall represent actual values obtained and are not modified or manipulated in any manner for which allowances have not been made for in the referenced method.

17.1.2 There will be no misrepresentation of another analyst's identity.

17.1.3 Altering the contents of logbooks and/or data sheets to misrepresent data is prohibited.

17.1.4 Altering any operating procedures or QC to make data "fit" is prohibited.

17.1.5 Failing to comply with SOPs without proper documentation and approval from the Laboratory Director and/or Quality Manager is prohibited.

17.1.6 Any attempt to misrepresent data or events as they actually occur in the course of data production, review or reporting is prohibited.

17.1.7 Deleting files, whether electronic or hard copy of raw data that was used in a reported value is prohibited.

17.1.8 Engaging in, or being a party to, any practice that ultimately misrepresents data or narratives in any way is prohibited.

17.2 SVL has established a zero-tolerance policy for improper, unethical, or illegal activities. Improper actions are defined as unapproved deviations from contract-specific or method-specific analytical practices, whether intentional or unintentional. Unethical or illegal actions are defined as

the deliberate falsification of analytical or quality assurance results where failed method or contractual requirements are made to appear acceptable. Some examples of improper, unethical, or illegal practices are listed below. Comments in parentheses should each be read as beginning with the phrase "including but not limited to…"

17.2.1 Improper use of manual integrations to meet calibration or method quality control criteria.

17.2.2 Intentional misrepresentation of the date or time of analysis.

17.2.3 Falsification of results to meet method requirements.

17.2.4 Reporting results without analysis.

17.2.5 Selective exclusion of data to meet quality control criteria (dropping calibration points).

17.2.6 Unwarranted manipulation of computer software.

17.2.7 Improper alteration of analytical conditions (changing voltages or run times).

17.2.8 Misrepresentation of quality control samples (not preparing them as samples).

17.2.9 Intentionally reporting results from one sample for those of another.

18.2.10 Reporting calibration or quality control data not linked to the reported samples.

17.3 Confidentiality

SVL's commitment to client confidentiality (including national security concerns) and any associated proprietary rights comes first and foremost. We understand the nature of doing business in a litigious society and will seek to protect our client's interest in all aspects of our work.

18.0 DATA REVIEW

SVL uses a three-tier system for data review via the LIMS. The first level is conducted by the analyst, the second level by a peer or supervisor, the third by a signatory, DCO, Technical Director or the Laboratory Director. Reviews

take place upon the review of raw data or within the LIMS (which uses a system of locks to assure data is secure from accidental overwritting). Most data is available in PDF, which can be reviewed at any work station. The process is governed by SOP SVL 2009.

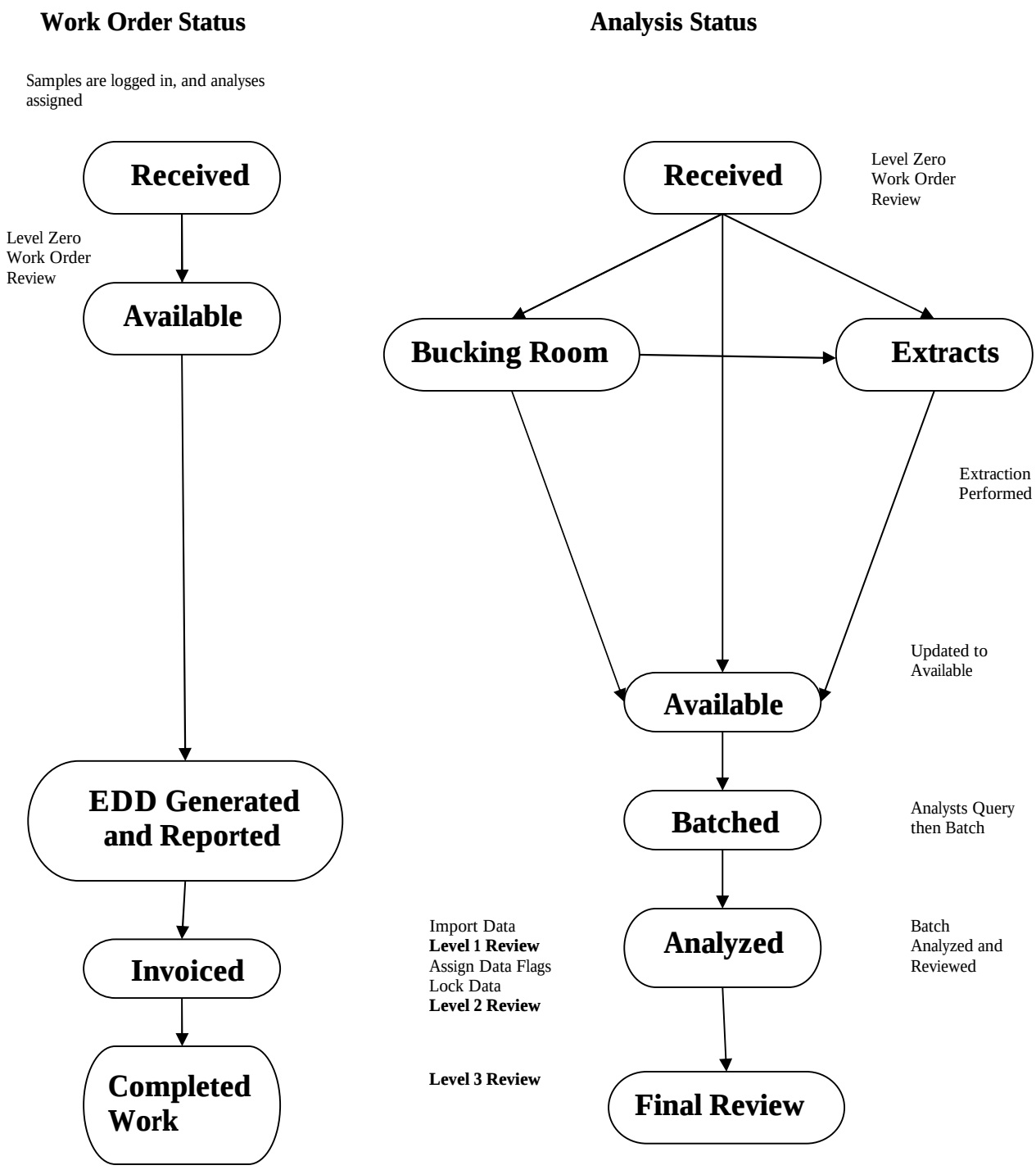
In the case that erroneous data does leave the lab, the Laboratory Director or Client Services will contact the affected clients as soon as all of the facts are available. SVL will work with the clients in seeking a new or alternative strategy to meet the client's needs.

18.1 Electronic Signatures

For all levels of review up to the final review Element provides an audit trail of who has uploaded and reviewed results. Employees are directed to log in and out of Element so that they are identified when conducting data uploads or reviews; it is not permissible to use another employee's password or misrepresent an analyst or reviewer by not logging in to a computer system under the correct username and password (see SOP SVL 1031).

The electronic signature affixed to the Final Report will be assigned by the Document Control Office dependent upon which reviewer signed the Work Order Review Checklist.

18.2 Data Review Flow Chart



19.0 REPORTING

SVL has a single standard report format for nearly all results (SVL_Sample) generated by Element. This includes a case narrative, sample report, and QC report.

Reports are also available in a number of routine and custom hardcopy formats. EDDs can be provided in ASCII, spreadsheet, and database formats, including EQWin, GIS/Key, and EnviroData Solutions. If a client has a specific format, SVL is usually able to provide data compatible with their preferred format.

Data that will be used to create EPA CLP-like deliverable packages may be done in Element or can be loaded into a third party data review and reporting system MARRS that will generate the forms required to complete a data package. SVL has the capability of providing a hardcopy and EDD format. EDDs are available in standard EPA CLP formats, as well as popular spreadsheet and database files.

20.0 AUDITS AND VERIFICATION PRACTICES

20.1 Performance Testing Program

SVL participates in two WS, two SOIL, and two WP Performance Testing (PT) studies each year. SVL uses the first WP Study to meet the DMRQA requirements of our clients. The PT samples are logged in as single-blinds and ran as if they were normal samples in all aspects. The Quality Manager is responsible for preparing all PT samples. QuiK™ Response samples are used when SVL does not pass an analyte required by our accreditation.

20.2 Internal System Audits

The Quality Manager conducts a minimum of one internal system audit per year per lab. The audit provides an overview of the implementation of procedures and policies set forth in the laboratory's QM and SOPs; ref, SOP SVL 1005. Other audits (that may be limited in scope) may be undertaken at any time in response to external audits, CARs, or at the request of the Laboratory Director.

The Quality Manager prepares an internal audit plan based on information garnered from previous audits both internal and external,

CARs, method changes, new instrumentation and requests or complaints from clients. The Quality Manager may use written checklists and/or quizzes to assess an analyst's knowledge of the QM, methods and current SVL SOPs.

The Quality Manager will interview the analyst(s) and conduct reviews of records, logbooks, and data packages.

At the close of the audit, a post-audit meeting is held to discuss the audit findings. The auditor or Laboratory Director can close a finding during this discussion if the laboratory staff can satisfactorily demonstrate that the finding is inappropriate or easily remedied.

The Quality Manager will deliver the audit report to the President, Laboratory Director, Technical Director, supervisor and appropriate staff. A report will contain at a minimum the following parameters: Date and location of the audit, personnel involved in the audit, laboratory operations audited, any minor or major findings that require corrective action (major findings require the issuance of a CAR) and the auditor's summation.

20.3 Reference Materials

Companies like ERA, High Purity, Fisher and Baker have been approved (see SVL's approved vendor list) to provide SVL with reference materials and reagents. SVL uses a second source verification for all calibrated methods. When there is not a secondary source provider available, SVL will verify and then purchase a separate lot from the primary vendor (lots must not be from the same parent batch).

20.4 Internal Quality Control Schemes

SVL has instituted a Reporting Limit Check Standard (RLCS) to verify recovery at the reporting limit; this check has been instituted at SVL for SDWA, CWA and Solid Waste analytical runs. SVL has also instituted a calibration curve verification policy where calibration standard recoveries are fitted back into the curve. A standard at the reporting level must be within 30% of the true value and the remaining standards must be within 10% of their true values. Any exception to this rule will be outlined in the appropriate SOP.

20.5 Data Audits

The Quality Manager performs a data audit of several data packages each year. Data audits can also be triggered by audits, CARs or requests from the Laboratory Director. The purpose behind the data audits is to

alert SVL to any errors, systemic problems or trends that may be developing.

21.0 MANAGEMENT REVIEW

The Management of SVL conducts a review of the adequacy of the quality system weekly. The reviews take into account reports from supervisory personnel, Client Services, Technical Directors, Document Control Officer, Systems Manager, LIMS Chemist, Quality Manager and President. Recent internal audits, external audits, the results of PT samples, changes to the volume or type of work undertaken, feedback from clients, instrumentation issues, personnel issues and CARs are a few of the items discussed. Conclusions or action items are addressed; any changes deemed necessary are then incorporated into revisions to the QM and SOPs as soon as practicable and communicated to relevant employees to provide direction for day-to-day operations. Notes from these meetings are kept in an electronic file located on our network.

22.0 CONTRACTS

SVL has established a Project/Bid Review Sheet to meet the TNI requirements of Section 4.4 “Review of Requests, Tenders, and Contracts”. Any differences between the request or tender and the contract shall be resolved before any work commences. Each contract will be acceptable to both the laboratory and the customer. Records of reviews (including significant changes) are maintained in the appropriate client files. Customers will be informed of any deviation from the contract including those by subcontractors. If a contract needs to be amended a new Project/Bid Review sheet will be utilized with all applicable parties being informed of the changes.

23.0 SUBCONTRACTING AND PURCHASING

23.1 Subcontracting

Prior to subcontracting work to another laboratory, the Laboratory Director or Client Services will ensure that the subcontracted laboratory is NELAP accredited, or is certified by the appropriate state (for the tests being subcontracted) if required. SVL will advise the customer in writing or email as to the need for subcontracting and will receive in return the client’s approval (to be placed in the client’s file). The Quality Manager will verify that the

subcontracting laboratory has an active Quality Assurance Program (QAP) that meets SVL's and our client's DQOs. The Sample Custodian is responsible for verifying that the subcontracting lab received the correct samples and that they were assigned the requested analyses. The subcontracting laboratory will be identified on the final report.

23.2 Purchasing

SVL maintains a vendor file which contains the vendors approved to supply products to SVL.

SVL ensures that purchase orders contain the required technical and quality specifications prior to submission. If a method or instrument requires specific technical and quality criteria (like grade or purity) then the Department Supervisor will ensure this is the product indicated on the purchase order. Identification of the product is by description and catalog number (see appropriate method SOPs).

SVL tests reagents and standards prior to analyzing samples and reporting data. New reagents will be used in a laboratory blank; if the QC requirements are met then those reagents are deemed to be acceptable. Standards will be diluted so as to fit into the current linear range of the instrument and prepared as a laboratory fortified blank to ensure that the standard is of sufficient quality and passes the grade and purity criteria as put forth by the manufacturer ; ref, SOP SVL 1015.

24.0 SERVICE TO THE CLIENT

SVL seeks to have an excellent working relationship with our clients. In order to monitor client's concerns, SVL will place both positive and negative feedback in the client's file. If clients do not provide feedback, Client Services will ask questions or provide clients with a written survey to assess any unspoken concerns.

24.1 Complaints

The Client Services Department strives to resolve all complaints from clients regarding analytical reports or service. Client Services will contact the appropriate Director, or Department Supervisor to investigate and resolve issues. Actions may include reanalysis of samples and/or explanations surrounding technical issues or lab procedures.

24.2 Reanalysis

Whether reanalysis is requested by a client or by SVL personnel, there must be justification for the request. The reasoning behind the justification requirement is to provide a baseline level under which the reanalysis can be compared and to provide a means of tracking quality within the lab. Reanalysis performed in order to "result hunt" is not conducted by SVL, but re-analysis performed to locate or confirm a possible error on the part of SVL or by any of the sample custodians listed on the COC, is valid. SVL will report out both values for a re-analysis if the sample results are scientifically indistinguishable and the client requests the new result or another report. Such data will be accompanied by a case narrative or data qualifier. SVL will issue a corrected report with only the re-analysis values if it can be determined that an error has occurred on the part of SVL (when this occurs a CAR must be generated). Re-analysis requested on a method that has multiple analytes shall result in the sample being re-analyzed for all of the analytes originally requested (the other analytes may not be re-reported if it is shown that they are scientifically indistinguishable from one another). Work order memos will be established when a client requests a reanalysis and may be updated throughout the reanalysis. Case narratives will be written up to explain any discrepancies between the original test and the reanalysis conducted. Samples that are reanalyzed in-house will have the reason for the request clearly identified on the reanalysis request form. Whether internal or external, the reanalysis request form must be filled out completely to assist with historical data reconstruction and to assist in writing up case narratives or CARs. See SOP SVL 2019.

25.0 TRANSFER OF ANALYTICAL REPORTS, RECORDS, and SAMPLES

In the event that SVL Analytical, Inc. (SVL) goes out of business or there occurs a transfer of ownership, the following plans will apply.

All current clients and past clients going back 5 years, longer if bound by contract, will be contacted by registered mail, return receipt requested, at their current or last known address, and made aware of the permanent closure or transfer of ownership of SVL.

Clients will be requested to respond in writing by return mail, fax or email within 10 business days with the instructions as to the final disposition of (in

the case of closure) or as to how they wish to proceed with the new ownership concerning, their reports, records and/or samples, including work that is in progress.

Options for the client may include complete transfer of all reports, records and samples to their business location, or complete destruction of all documents and samples. SVL does not take ownership of client samples at any time or under any circumstances, and title to all reports, records and samples resides with the client. SVL will not be responsible for disposal of hazardous materials.

Methods of reports and records transfer may be by hard copy purge file, hard copy reports only, or by electronic data deliverables (EDD) for all date accessible records stored in SVL's database. No customized EDDs will be available.

Should a client decide to stay with the new ownership, any business relationship between the two parties will constitute a new relationship independent of any involvement by SVL. The maintenance of reports and records, and the completion of the work in progress (but not completed by SVL) shall be under the sole control of the new owner. SVL will be relinquished from any and all responsibilities concerning the business relationship between the parties.

26.0 GLOSSARY

Calculations are for definitions may be found in SOP SVL 1028.

Acceptance Criteria: Specified limits placed upon characteristics of an item, process, or service defined in required documents.

Accuracy: The degree of agreement of a measured value with the true or expected value of the quantity of concern.

Acid Base Accounting (ABA): The Acid-Base Account is determined by calculation from the ANP and AGP results. The Acid-Base Account may be reported as the ABA, Acid Base Potential (ABP), or Net Neutralizing Potential (NNP) at a client's request.

Acid Generating Potential (AGP): The acid generating potential is established by determining three sulfur content numbers, the "Total Sulfur", "Non-Extractable Sulfur", and "Non-Sulfate Sulfur" or "Non-Sulfate Sulfur-HCl". Total Sulfur is determined from analysis of a 0.2 g aliquot taken from a sample that has undergone a 200 mesh screening. Non-Extractable Sulfur is

determined after digestion with 2N nitric acid, then filtered, and analyzed by a LECO analyzer. Non-Sulfate Sulfur is determined after digestion with hot water, then filtered, and analyzed by a LECO analyzer. Non-Sulfate Sulfur-HCl is determined after digestion with a 2:3 HCl solution, then filtered, and analyzed by a LECO analyzer.

Acid Neutralizing Potential (ANP): The amount of neutralizing bases, including carbonates, present in overburden materials is found by treating a sample with a known excess of standardized hydrochloric acid. The sample and acid are heated to insure that the reaction between the acid and the neutralizers goes to completion. The calcium carbonate equivalent of the sample is obtained by determining the amount of unconsumed acid by titration with standardized sodium hydroxide.

Aliquot: A portion of a sample.

Alkalinity: A measure of the acid-neutralizing ability of the sample.

Analytical Spike: An aliquot of sample to which a known amount of analyte has been added after sample preparation. It is a measure of the effect of the matrix of a digest or extract. It is sometimes known as a post-digestion spike.

Batch: Environmental samples that are prepared and/or analyzed together with the same process and personnel, using the same reagents. For SVL's purposes a batch will not include more than 20 samples.

Bias: A systematic error inherent in a method or caused by some idiosyncrasy of the measurement system. Temperature effects, extraction efficiencies, contamination, mechanical losses, and calibration errors create bias. Bias may be either positive or negative.

Blank: An artificial sample designed to monitor the introduction of contamination into the process. For aqueous samples, reagent water is used as a blank matrix.

Blind Sample: A sample submitted for analysis whose concentration is unknown to the analyst.

Buffers: Solutions of a weak acid and a salt of the acid or weak base and a salt of the base that are capable of maintaining pH on addition of acid or base.

Calibration: Comparison of an instrument response with a standard or a certified instrument. Commonly it is performed with a set of known standards plotted versus a response.

Calibration Blank: See Section 14.0 Quality Control.

Calibration Curve: Graphical plot of instrument response against amount of analyte in standards. The relationship can usually be modeled as linear or quadratic.

Completeness: The percentage of measurements that meet quality control acceptance criteria for requested determinations. Percentage completeness is defined by client DQOs.

Continuing Calibration Verification (CCV): See Section 14.0 Quality Control.

Continuing Calibration Blank (CCB): See Section 14.0 Quality Control.

Control Chart: A graphical plot of test results with respect to time or sequence of measurement, together with limits within which they are expected to lie when the system is in a state of statistical control.

Custody Log: A system for tracking samples from the time they enter the lab until a final report is generated.

Digestion: Solubilizing of metal analytes through heating with a variety of acids or oxidizers.

Dissolved Analytes: An aqueous sample that has been passed through a 0.45 µm filter. The filtered portion is then run for dissolved analysis.

Double Blind Sample: A sample known by the submitter but submitted to an analyst in such a way that its identification as a check sample is unknown.

Duplicate Sample: See Section 14.0 Quality Control.

Extraction: The process of removing analytes through the addition of acids or water from a solid/semi-solid matrix. SVL performs TCLP, SPLP, CA-WET and Meteoric Water Mobility extractions.

Field Blank: See Section 14.0 Quality Control.

Field Duplicate: Duplicate samples obtained in the field and analyzed in the lab to assess field precision in sampling.

Hardness: Dissolved metal content of water, expressed as calcium carbonate equivalents.

Homogeneity: The degree to which a property or substance is evenly distributed throughout a material.

Initial Calibration Verification (ICV): See Section 14.0 Quality Control.

Instrument Detection Limit (IDL): The smallest concentration detectable on a specific instrument. It is statistically determined by analysis of at least seven replicates of a blank that has not been digested.

Interference Check Sample (ICS): A sample with known concentrations of elements used to determine if the inter-element correction factors of the ICP are accurate.

Inter-element Correction Factor (IECs): The effect one element has on other elements due to wavelength overlap. These effects are accounted for and subtracted out resulting in a less biased result.

Internal Standard: Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not in the sample.

Initial Calibration Blank (ICB): See Section 14.0 Quality Control.

Instrument Performance Check (IPC) Solution: A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria. The CCV or LCS may fit this criteria.

Laboratory Control Sample (LCS): See Section 14.0 Quality Control.

Laboratory Fortified Blank (LFB): Another term for a laboratory control sample.

Laboratory Fortified Matrix (LFM): Another term for a matrix spike.

Laboratory Information Management System: A software-based laboratory and information management system that offers a set of key features that support a modern laboratory's operations.

Laboratory Reagent Blank (LRB): Another term for a method blank.

Langlier's Index: An analytical measure of the corrosivity of water.

Limit(s) of Detection (LOD): A laboratory's estimate of the minimum amount of an analyte in a given matrix that an analytical process can reliably detect in their facility.

Limit(s) of Quantitation (LOQ): The minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.

Linear Calibration Range (LCR): The calibration range over which the instrument response to analyte is linear.

Linear Dynamic Range (LDR): The concentration range over which the instrument response to analyte is linear.

Manual Integration: Anytime a chromatogram is altered by an analyst from the original software determined chromatogram, usually performed by adjusting how the baseline was assigned.

Material Safety Data Sheet: Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire and reactivity data including storage, spill and handling precautions.

Matrix: The substrate of a test sample.

Matrix Spike (MS): See Section 14.0 Quality Control.

Matrix Spike Duplicate (MSD: See Section 14.0 Quality Control.

Maximum Contaminant Levels: Regulatory action levels for primary drinking water analytes.

Mean: The sum of all observations divided by the number of observations.

Method: A body of procedures and techniques for performing an activity (e.g., sampling, chemical analysis, quantification), systematically presented in the order they are to be performed.

Method Blank: See Section 14.0 Quality Control.

Method of Standard Addition: Commonly used to determine the concentration of an analyte in a complex matrix. The matrix may contain other components that interfere with the analytical signal causing inaccuracy in the determined concentration. Known concentrations are added to a volume of sample to develop a curve based upon the interferences from that sample, so that a reliable concentration can be derived for the sample.

Method Detection Limit (MDL): The smallest concentration detectable on an instrument with 99% certainty by a specific method. It is statistically determined by analysis of seven replicates of a low-level standard, prepared in the same way as a sample.

NTU: Nephelometric turbidity unit.

Net Carbon Value (NCV): A method used in the determination of Acid Generation Potential and Acid Neutralizing Potential using the Net Carbonate Value method AGP is calculated via sulfur pyrolysis and ANP is calculated using digestion with hydrochloric acid.

Net Acid Generation (NAG): A solution of hydrogen peroxide is added to rock samples which have been reduced to pass through a -200 mesh screen. The sample and the hydrogen peroxide are heated to ensure the reaction goes to completion. The hydrogen peroxide reacts with the sulfides, carbonates and other materials in the sample to produce a net pH.

Performance Test (PT) sample: A sample, the composition of which is unknown to the laboratory is provided to test whether the laboratory can produce analytical results within the specified acceptance criteria.

pH: The negative log of activity of the hydrogen atom.

Precision: The degree of agreement of independent measurements under specified conditions.

Quality Assurance: A system of activities used to ensure defined standards of quality.

Quality Control: A system for verifying and maintaining the desired level of accuracy and precision of an analytical method.

Quality Control Sample (QCS): A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is prepared from a secondary source. The ICV fits these criteria.

Relative Standard Deviation (%RSD): The Standard Deviation divided by the Mean and multiplied by 100.

Relative Percent Difference (%RPD): The difference between two values divided by the average of the values, expressed as a percent.

Reporting Limit (RL): The smallest concentration usually reported for an analyte. It is usually at least three times the Method Detection Limit.

Reporting Limit Check Standard (RLCS): See Section 14.0 Quality Control.

Residues: Remainder after removal of water or other liquids, see solids and total solids.

Retention Time: Elapsed time between the injection of sample to the elution of the sample.

Run Logs: A log book for each instrument listing consecutively what was run, when, by whom, and what file name the raw data is filed under.

Serial Dilution: See Section 14.0 Quality Control.

Standard Operating Procedure (SOP): A written procedure that defines a laboratory operation or analytical method.

Sub-sample: A portion taken from a sample.

Standard Deviation: The square root of the variance. A measure of the average spread around the mean.

Titration: Any number of methods for determining volumetrically the concentration of a desired substance in solution by adding a standard solution of known volume and strength until the reaction is complete, usually as indicated by a change in color due to an indicator.

Total Recoverable Metals: Follow the digestive method outlined in 40 CFR 136 Appendix C Section 9.4. Results are reported as "total metals". This is SVL's default total metals method unless both total and total recoverable metals are requested.

Traceability: The ability to trace the history, application, or location of an entity (e.g., standard, reagent, sample). SVL tracks the entities from the moment it enters the premises until the time it is disposed of.

Trip Blank: See Section 14.0 Quality Control.

Tuning Solution: A solution which is used to correct instrument performance prior to calibration and sample analysis.

Variance: The value approached by the average of the sum of the squares of deviations of individual measurements from the mean.

27.0 CERTIFICATIONS

SVL maintains certification for analysis of drinking water in the following states:

Arizona
Florida
Idaho
Nevada
Washington

SVL maintains certification for analysis of environmental samples in the following states:

Arizona
California
Florida
Nevada
Washington

NELAC Certification Awarded – Primary Accreditation Florida

27.1 Copies of the Scopes of Accreditation can be located at www.svl.net .

Appendix 1 Resumes

WAYNE R. SORENSEN

PROFESSIONAL EXPERIENCE:

SVL Analytical, Inc. - Kellogg, ID 1991- Present
President / CEO - Administers company policies and formulates business strategies.

SVL Analytical, Inc. – Kellogg, ID 1987-1991
Laboratory Director: Responsible for all analytical and operational activities of the laboratory; supervised personnel

SVL Analytical, Inc. – Kellogg, ID 1973-1987
Analytical Chemist: Analyzed soils and water for metals by flame atomic absorption and graphite furnace (7000 methods), for mercury by cold vapor atomic absorption (methods 7470 and 7471); for cyanide (method 9012), fluoride (method 340.2), phosphate (method 365.2), pH (method 150.1), turbidity (method 180.1), and conductivity (120.1); analyzed soils and house dusts for lead, arsenic, cadmium; analyzed hi-vol filters for metals by flame atomic absorption; performed baseline study analyses for permitting mine sites; conducted analysis for Remedial Investigation and Feasibility Study for Bunker Hill Superfund Site..

The Bunker Hill Company - Kellogg, ID October 1969-April 1973
Supervised a large integrated mine, mill and smelter analytical laboratory and trained personnel.

Kennecott Copper, Ray Mines Division March 1968-October 1969
Chief Chemist: Supervised an assay lab, trained assayers for new analytical methods and conducted applied research.

Kennecott Copper, Western Mining Division Research Center May 1965-March 1968
Analytical Chemist: Analytical methods development and applied metallurgical research on copper.

EDUCATION:

Utah State University - Logan, UT 1958-1962
B.S. Chemistry (minor: mathematics, physics)

Salt Lake Trade Tech - Salt Lake City, UT 1965
Basic Industrial Statistics

John R. Kern

PROFESSIONAL EXPERIENCE:

SVL Analytical, Inc. - Kellogg, ID October 2007 - present

Laboratory Director: Manage and direct the activities of the laboratory; establish ethical norms; evaluates personnel performance; conduct QA/QC reviews of incoming work and completed reports; work with the QA Manager to evaluate compliance with SOPs and methods.

P3 Scientific - Oakdale, MN September 2005 - April 2007

Laboratory Manager – Chemistry: Management and operation of a laboratory at a cGMP/GLP compliant CRO, providing analytical (organic and inorganic analysis) and microbial services to the chemical industry.

Arena Pharmaceuticals, - Inc. San Diego, CA January 2003 - August 2005

Associate Director, Analytical Chemistry – Pharmaceutical Development: Direct the analytical chemistry laboratory within the pharmaceutical development unit at a start-up biotech/pharmaceutical company.

LC Resources - McMinnville, OR 1991 - 2003

Laboratory Director: Started and built up a contract research laboratory specializing in HPLC and LC/MS/MS services for the pharmaceutical and chemical industries. Oversaw the growth of the lab from 2 to 20 employees, with annual sales of over 3 million. Directly responsible for the day-to-day operation of the lab including project management, experimental design, preparation of proposals, client interface, contracts, budget, oversight of QA and QC departments, SOP and protocol preparation. This position involved extensive interaction with major pharmaceutical companies in negotiating contracts, planned studies, allocating resources, report preparation, and discussing technical issues. Experience was also gained in the direction of projects involving analysis of a wide variety of pharmaceutical products from OTC to complex proteins, and drugs in biological matrices.

Syntex USA, Inc. – Palo Alto, CA 1984 - 1991

Senior Chemist: Development of analytical methods for the analysis of active pharmaceutical ingredients (AIP) and determining release specifications. Prepared analytical sections for IND and NDA applications. Supervised laboratory staff and project team membership.

EDUCATION:

Montana State University - 1982

M.S. Chemistry

Eastern Michigan University - 1978

B.S. Biochemistry

Professional Memberships:

American Chemical Society since 1980

Professional Honors:

Syntex Research Fellow, University of Illinois, 1984
Research on chiral separations under the direction of Dr. William Pirkle

KIRBY L. GRAY

PROFESSIONAL EXPERIENCE:

SVL Analytical, Inc. - Kellogg, ID Dec. 2004-present
Technical Director - Conducts QA/QC reviews of commercial and EPA (ILMO5.4) incoming work and completed reports: supervises laboratory activities related thereto: primary contact with EPA (SMO); verifies SDGs, and responsible for MARRS (electronic data deliverable system) in coordination with DCO prior to reporting.

SVL Analytical, Inc. - Kellogg, ID March 1987-2004
Inorganic Instrumental Chemistry Department Supervisor -- Responsible for sample analysis by ICP, GFAA, FLAA, IC and CVAA.

Radersburg Mining Co. - Toston, MT September 1986-March 1987
Chemist: -- Responsible for fire assay, FLAA, and sample preparation.

IDHW, State of Idaho - Kellogg, ID August1986
Environmental Technician: --Operated X-ray fluorescence meter and collected soil samples.

Sunshine Mining Co. - Kellogg, ID May 1984-May 1986
Chemist -- Responsible for fire assay, FLAA, and classical chemistry.

The Bunker Hill Co. - Kellogg, ID May 1972-May 1982
Material Recovery Supervisor -- Responsible for operation and maintenance of water treatment plant, sulfuric acid plant, baghouse, cadmium refinery, and electric reverbatory furnace at a lead smelter.

EDUCATION:

University of Idaho - Moscow, ID Sept 1968-May 1972
B.S. Geological Engineering

North Idaho College-Coeur d'Alene, ID Sept 1966-June 1968
Engineering major

Nan Wilson

PROFESSIONAL EXPERIENCE:

SVL Analytical, Inc. - Kellogg, ID March 2003 – present

Technical Director October 2007 – present: Conducts QA/QC reviews of incoming work and completed reports, supervises laboratory activities.

Laboratory Director - October 2006—October 2007: Manage and direct the activities of the laboratory; establish ethical norms; evaluates personnel performance; conduct QA/QC reviews of incoming work and completed reports; work with the QA department to evaluate compliance with SOPs and methods.

QA Coordinator - April 2006-October 2006: maintain Quality Systems, draft & approve SOPs, coordinate Quality System Audits, coordinate PT testing.

QA Chemist - September 2004 – March 2006: maintain Quality Systems, draft SOPs, assisted with Quality System Audits.

Safety Director - September 2004-October 2006: maintain Chemical Hygiene Plan, coordinate safety training and record keeping.

LC Resources—McMinnville, OR September 1997-January 2003

Manager, Pharmaceutical Analysis - January 2001-January 2003: Supervised HPLC method development; coordinated work for chemists and technicians; directed method validation; wrote SOPs and validated protocols; prepared client reports; trained chemists and technicians on SOPs and computer software; presented data and reports; responsible for client contact; administered Millennium32 chromatography software.

Chemist - September 1997-January 2001: Developed HPLC methods for pharmaceuticals; operated, calibrated, and maintained HPLC, UV/Vis, pH meters, balances, pipettes; wrote client reports; administered Millennium32 chromatography software.

Willamette University - Salem, OR 1995-1996

Laboratory Teaching Assistant - Assisted organic chemistry students in successfully carrying out lab experiments.

EDUCATION:

Willamette University - Salem, OR 1992-1996

B.A. Chemistry and Russian

Simferopol State University - Simferopol, Ukraine 1995

Semester abroad

Brandon A Borgias

PROFESSIONAL EXPERIENCE:

SVL Analytical, Inc. – Kellogg, ID 1991-Present
Systems Manager, Computational Chemist – Oversees the Laboratory's Information Management System (LIMS) and works with our clients on custom reporting and electronic deliverables.

Cray Research– San Ramon, CA Jan 1989-1990
Software Technical Support Analyst 0 Co-administrator of network, composed of eight file servers and over 50 client work stations distributed throughout the western U.S. Unix (Sun OS and Cray UNICOS) operating systems experience

University of California, UCSF – San Francisco, CA 1985-1989
Postdoctoral Scholar – Developed computer programs (FORTRAN) for the refinement and analysis of macromolecular structure. VAX, Sun, and Cray computers and VMS and UNIX operating systems.

EDUCATION:

University of California, Berkley – Berkley, CA 1979-1985
Ph.D. Chemistry

Reed College – Portland, OR 1975-1979
B.S. Chemistry/Physics

MICHAEL S. DESMARAIS

PROFESSIONAL EXPERIENCE:

SVL Analytical, Inc. - Kellogg, ID Oct. 2006 - Present

Quality Assurance Manager -- Coordinates and develops quality assurance and training programs for the laboratory, maintains laboratory accreditations, writes standard operating procedures, reviews data, conducts audits, performs root cause analysis.

SVL Analytical, Inc. - Kellogg, ID June 2004 – Oct. 2006

Chemist Inorganic Instrument Department – Responsible for analysis of samples for trace metals by EPA methods 200.7 and 6010B. Interprets and reports data.

SVL Analytical, Inc. - Kellogg, ID April 2004 – June 2004

Chemist Organic Chemistry Department – Responsible for analysis of samples for pesticides and PCBs by EPA methods 608, 8081A, and 8082. Interprets and reports data.

U.S. Army Engineer District-Alaska – Umiat, AK May 2003 - Sept. 2003

Alaska Dept. Environmental Conservation approved field chemist. Established field laboratory, developed and implemented QA/QC under USACE and ADEC requirements. Surveyed, sampled and tested soils and waters under a Total Environmental Restoration Contract (TERC).

North Creek Analytical Oct. 1997 - Dec. 2002

Senior Metals Chemist and Health/Safety Officer - Developed, revised and implemented safety and HAZMAT procedures. Developed and documented standard operating procedures. Maintained analytical instrumentation and analyzed samples for trace metals (ICP, AA and GFAA) and BTEX/GRO.

EDUCATION:

Eastern Washington University – Cheney, WA 1996-1997

Graduate coursework in Hydrology and Fisheries.

Washington State University – Pullman, WA August 1993-June 1995

B.S. in Physical Science (emphasis in Chemistry, Geology, and Environmental Science).

Yakima Valley Community College 1991

A.A.

Dianne Gardner

PROFESSIONAL EXPERIENCE:

SVL Analytical, Inc. - Kellogg, ID May 2011 - Present

Classical Chemistry Department Supervisor -- Supervises the staff and operation of SVL's TDS, Nutrient, TKN, cyanide, NOX/NH4, Leco, and extraction labs. Ensures that EPA, ASTM and Standard Method methods are correctly followed. Requisitions instrumentation and supplies. Reviews manually entered lab data prior to entry into Element (LIMS). Reviews level 1 data entry prior to submission to DCO for reporting.

SVL Analytical, Inc. -- Kellogg, ID January 2007- May 2011

Instrument Department Analyst – Responsible for analysis of digested samples by ICP-AES and ICP-MS for trace metals by EPA methods 200.7, 200.8, 6010B, 6020B, and EPA SOW ILMO5.4. Interprets and up loads data to Element (LIMS). Back up analyst for GFAA.

SVL Analytical, Inc. - Kellogg, ID – April 2004 to January 2007

Classical Chemistry Department Chemist—Analyzed soil and aqueous samples for Cyanide.

EDUCATION:

Cedarville University – Cedarville, OH June 1987

B.A. Chemistry

North Idaho College – Coeur D'Alene, ID 1997

Coursework in Microbiology

DANNY J. SEVY

PROFESSIONAL EXPERIENCE:

SVL Analytical, Inc. - Kellogg, ID Dec 2004-present
Instrument Department Supervisor – Supervises staff and operation of SVL's ICP-AES, ICP-MS, CVAA, GFAA, FLAA, and IC labs and their respective sample preparation labs. Ensures that EPA and Standard Method methods are correctly used, including EPA SOW ILMO5.4. Approves lab data in Element (LIMS) prior to submission to DCO for reporting.

SVL Analytical, Inc. - Kellogg, ID 1996-2004
Inorganic Instrument Operator -- Performs metals analysis by ICP and IC.

SVL Analytical, Inc. - Kellogg, ID 1994-1996
Classical Chemistry Analyst -- Performed classical Wet Chemistry analyses on water and soil sample, including the preparation and analysis of cyanide and nitrate/nitrate (as N) tests for soil and water samples.

SVL Analytical, Inc. - Kellogg, ID 1988-1994
Instrument Operator -- Analyzed samples using Cold Vapor Atomic Absorption and Ion Chromatography

SVL Analytical, Inc. - Kellogg, ID 1987-1988
Laboratory Technician -- Performed inorganic sample preparation and operated CVAA and GFAA instruments.

EDUCATION:

Perkin Elmer April 2008
Inorganic Workshop Series

Perkin Elmer July 2004
ICP-MS with Elan Software & Elan DRC Accessory Training Course

Perkin Elmer November 2001
Optima Instrument Series with ICP WinLab Software

OI Corporation January 2001
Operation of FS-3000 Auto-analyzer

North Idaho College - Coeur d' Alene, ID 1989-1990
Chemistry and Mathematics courses

Heather Green

PROFESSIONAL EXPERIENCE:

SVL Analytical, Inc. -- Kellogg, ID June 2011 – Present
Acid/Base Department Supervisor – Responsible for analysis and technicians within the department. Responsible for method interpretation and development.

SVL Analytical, Inc. -- Kellogg, ID Sept. 2010 – June 2011
Leco Analyst – Responsible for the following methods: ABA, AGP, ANP, NCV, NAG, total carbon and total sulfur.

SVL Analytical, Inc. -- Kellogg, ID Sept. 2009 – Sept, 2010
Classical Chemistry Floater – Responsibilities will include becoming certified in multiple disciplines in order to back-up primary analysts and technicians.

Bio Medics Plasma Center - Moscow, ID – Nov. 2007 to May 2009
Duties included: calibrating equipment, screening donors, conducting historical surveys and performing various test on blood samples.

Worked under highly regulated guidelines with strict adherence to SOPs.

EDUCATION:

University of Idaho, Moscow, ID 2005-09
B.S. Microbiology

Sherry Maine

PROFESSIONAL EXPERIENCE:

SVL Analytical, Inc. - Kellogg, ID Sept. 2011 - Present
Safety/Hazmat Officer - Responsible for revising the Chemical Hygiene Plan annually, conducts safety training and oversees response teams. Other duties include providing accident reports to the state and overseeing SVL's hazardous waste program (including setting up 8-hour refresher courses annually).

SVL Analytical, Inc. - Kellogg, ID Nov. 2005 - Present
Classical Chemistry Department Chemist—Analyzes and interprets soil and aqueous samples for: Total and ortho phosphorous, COD, TOC/TN, sulfide, MBAS, ammonia, nitrate/nitrite, TKN, hexavalent chromium, TOM, LOI and gravimetric silica.

UNR-Chem. – Reno, NV Aug. 2001 – June 2004
She synthesized and analyzed compounds to determine their chemical structure. She also tested soils and water for inorganic analysis.

Nestle/Simplot – Nampa, ID April 1999 – July 2001
Quality Assurance Technician – Tested and evaluated product throughout entire course of production.

ESI – Grandview, ID Dec. 1995 – Aug. 1997
Hazardous Waste Technician - Identified incoming hazardous waste samples (GC and ICP technician). Assisted in the development of formulas to stabilize hazardous waste in accordance with federal standards.

EDUCATION:

University Of Nevada – Reno, NV 2004
M.S. Chemistry

Northwest Nazarene College – Nampa, ID 1995
B.S. Chemistry

Southern Nazarene University – Bethany OK 1986-1989
Took classes towards a nursing degree.

CRYSTAL SEVY

PROFESSIONAL EXPERIENCE:

SVL Analytical, Inc. - Kellogg, ID 2006-Present
Sample Receiving Department Supervisor— Supervises SVL's sample receiving staff and is Sample Custodian for samples received under EPA SOW ILMO5.4. Responsible for setting up Work Orders within Element (LIMS), case narratives and point of contact with clients and their representatives. Works closely with SVL's Client Services and Technical Director to ensure that projects are setup and priced correctly.

SVL Analytical, Inc. - Kellogg, ID 1996-2006
Sample Receiver—Verifies sample temperature, integrity and security on receipt; creates laboratory jobs; ensures proper sample storage prior to analysis supervises sample disposal; ships sample containers to clients.

MELBA BENCICH

PROFESSIONAL EXPERIENCE:

SVL Analytical, Inc. - Kellogg, ID, February 1988 - Present
Document Control Manager – Supervises data reporting using Element (LIMS) for commercial clients and SDG reporting for EPA's CLP SOW ILMO5.4.

Shoshone Insurance – Kellogg. ID, 1984 – 1988
Duties included accounting, customer service relations and updating manuals

Travel People – Coeur d' Alene, ID, 1982 – 1984
Travel Consultant

Farmer's Insurance – Kellogg, ID 1982-1984
Duties included accounting, customer service relations and updating manuals

The Bunker Hill Company – Kellogg, ID, 1974 – 1981
Data Control Analyst

EDUCATION:

North Idaho College – Coeur d' Alene, ID, 1967 – 1968

General studies

International Correspondence School, 1980

Mathematics

28.0 Quality Manual Releases

Date
January 2010
January 2011
February 2012
February 2013
February 2014

ARCADIS

ALS SOPs

ALS Standard Operating Procedure

DOCUMENT TITLE:	SYNTHETIC PRECIPATATION LEACHING PROCEDURE (SPLP) FOR THE ANALYSIS OF METALS AND SEMI-VOLATILE ORGANICS
REFERENCED METHOD:	SW 1312
SOP ID:	668
REV. NUMBER:	5
EFFECTIVE DATE:	NOVEMBER 6, 2012

ALS Environmental

ALS STANDARD OPERATING PROCEDURE 668 REVISION 5

TITLE: SYNTHETIC PRECIPITATION LEACHING PROCEDURE (SPLP) FOR THE ANALYSIS OF METALS AND SEMIVOLATILE ORGANICS -- METHOD SW1312

FORMS: APPENDIX A, B, C, D

APPROVED BY:

TECHNICAL MANAGER_____ DATE _____

QUALITY ASSURANCE MANAGER_____ DATE _____

LABORATORY MANAGER_____ DATE _____

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) and the method it references -- SW-846 Method 1312 -- are designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. Application of these procedures to matrices other than those specified will be handled individually to simulate the leaching procedure as best as possible.

Procedures for ZHE SPLP extractions are described in SOP 669.

2. SUMMARY

For liquid wastes (i.e., <0.5% solids), the sample is filtered through a 0.7μm glass fiber filter, and the filtrate is defined as the SPLP leachate.

For samples containing ≥0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis. If necessary, the particle size of the solid phase is reduced. The solids are then leached with an amount of extraction fluid (the extraction fluid employed is a function of the region of the country where the sample site is located, and of the type of matrix and analyses required), equal to twenty (20) times the weight of the solid phase. Following the SPLP extraction, the leachate is separated from the solids by filtration through a 0.7μm filter.

If a liquid phase was present in the sample and set aside as described above, then this liquid is combined with the leachate from the solid phase, if the two are miscible, before metals or semivolatile organic preparation for analysis. If the liquid and the leachate are not miscible, the liquid and the leachate are analyzed separately, and the results are mathematically combined to yield a volume-weighted average concentration.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysts must demonstrate the capability to generate and interpret results acceptably to utilize this method. Demonstration of performance may include Supervisory/training review, results of precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 ALS's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede ALS standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the file documentation indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notifying the technician/analyst who performed the work of the errors and documentation of the measures taken to correct those errors.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by processing and analyzing method blanks.

5. APPARATUS AND MATERIALS

Extraction vessels and filtration devices shall be made of inert materials that will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) are to be used only when evaluating the mobility of metals.

5.1 Rotary tumbler with 30±2rpm capability, Associated Design and Manufacturing Model 3740 or equivalent

5.2 pH meter, accurate to ±0.05 pH units @ 25°C
Meter must be calibrated prior to use (see Form 825).

5.3 Pressure filtration device, Associated Design and Manufacturing Model 3750-LHWF or equivalent. A.K.A. “lunar lander”.

5.4 Fiber filters, borosilicate glass, Gelman™ #66256, 0.7µm nominal or equivalent

NOTE: The glass fiber shall contain no binder materials and shall have an effective particle size of 0.6 to 0.8µm. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1.0M HNO_3, followed by three consecutive rinses with deionized water (a minimum of 1000mL per rinse is recommended). Glass fiber filters are

fragile and should be handled with care.

5.5 Bottle extraction vessel, 2L or slightly larger. Borosilicate glass, 2200mL Kontes™ #332100-021 or equivalent. If PVC coated for safety, do not place in kiln. HDPE plastic, 2000mL Eagle Picher #EP150-02WM or equivalent

ALS typically uses disposable HPDE extraction bottles for metals and semivolatile organics. The use of HDPE extraction bottles has been demonstrated to generate leachates that are free of contaminants for the analyses being conducted.

5.6 Balance, accurate to within ±0.01g

5.7 Beakers or Erlenmeyer flasks, glass 500mL (or 4.5oz plastic cups)

5.8 Watch glass, appropriate diameter to cover beaker or Erlenmeyer flask (or cap for plastic cup)

5.9 Carboys for containerizing extraction fluids

5.10 Stirring hot plate, with magnetic stir bar

5.11 Graduated cylinders, sized as appropriate

5.12 Centrifuge

5.13 Drying oven, capable of maintaining 100±20°C

6. REAGENTS AND STANDARDS

6.1 Water, of sufficient purity that target analytes or interferences are not observed at levels of interest for the analytes of interest. For semivolatile organics and metals analysis, laboratory deionized (DI) ASTM Type II water meets the definition of reagent water. Prior to being used for this procedure, this water is filtered through a Millipore Synergy 185® filtration system for further purification.

6.2 Sulfuric acid (H_2SO_4), used in combination with nitric acid to adjust pH of leaching solution.

6.3 Nitric acid (HNO_3), used in combination with sulfuric acid to adjust pH of leaching solution, as well as to prepare 1N HNO_3 for rinsing metals from containers and filters.

6.4 Sulfuric acid/nitric acid (60/40% w/w). Carefully mix 60g of concentrated sulfuric acid with 40g of concentrated nitric acid. If preferred, a more dilute acid mixture may be prepared and used to more easily adjust pH of the extraction fluids.

6.5 **SPLP Extraction fluid 1**: Make by adding the 60/40 weight percent mixture of sulfuric and nitric acids (or a suitable dilution) to water until the pH is 4.20 ±0.05. This fluid is used to determine the leachability of soil from a site that is east of the Mississippi River, and the leachability of wastes and wastewaters.

6.6 **SPLP Extraction fluid 2**: Make by adding the 60/40 weight percent mixture of sulfuric acid and nitric acids (or a suitable dilution) to water until the pH is 5.00 ±0.05. This fluid is used to determine the leachability of soil from a site that is west of the Mississippi River.

6.7 **SPLP Extraction fluid 3**: This fluid is laboratory deionized water and is used to determine cyanide leachability.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 All samples should be collected using an appropriate sampling plan. Since samples that are predominantly liquid may not have enough solids to obtain 100g by filtration, several hundred grams of sample may be necessary to properly conduct this procedure.

7.2 Chemical preservatives are not added to solid samples. Some liquid samples may contain residual chlorine and the free chlorine should be deactivated with sodium thiosulfate or another dechlorinating reagent while in the field. Preservatives shall not be added to samples before extraction.

7.3 Samples should be collected in Teflon-lined septum capped bottles and stored at 4±2°C. Samples may be refrigerated unless refrigeration results in irreversible physical change of the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

7.4 SPLP leachate should be prepared for analysis and analyzed as soon as possible following extraction. Leachates or portions of leachates for metallic analyte determinations must be acidified with nitric acid to a pH<2, unless precipitation occurs. Refrigeration is generally the only preservation technique applied to the leachates intended for semivolatile organic analysis. Maximum hold times are:

MAXIMUM HOLD TIMES (DAYS)

Leachate Analysis	From Field Collection to SPLP Leaching	From SPLP Leaching to Preparation for Analysis	From Preparation to Analysis
Semivolatile organics (including Pesticides, Herbicides)	14	7	40
Mercury (Hg)	28	NA	28
Metals (except Hg)	180	NA	180

NA=Not Applicable

8. PROCEDURES

8.1 PRELIMINARY EVALUATION

Preliminary evaluation includes: (1) determination of the percent solids (8.1.1); (2) determination of whether the sample contains insignificant solids and is, therefore, its own leachate after filtration (8.1.2); (3) determination of whether the solid portion of the sample requires particle size reduction (8.1.3) and (4) determination of which extraction fluid is to be used for the nonvolatile SPLP extraction of the waste (8.1.4).

Select samples to be analyzed and record on benchsheet. Perform preliminary SPLP evaluations on a minimum 100g aliquot of sample, assuming adequate volume of sample has been provided (notate on benchsheet if otherwise); this aliquot may not actually undergo SPLP extraction.

8.1.1 DETERMINATION OF PERCENT SOLIDS
PHASE SEPARATION

8.1.1.1 Percent solid is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out under applied pressure, as described below. Visual inspection may be sufficient for this determination.

If the sample will obviously yield no liquid when subjected to pressure filtration (i.e., it is 100% solids), then proceed to Section 8.1.3 - Particle Size Reduction Determination.

8.1.1.2 **Phase Separation**. If the sample is liquid or multiphasic, liquid/solid separation is required to make a preliminary determination of percent solids. Phase separation involves the filtration device discussed in Section 5.3, and is accomplished per the procedure outlined below:

8.1.1.2.1 Weigh the filter paper for each sample and record this weight on the benchsheet (Form 623). Weigh the collection flask for each sample and record this weight on the benchsheet. Acid wash the filter if evaluating the mobility of metals (5.4).

Place the filter on the support screen. Assemble the filtration device.

8.1.1.2.2 Transfer an aliquot of the waste (100g minimum) into a beaker. Record the combined weight of the sample, beaker and spatula on the benchsheet.

8.1.1.2.3 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If centrifugation is used, then the liquid should be decanted and filtered, followed by filtration of the solid portion of the waste through the same filtration system.

8.1.1.2.4 Quantitatively transfer the waste sample to the filtration device (liquid and solid phases).

8.1.1.2.5 After transferring the sample to the filtration

device, place the spatula in the beaker and record the combined weight of both. Then continue with the calculations prompted on the benchsheet.

8.1.1.2.6 Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4±2°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm to room temperature before filtering.

8.1.1.2.7 Gradually apply vacuum or gentle pressure of 1-10psi, until air or pressurizing gas moves through the filter. If gas or air does not move through the filter at this range of pressures and if no additional liquid has passed through the filter in a 2-minute interval, slowly increase the pressure in 10psi increments to a maximum pressure of 50psi. **Note that instantaneous application of high pressure can rupture the glass fiber filter and may cause premature plugging.**

If after each incremental increase of 10psi, the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in a 2-minute interval, proceed to the next 10psi increment.

When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50psi (i.e., filtration does not result in any additional filtrate within a 2-minute period), stop the filtration.

8.1.1.2.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase.

Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. However, even after applying vacuum or pressure filtration as outlined previously, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. **Do not**

replace the original filter with a fresh filter under any circumstances; use only one filter.

8.1.1.2.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (8.1.1.1) from the total weight of the filtrate-filled container; record on benchsheet.

8.1.1.2.10 Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase (8.1.1.9) from the weight of the total waste sample; record on benchsheet.

8.1.1.3 Calculate the percent solids as follows:

$$\%\ \text{solids} = 100 * \frac{\text{weight of solids (8.1.1.10)}}{\text{total weight of waste (from benchsheet)}}$$

8.1.2 DETERMINATION OF INSIGNIFICANT SOLIDS

If the percent solids as determined above (8.1.1.3)is equal to or greater than (≥) 0.5%, then proceed either to Section 8.1.3 (particle size reduction determination) or continue as outlined below (8.1.2.1), if it is noticed that a small amount of the filtrate is entrained in the wet filter.

If the percent solids determined (8.1.1.3) is less than (<) 0.5%, then proceed to Section 8.2 (Aliquots for Leaching).

8.1.2.1 Remove the solid phase and filter from the filtration apparatus.

8.1.2.2 Dry the filter and solid phase at 100±20°C until two successive weighings yield the same value (±1%). Record the final weight.

NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. If it is suspected that the material is flammable, drying in the hood overnight is recommended. When the filter paper is dry, re-weigh and calculate the % solids with the new value. This Step is performed when it is suspected that the weight from the moisture in the filter paper has caused the % solids value to rise above 0.5%. Perform this Step only in borderline cases.

8.1.2.3 Calculate the percent dry solids as follows:

$$\%\,\text{dry solids} = 100 * \frac{\text{(dry waste + filter) - (initial weight of filter)}}{\text{initial weight of waste (8.1.1.6 or 8.1.1.8)}}$$

8.1.2.4 If the percent dry solid is < 0.5%, then proceed to Section 8.2 if the nonvolatile SPLP is to be performed.

If the percent dry solid is ≥0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 8.1.3). **The portion of sample that has been dried is not to be used in the leaching procedure.**

8.1.3 PARTICLE SIZE REDUCTION DETERMINATION

8.1.3.1 Using the solid portion of the sample, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1cm^2, or is smaller than 1cm in its narrowest dimension (i.e., is capable of passing through a 9.5mm [0.375 inch] standard sieve). If the particle size is larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above.

8.1.3.2 Note that the surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

8.1.3.3 Safety concerns such as dust control may preclude the grinding of samples for particle size reduction. These safety concerns must always be addressed before attempting to grind any sample. Generally due to health and safety concerns, grinding to reduce particle size is not practiced in the extractions area. Samples requiring particle size reduction have been sent to an appropriate facility before an extraction was performed.

8.1.3.4 If a particle size reduction of the solid portion of the waste is required, continue as follows:

8.1.3.4.1 Prepare the waste for extraction by crushing, cutting or grinding the solid portion of the waste to a suitable surface area or particle size.

8.1.3.4.2 Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4±2°C prior to particle size reduction.

8.1.3.4.3 The means used to effect particle size reduction must not generate heat in and of itself.

8.1.3.4.4 Work carefully and quickly, as exposure of the waste to the atmosphere should be avoided to the extent possible.

8.1.3.4.5 Note that sieving of the waste is not normally required. If sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth and similar) waste materials. Actual measurement of surface area is not recommended.

If the waste as received passes a 9.5mm sieve, quantitatively transfer the solid material into an extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to 8.4 - Tumbling.

8.1.3.4.6 When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into the extractor bottle. Include the filter used to separate the initial liquid from the solid phase. Then proceed to 8.3 - Filtration..

8.1.4 EXTRACTION FLUID DETERMINATION

If the solid content of the waste is ≥0.5%, then determine the appropriate fluid for the nonvolatiles extraction as follows:

8.1.4.1 For soils, if the sample is from a site that is east of the Mississippi River, Extraction fluid #1 should be used. If the sample is from a site that is west of the Mississippi River, Extraction fluid #2 should be used.

8.1.4.2 For wastes and wastewater, Extraction fluid #1 should be used.

8.1.4.3 For cyanide-containing wastes and/or soils, Extraction fluid #3 (reagent water) must be used, because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

8.2 DETERMINATION OF ALIQUOTS FOR LEACHING

8.2.1 Label a 2000mL container with work order number, sample number, and fluid number (for metals, rinse the container with 0.1N HNO_3, followed by a rinse with deionized water). For each reagent blank, label a container with the date of tumbling, reagent blank number and fluid number.

8.2.2 Determine the number of analyses to be performed upon each sample: Herbicides, organochlorine pesticides, and semivolatiles analysis each require 100mL of tumbled fluid. Metals analysis requires 50mL of tumbled fluid. Each analysis also requires one (1) matrix spike sample/fluid/day tumbled, so these amounts may be doubled to ensure sufficient amount of fluid for all analyses and matrix spike quality control samples.

Each analysis also requires a reagent blank/fluid/day tumbled, which consists of the appropriate fluid placed in a container (no solid added) and tumbled with the samples. The reagent blank should also be put on the benchsheet and carried through the tumbling/filtering/extracting (and analysis) process.

The amount of fluid added to the sample is equal to 20 times the weight of the solid (e.g., 20g of sample requires 400mL of fluid).

8.2.3 If the aliquot of the sample used for the preliminary evaluation was determined to be 100% solid (8.1.1.1), then that aliquot can be used for the nonvolatile extraction (assuming that aliquot is sufficient to generate enough leachate to support the requested analyses).

Do not use leach solid that was dried in the oven.

8.2.4 The amount of solid necessary is dependent upon whether a sufficient amount of leachate will be produced to support the required analyses. If an adequate amount of solid remains, proceed with the nonvolatile SPLP extraction (Section 8.4).

A minimum sample size of 100g (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content (8.1.1.3) of the waste sample, whether the initial liquid phase of the waste will be miscible with the aqueous leachate of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough SPLP solids should be generated for extraction such that the volume of leachate will be sufficient to support all of the analyses required. Generally, 100g sample to 200mL leachate is sufficient to accomplish this.

If the amount of leachate generated by a single SPLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed, and the leachates from each combined and aliquoted for analysis

8.2.5 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid), weigh out a subsample of the waste (100g minimum) and proceed to Section 8.3 – Filtration.

8.2.6 If the sample is liquid or multiphasic, liquid/solid separation is required as

outlined in Section 8.1.1.2..

8.2.7 Weigh out an aliquot of the sample (100g minimum) and record the weight. If the waste contains <0.5% dry solids (Section 8.1.2.3), the liquid portion of the waste, after filtration, is defined as the TCLP leachate. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required.

8.2.8 For wastes containing ≥0.5% solids, use the percent solids information obtained in Section 8.1.1.3 to determine the optimum sample size (100g minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP leachate.

8.2.9 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the sample is centrifuged, the liquid should be decanted and filtered, followed by filtration of the solid portion of the waste through the same filtration system.

8.3 FILTRATION

8.3.1 Pre-weigh the container that will receive the filtrate; record weight.

8.3.2 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Section 5.4).

NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

8.3.3 Quantitatively transfer the sample (liquid and solid phases) to the filter holder. Spread the sample evenly over the surface of the filter. If filtration of the waste at 4±2°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm to room temperature in the device before filtering.

NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 8.3.6, to determine the weight of the waste sample that will be filtered.

8.3.4 Gradually apply vacuum or gentle pressure of 1-10psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10psi increments to a maximum of 50psi. **Note Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.**

8.3.5 When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50psi (i.e., filtration does not result in any additional filtrate within a 2-minute period), stop the filtration.

8.3.6 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in the Section 8.2, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. **Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.**

8.3.7 Weigh the filtrate; record weight.

8.3.8 If the sample contains <0.5% dry solids, proceed to Section 8.5 - Preparation for Analysis.

If the sample contained no initial liquid phase, the filtrate is defined as the SPLP leachate; proceed to Section 8.5 - Preparation for Analysis.

8.3.9 EXTRACTION FLUID ALIQUOT DETERMINATION
Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (8.1.1.3)} \times \text{weight of waste filtered (8.3.3)}}{100}$$

8.4 EXTRACTION (TUMBLING)

8.4.1 Slowly add the calculated amount of appropriate extraction fluid to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal).

8.4.2 Secure the extractor bottle in the rotary tumbler, and rotate at 30±2 rpm for 18±2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23±2°C during the extraction period. SOP 663 describes the procedures for monitoring tumbler revolutions and room temperature.

NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically vented (e.g., after 15 minutes, 30 minutes, and 1 hour), into a hood.

8.4.3 Following the 18±2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter.

8.4.4 For final filtration of the SPLP leachate, the glass fiber filter may be changed, if necessary, to facilitate filtration.

Filter(s) shall be acid-washed (see Section 5.4) if evaluating the mobility of metals.

8.4.5 Following collection of the SPLP leachate, the pH of the leachate should be recorded. Immediately aliquot and preserve the leachate for analysis.

8.4.6 The liquid phase may now be either analyzed (8.5) or stored at 4±2°C until time of analysis. If miscible, the initial liquid phase may be combined with the SPLP leachate. If the initial liquid phase of the waste is not or may not be compatible with the filtrate, do not combine these liquids. Although they are collectively defined as the SPLP leachate, they are to be analyzed separately, and their analysis results combined mathematically (8.5.2).

8.5 PREPARATION FOR ANALYSIS

8.4.1 Metals aliquots must be acidified with nitric acid to pH<2. If precipitation is observed upon addition of nitric acid to a small aliquot of the leachate, then the remaining portion of the leachate for metals analyses shall not be acidified, and the leachate shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4±2°C) until analyzed.

8.4.2 The SPLP leachate shall be prepared and analyzed according to appropriate analytical methods. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ±0.5%), conduct the appropriate analyses, and combine the results mathematically by using a volume-weighted average as shown below:

$$\text{Final Analyte Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = volume of the first phase (L)

C_1 = concentration of the analyte of concern in the first phase (mg/L)

V_2 = volume of the second phase (L)

C_2 = concentration of the analyte of concern on the second phase (mg/L)

9. QUALITY CONTROL

9.1 A minimum of one blank (using the same extraction fluid as used for the samples) must be analyzed for every 20 extractions that have been conducted in an extraction vessel. No more than 20 field samples may be included in a batch.

9.2 A matrix spike shall be performed for each waste type (e.g., wastewater treatment

sludge, contaminated soil, etc.). A minimum of one matrix spike must be analyzed for each analytical batch. As a minimum, follow the matrix spike addition guidance provided in each analytical method.

9.2.1 Matrix spikes are to be added after filtration of the TCLP leachate and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

9.2.2 In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may not be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal volume of TCLP leachate as that which was analyzed for the unspiked sample.

9.2.3 Matrix spike recoveries are calculated by the following formula:

$$\%R\ (\%\ \text{Recovery}) = 100\ (Xs - Xu)/K$$

where:

Xs = measured value for the spike sample

Xu = measured value for the unspiked samples

K = known value of the spike in the sample

10. DEVIATIONS FROM THE METHOD

There are no known deviations from the SW-846 Method 1312 with the following exception: ALS allows for the use of HDPE bottles for metals and semivolatile organics leaching, if approved by the client (see LIMS program specifications), and if this type of container can be shown to meet the criteria discussed in Section 5.5 (i.e., inert and does not adsorb or release target analytes).

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

All Safety and Hazards are managed in accordance with the current facility plans:

- Chemical Hygiene Plan (CHP)
- Radiation Protection Plan (RPP).
- Emergency and Contingency Plan (ECP)
- Respiratory Protection Plan (RESPP)

11.2 WASTE DISPOSAL

All Wastes are disposed of in accordance with the Waste Management Plan (WMP)

12. REFERENCES

Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, US EPA SW-846, 3rd Edition, Final Update III, Volume 1c, Method 1312, Rev 0, September 1994.

APPENDIX A(1)

EXAMPLE

PERCENT SOLIDS (% SOLIDS) DETERMINATION

Logbook No./Page _____ A **(For Samples on Following Logbook Page)**
Balance ID _____

Units = grams	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)
Sample No.	**Weight of Beaker, Spatula & Sample**	**Weight of Beaker, Spatula & Residue**	**Total Sample Weight (a - b)**	**Weight of Filter**	**Weight of Collection Flask**	**Weight of Flask & Filtrate**	**Filtrate Weight (f - e)**	**Total Solids Weight (c - g)**	**% Solids (Wet) (h / c) * 100**	**Weight of Filter & Dried Solids**	**Weight of Dried Solids (j - d)**	**% Solids (Dry) (k / c) * 100**

APPENDIX A(2)
EXAMPLE

Logbook No./Page _____ B

LEACHING PROCEDURE WORKSHEET

Work Order # _____	**(Start) Date** _____ **Time** _____	**(Stop) Date** _____ **Time** _____ **RPM** _____
Batch ID # _____	**(Start) RPM** _____ **Temp.** _____ **°C**	(Stop) Temp. ____ °C Tumble
Method _____ **SOP** _____ **Rev** ____	**(Start) Analyst** _____ RESET MIN/MAX AFTER READING OBTAINED	Min/Max ___/___ °C
Extraction Fluid ID _____	**Filtration Date/Time/** _____ **Initials** _____	1-1 Reviewed By / Date

Solids[a]	Particle Reduction[b]	Sample Number	Initial pH	Fluid Determination				Sample Weight (g)	Fluid (mL)	Final pH	Leachate No.	Comments
				HCl (mL)	Final pH	Fluid #	Fluid pH					
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											
I S M	Y N											

[a] I = insignificant (< 0.5%); S = 100%; M = Multiphasic (see attached % Solids Determination form).

[b] Y = Yes - reduction required / performed; N = no partical size reduction required.

INTERNAL COC TRANSFER: Relinquished by _____ (initials) to _____ (RU# & location) _____ (Date & Time) **Form 623r12.doc (10/25/11)**

APPENDIX B
EXAMPLE

TCLP/SPLP/CAL-WET EXTRACTION FLUIDS

Lot Nos.: Sodium Hydroxide: _____ Glacial Acetic Acid: _____ Citric Acid: _____ H_2SO_4:_____
HNO_3:_____

Solution Name	Date Prepared	Initials	Volume NaOH Used (mL)	Volume Glacial Acetic Acid (or other) Used (mL) (see comments)	Total Volume Made (mL)	Final pH	Comments

Reviewed by _____ Date _____

FORM 646r2.doc (08/08/2012)

APPENDIX C
EXAMPLE

ALS Laboratory Group

Mettler Toledo Delta-320 pH Meter
Calibration & Maintenance Log

Result Units = pH units

Date	Time	Initials	4.00 Solution **Lot No.**/ Result	10.01 Solution **Lot No.**/ Result	% Slope	7.00 **Check** Sln **Lot No.**/ Result	Comments / **Maintenance Notes**
			/	/		/	
			/	/		/	
			/	/		/	
			/	/		/	
			/	/		/	
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			/	/		/	

Reviewed by / date _____

Form 825r1.xls (3/26/08)

APPENDIX D
EXAMPLE
TEMPERATURE LOGBOOK
ORGANIC EXTRACTIONS - TCLP ROOM
Acceptable Range 23 ± 2 °C

A current temperature reading must be recorded at the onset of TCLP tumbling, and the min/max memory must be reset. DO NOT initiate tumbling if temperature is not within acceptable limits. The current temperature and min/max information must be recorded at the completion of tumbling. Both the Department and QA Managers must be notified in a timely manner if an excursion occurs.

		Thermometer: 41406316 (min/max)				
DATE	TIME	Current Temp. (°C)	Temp. Min (°C) Date/Time Occurred	Temp. Max (°C) Date/Time Occurred	INITIALS	COMMENTS

Reviewed by / date _____ **Form 345r1.doc (7/10/06)**

ALS Standard Operating Procedure

DOCUMENT TITLE:	PREPARATION OF GROSS ALPHA AND GROSS BETA IN ENVIRONMENTAL MATRICES
REFERENCED METHOD:	EPA 900.0 AND SW9310
SOP ID:	702
REV. NUMBER:	20
EFFECTIVE DATE:	JANUARY 31, 2013

ALS
STANDARD OPERATING PROCEDURE 702 REVISION 20

TITLE: PREPARATION OF GROSS ALPHA AND GROSS BETA IN ENVIRONMENTAL MATRICES -- EPA METHOD 900.0 AND SW9310

FORMS: APPENDIX A, B
APPROVED BY:

TECHNICAL MANAGER _____ DATE _____

QUALITY ASSURANCE MANAGER _____ DATE _____

LABORATORY MANAGER _____ DATE _____

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the methods it references, EPA 900.0 and SW-846 Method 9310, describe the procedure used to determine non-volatile gross alpha and beta activity of waters, liquids, soils, non-soil solids, air filters and air filter composites, and certain non-aqueous liquids. The solids procedure is amenable to the preparation of suspended solids that have been removed by filtration from waters or other liquid matrices.

The gross alpha and gross beta activity are determined simultaneously in the same sample preparation by counting on the beta plateau. The raw count results are corrected for detector background, efficiency (referenced to ^{241}Am for alpha -or ^{230}Th to meet National Primary Drinking Water Standards using Method EPA 900.0- and ^{90}Sr/Y for beta), mass attenuation (sample self-absorption), and alpha and beta cross-talk. Default reporting units are picoCuries per liter (pCi/L) on an unfiltered basis, (waters), or per gram (pCi/g) on a dry weight basis (solids), or per filter or composite as appropriate to meet the client's data quality objectives.

This procedure is substantially compliant with methods EPA 900.0, SW-846 Method 9310, and Standard Methods (SM) Method 7110B for aqueous matrices.

2. SUMMARY

2.1 WATERS

Waters samples are routinely analyzed on a "filtered" or "unfiltered" basis. Samples containing visible sediment are routinely filtered prior to preparation according to SOP 721 unless EPA drinking water protocols are requested by the client. In this case, the sample must not be filtered so that the actual consumer dose can be accurately measured. The aliquot size is determined for each sample by gravimetric measurement of the total solids. This aliquot is then evaporated to near dryness and a small volume (i.e., <5mL) is quantitatively transferred into a tared stainless steel planchet. The contents of the planchet are evaporated on a hot plate and cooled in a desiccator. After cooling, the planchet is weighed to determine the residual mass of nitrated sample solids. If the mass of solids is greater than 100 milligrams for alpha-only and simultaneous alpha/beta

measurements, or greater than 200 milligrams for beta-only measurements, the sample is re-prepared using a proportionately smaller aliquot. Planchets containing solids in the acceptable range are sent to the Radiochemistry Instrument Group for analysis per SOP 724.

2.2 LEACHATES OR DIGESTATES

Following preparation, sample leachates or digestates are determined as described in Section 2.1 above for waters. The total solids spot check may be omitted at the analyst's discretion. The sample aliquot is adjusted to reflect the equivalent sample concentration (grams or mL sample per gram or mL leachate).

2.3 NON-AQUEOUS OR MIXED PHASE LIQUIDS

Non-aqueous liquids are analyzed and reported on an "as received" basis. They may be treated as waters as long as the physical or chemical characteristics of the sample are amenable to safe evaporation with the eventual addition of nitric acid. Questionable cases should be addressed to the Senior Scientist, Technical Manager, Project Manager, or Health and Safety Officer prior to initiation of analysis.

2.4 SOILS AND NON-SOIL SOLIDS (hereafter referred to as "solids")

Solids are analyzed on a "dry weight" basis. Routinely, a 3g aliquot (or other appropriate quantity) of the solid is digested in a known volume (usually 30mL) of 8N nitric acid in a 50mL centrifuge tube. The sample is then centrifuged. A volume aliquot which yields <100mg of nitrated solid residue is determined gravimetrically. This aliquot is then evaporated onto a tared stainless steel planchet, dried, flamed, and weighed. The planchet is then sent to the Radiochemistry Instrumentation Group for analysis. Results are reported on a default basis of pCi/g dried solids.

2.5 AIR FILTERS

Air Filters are processed in a manner similar to solids except they need not be weighed and the units are reported on a default basis as "per filter".

2.6 SUSPENDED SOLIDS

Solids suspended in aqueous solutions are filtered from a known quantity of sample onto tared glass fiber filters. The filters are dried and weighed to determine the mass of the suspended fraction. The entire filtered suspended solid sample, up to 5 grams, is then treated as a solids sample. Results are reported on a default basis as pCi/g dried solids.

2.7 SWIPES

Swipes and some filters that are counted directly, or on an "as received" basis, are placed onto a clean stainless steel planchet and relinquished to the Radiochemistry Instrument Group for counting. Results are typically reported on a per sample basis, but may also be reported as pCi/air volume for filters at the client's request.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.2 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. The demonstration may come in the form of supervisory/training review, precision and accuracy tests performed, or the successful completion of an unknown proficiency test sample.

3.3 ALS's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede ALS's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.4 Final review and sign-off on the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.5 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events. Any discrepancies must be noted and brought to the attention of a Senior Scientist or Manager. Corrective actions taken must be approved, and promptly and thoroughly documented.

4. INTERFERENCES

4.1 Radionuclides that are volatile during evaporation in nitric acid or flaming of planchets will not be dependably measured. This method is not applicable to the determination of Tritium (^{3}H) or Carbon 14 (^{14}C). Other problematic nuclides include Technetium 99 (^{99}Tc) and radioisotopes of iodine, cesium, and polonium.

4.2 If the radionuclides are not separated from the solids of the sample, the solids concentration is a primary limiting factor in the sensitivity of the method for any given water sample. Also, for samples with very low concentrations of radioactivity, it is essential to analyze as large a sample aliquot as possible to allow reasonable counting times.

4.3 The largest sample aliquot that should be counted for gross alpha activity is that size aliquot which gives a solids density thickness of $5mg/cm^2$ in the counting planchet. For a 2in diameter counting planchet, an aliquot containing 100mg of nitrated (sample evaporated with nitric acid present) dissolved solids would be the maximum aliquot size for that sample which should be evaporated and counted

for gross alpha activity.

4.4 The largest sample aliquot that should be counted for gross beta activity is that size aliquot which gives a solids density thickness of $10mg/cm^2$ in the counting planchet. For a 2in diameter counting planchet, an aliquot containing 200mg of nitrated dissolved solids would be the maximum aliquot size for that sample which should be evaporated and counted for gross beta activity.

4.5 In some areas of the country, the nitrated water solids will not remain at a constant mass after being brought to dryness. Those types of water samples need to be heated to a dull red heat for a few minutes to convert the salts to oxides. Sample masses are then usually sufficiently stable to give consistent counting rates, and a correct counting efficiency can then be assigned. Some radioactive species, such as the cesium radioisotopes, may be lost when samples are heated to a dull red color. Such losses are limitations of the method.

4.6 This method is applicable to the measurement of alpha emitters having energies above 3.9MeV and beta emitters having maximum energies above 0.1MeV. Lower detection efficiency for emitters such as ^{99}Tc or ^{63}Ni will lead to an underestimation of the actual isotopic concentration for these species, if present in the sample.

4.7 Non-uniform distribution of the sample residue in the counting planchet interferes with the accuracy and precision of the method.

4.8 Moisture absorbed by the sample residue may interfere because it may change the sample residue mass affecting self-absorption characteristics. While the presence of hydrated solids is non-problematic to counting, residue mass should be stable enough to allow application of self-absorption corrections which meet the precision and accuracy requirements of the work being performed.

4.9 The minimum detectable concentration (MDC), applicable to this method, depends on sample size, counting system characteristics, background, and counting time. The formula for calculating an MDC is derived from ANSI N42.23 (rev. February 10, 1995). Due to industry-wide practice, and the need to demonstrate compliance with regulatory requirements, the “sample specific MDC” is routinely calculated and often reported in conjunction with sample activity and total propagated uncertainty values. The sample specific MDC makes a priori assumptions regarding the variance in the background count rate, but also reflects the actual conditions employed for the analysis, including aliquot, detection efficiency, solids residue, and count time. The routine solids digestion procedure will not completely remove radioactive elements from silica or absorbed radioactive materials. More aggressive digestion procedures may be necessary if determination of matrix constituents is required (see SOP 721).

4.10 Non-aqueous liquid, non-soil solids, and samples with high organic content may not be amenable to this procedure.

4.11 The presence of significant quantities of chloride salts in aqueous samples may lead to corrosion of the stainless steel planchet if the solution is not fully converted to a nitrate system prior to transfer. Repeated additions of concentrated nitric acid followed by evaporation are usually sufficient to address the problem.

4.12 Sample solution should be slowly evaporated to near dryness (≤5mL). Avoid evaporating the sample to complete or hard dryness that could lead to analyte loss resulting from poorly soluble residues in the beaker.

5. APPARATUS AND MATERIALS

5.1 2in stainless steel ringed planchets. Prior to use, the planchets are placed in a beaker and muffled at approximately 550°C for a minimum of 2 hours. This is done as a cleaning procedure.

5.2 pipettors, Eppendorf™ or equivalent

5.3 centrifuge tubes with caps, plastic, 50mL

5.4 polypropylene beakers, 250mL

5.5 balance, top loading, 0.1g sensitivity

5.6 balance, analytical, 0.1mg sensitivity

5.7 pleated filter paper

5.8 plastic funnels

5.9 hot plate

5.10 wash bottles

5.11 drying oven

5.12 graduated cylinders

5.13 desiccator

5.14 Meeker burner

5.15 tongs

5.16 glass rods

5.17 rubber policeman

5.18 disposable transfer pipettes, plastic, ~3mL and disposable pipette tips

5.19 filtering apparatus and 47mm glass fiber filters

6. REAGENTS

- TLV and other hazard information may also be given here. Any chemical with a TLV below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is non-hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Deionized (DI) water, ASTM Type II, minimum

6.2 Nitric acid, concentrated, 16N, ACS grade
TLV = 2 ppm (TWA) Irritant, corrosive

6.3 Nitric acid, 8N: Cautiously add 500mL of reagent grade concentrated HNO_3 to approximately 400mL of DI water and dilute to 1.0L.

6.4 Nitric acid, 1N: Cautiously add 62.5mL of reagent grade concentrated HNO_3 to approximately 500mL of DI water and dilute to 1.0L.

6.5 ^{90}Sr spiking solution, NIST-traceable. A second source should be used, independent of the source used for calibration (*required* for DOD samples per LIMS program specification).

6.6 ^{241}Am spiking solution, NIST-traceable. A second source should be used, independent of the source used for calibration (*required* for DOD samples per LIMS program specification).

6.7 ^{230}Th spiking solution, NIST-traceable. A second source should be used, independent of the source used for calibration (*required* for DOD samples per LIMS program specification).

6.8 Modified USGS Simulated River Water Reagent (salt solution): Dissolve 3.72g $MgSO_4$, 3.10g NaCl, and 3.24g $CaCl_2$ in 200mL 1N HNO_3.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Although the client is responsible for conducting the sampling process, it is emphasized that water samples be collected in a manner that addresses the considerations discussed in EPA 900.0 Section Three or Chapter Nine of EPA SW-846, as appropriate. Also, it is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 to the sample to bring it to pH 2 (15mL of 1N HNO_3 per liter of sample is usually sufficient). If water samples are collected without preservation, they should be brought to the laboratory within 5 days, and then be preserved and held in the original container for a minimum of 24 hours before analysis or transfer of the sample.

7.2 The container should be plastic rather than glass to prevent loss due to breakage during transportation and handling.

7.3 SW-846 specifies the holding time for Method 9310 as 180 days.

8. PROCEDURE

8.1 PREPARATION OF CALIBRATION STANDARDS

8.1.1 EFFICIENCY CALIBRATIONS

8.1.1.1 Gross Alpha Efficiency Planchets: Spike five ringed stainless steel planchets directly with ~8,000 to 15,000 dpm each of NIST-traceable ^{241}Am. Submit to the Radiochemistry Instrument Group with appropriate documentation.

8.1.1.2 Gross Alpha Efficiency Planchets for Drinking Water Protocols: Spike five ringed stainless steel planchets directly with ~8,000 to 15,000 dpm each of NIST-traceable ^{230}Th. Submit to the Radiochemistry Instrument Group with appropriate documentation.

8.1.1.3 Gross Beta Efficiency Planchets: Spike five ringed stainless steel planchets directly with ~8,000 to 15,000 dpm each of NIST-traceable ^{90}Sr. Submit to the Radiochemistry Instrument Group with appropriate documentation.

NOTE: If the standard matrix is HCl, convert to the nitrate system before planchetting to avoid corroding the planchet.

8.1.2 MASS ATTENUATION CALIBRATION

8.1.2.1 Supply the Radiochemistry Instrument Group with a series of planchets containing a range of mass from ~10mg to ~145mg, including a duplicate for each mass. The approximate target masses in mg are: 10, 25, 40, 55, 70, 85, 100, 115, 130, and 145.

NOTE: A separate set of planchets must be prepared for gross alpha, gross alpha for drinking water protocol, and for gross beta calibrations

8.1.2.2 Label and tare weigh 10 stainless steel ringed planchets. Label a plastic disposable cup for each sample.

8.1.2.3 Add the appropriate amount of Simulated River Water Reagent to give the target mass to each cup (1mL of reagent typically gives 35-40mg dried mass on the planchet).

8.1.2.4 Spike each sample cup with ~8,000 to ~15,000dpm of the appropriate NIST-traceable radionuclide (routinely ^{241}Am for gross alpha and ^{90}Sr for gross beta).

8.1.2.5 Add ~5mL of concentrated nitric acid to each to convert chloride salts to nitrate salts.

8.1.2.6 Take to near dryness on Hot Blocks.

8.1.2.7 Transfer with at least three rinses of 1N nitric acid to a tared

stainless steel planchet.

8.1.2.8 Dry on a hot plate set at 3.

8.1.2.9 Once dry, continue heating for 20-30 minutes with the hot plate set at 10.

8.1.2.10 Cool in a desiccator.

8.1.2.11 Weigh on an analytical balance and record the data on a benchsheet

8.1.2.12 Submit to the Radiochemistry Instrument Group with the appropriate documentation, where the planchets will be analyzed per SOP 724.

8.2 CALIBRATION PROCEDURES

8.2.1 Efficiency and Attenuation Calibration: Analysis systems will be calibrated at least annually or as indicated by routine instrument response check results.

8.2.2 Gross Alpha measurements are routinely referenced to ^{241}Am.

8.2.3 Gross Beta measurements are routinely referenced to ^{90}Sr/Y.

8.2.4 EPA drinking water compliance testing for gross alpha requires that the gross alpha measurement be referenced to ^{230}Th instead of ^{241}Am. (EPA 816-D-00-002, December 2000).

8.2.5 All standards used to develop efficiency and attenuation curves shall be traceable to the National Institute for Standards and Technology (NIST).

8.2.6 Detectors must be calibrated to obtain the ratio of net count rate to disintegration rate. ^{241}Am has higher alpha particle energy (5.49MeV) than those emitted by the naturally occurring uranium and ^{226}Ra radionuclides, but is close to the energy of the alpha particles emitted by naturally occurring ^{228}Th and ^{224}Ra.

8.2.7 ^{90}Sr/Y and ^{137}Cs have both been used quite extensively as standards for gross beta activity. Cesium, however, may become volatile at elevated temperatures (above 450ºC) and may volatilize at temperatures observed while flaming a sample containing hygroscopic salts.

8.2.8 Each instrument used for the analysis of gross alpha and beta shall be calibrated to correct for alpha and beta sample self-absorption (residue mass vs. zero mass normalized efficiency). Mass attenuation curves will be prepared for this purpose. The mass stable standards should be alpha or beta counted (as appropriate) until 10,000 counts have been

accumulated. A single set of standards for each nuclide (^{241}Am, ^{230}Th, and ^{90}Sr/Yis suitable for calibration of instruments and re-verification of curves, whenever needed.

8.2.9 Data acquisition is conducted according to instrument manufacturer instructions.

8.2.10 Calculations for attenuation and crosstalk are defined in Section 9. Meticulously document steps taken to produce calibration data.

8.3 PROCEDURE FOR WATERS

8.3.1 Verify with pH paper that the sample has been properly preserved to a pH <2. Record the pH on the sample condition form (Form 631).

8.3.1.1 If the pH is > 2, notify the appropriate Project Manger to determine if further analysis will be acceptable to the client and whether the sample should be (re-)preserved prior to continuing with analysis. If the Project Manager determines that the situation is acceptable to the client's DQOs, acidify to pH<2 with conc. HNO_3. Wait for two (2) minutes and retest pH. Record the acid addition and the final pH on a Quality Assurance Summary Sheet (QASS) or NCR form (Form 313), as appropriate. The date and time of acidification must be noted.

8.3.1.2 Return the sample to storage for at least 24 hours before proceeding. Record the beginning date and time on a Sample Condition Form. If twenty-four (24) hours causes a scheduling difficulty, notify the Project Manager to determine if a deviation from this requirement is acceptable. Document any deviations thoroughly on a QASS that accompanies the project file.

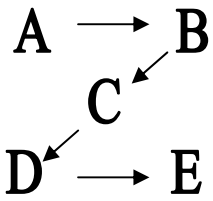
8.3.1.3 When resuming the analysis, record the date/time of resumption on the Sample Condition form. Also, calculate and record the number of elapsed hours since acidification.

8.3.2 To determine the mass of solids in 10mL of the sample, proceed as follows:

8.3.2.1 Place all planchets to be used onto a steel desiccator tray. Each space on the tray is numbered and that number corresponds with the sample ID on the mass benchsheet.

8.3.2.2 Label and tare a planchet on an analytical balance to nearest 0.1mg. Record the mass in the appropriate column on the mass benchsheet.

8.3.2.3 Place the planchets in the following order on the hotplate:



Where ‘A’ corresponds to the first planchet, ‘B’ to the second, and so on.

8.3.2.4 Shake the sample well and pipet 10.0mL of sample into the labeled, tared planchet using a calibrated pipettor. Place on hotplate set at 3.

8.3.2.5 When dry, turn the hotplate setting to 10 and maintain at this heat for 20-30 minutes.

8.3.2.6 Transfer the planchets to the steel tray, making sure that each sample is returned to its proper numbered space, and place the tray directly in the desiccator to cool. Be sure to note which numbered space in the pan corresponds to which sample on the benchsheet.

8.3.2.7 When the planchets are cool, weigh each one to the nearest ±0.1mg. Record the mass in the appropriate column on the mass benchsheet.

8.3.2.8 The solid mass and volume aliquot will be calculated using Equation 1 (shown below), and the results will be shown in the respective cells in the “Init Mass” and “Sugg. Alq” columns in the Mass section of the electronic benchsheet. The “Sugg. Alq” column shows the calculated aliquot plus the 10mL used for aliquot determination as final aliquot used. (V is the volume of the spot check used, in mL and W is the mass calculated in the “Init Mass” column, in g.)

$$V(g) = \frac{0.75}{W(g)}$$

EQUATION 1

8.3.2.9 If the planchet mass is unstable, flame the 10mL planchet and recalculate. If that is done, the resultant sample planchet needs to be flamed also.

8.3.2.10 The default maximum aliquot size for water samples is 200mL. If the calculated aliquot volume is greater than 200mL, use the default aliquot size unless DQOs demand a higher aliquot to achieve required detection limits.

8.3.2.11 If the predicted final residue mass for a sample is estimated to be below 20 milligrams (1.0mg residue for 10mL spot check), simulated river water reagent is added, in Step 8.3.4 below, to provide between 20 and 100 milligrams equivalent of final residue.

8.3.2.12 1mL of simulated river water reagent is added to provide between 20 and 100 milligrams equivalent of final residue for each of the batch QC samples (Method Blank and LCS).

8.3.3 Measure the calculated sample aliquot from a well-shaken sample container into a labeled disposable poly beaker. If DQOs demand the use of a larger sample size, a glass beaker may be used and taken to near dryness on a hotplate.

NOTE: The same planchet will be used for the sample as was used for the determination of the residue. Thus only 190 additional mL would be necessary to make up the final volume to 200mL.

8.3.4 Add the appropriate spike and amount of spike per Section 10. Add simulated river water reagent to the blank, LCS, and any samples that require it (see Section 8.3.2.11). Typically, 1mL of simulated river water reagent is added for waters analysis to produce 35-40mg of nitrated solids on the planchet.

8.3.5 Add concentrated HNO_3 in the ratio of 1/10th the sample volume. (e.g., 19mL acid per 190mL of sample). The samples may be diluted to a single volume (e.g., to the largest volume of any sample in the batch).

8.3.6 Slowly evaporate the sample solution to near dryness (≤5mL). Avoid evaporating the sample to complete or hard dryness that could lead to analyte loss resulting from poorly soluble residues in the beaker.

8.3.7 If significant concentrations of chlorides are suspected to be present, a second 5mL portion of concentrated nitric acid may be added to complete conversion of the sample to a nitrate system. The sample is once again evaporated to near dryness.

8.3.8 Using a disposable plastic transfer pipet, quantitatively transfer the solution to the labeled stainless steel planchet used for the 10mL aliquot determination. If solid residues are present, it may be necessary to use a rubber policeman to effect the transfer.

NOTE: Any rubber policeman that shows signs of deterioration should not be used.

8.3.9 Rinse the beaker with three successive 2mL portions of 1N HNO_3 transferring each of the rinses to the appropriate planchet on a hotplate

in a fume hood. If the planchet cannot hold all rinses, add them as planchet volume is evaporated in the next Step.

8.3.10 Take the solution to dryness as in Step 8.3.6. Avoid excess heating that can cause spattering or boiling during drying. Turn the hotplate setting to highest and maintain at this heat for 20-30 minutes.

8.3.11 Flame the planchet if the 10mL planchet was flamed.

NOTE: Be sure the sample is well distributed on the planchet. This will assure proper counting efficiency.

8.3.12 When all the planchets are dry, remove and cool in a desiccator for at least 30 minutes. Note the time and date of the desiccation in the Notes section on the benchsheet.

8.3.13 Remove the samples from the desiccator and weigh them on an analytical balance. Record the mass to the nearest 0.1mg in the designated cell mass benchsheet. If the planchet mass is unstable on the balance and noticeably gains weight proceed with Step 8.3.15.

8.3.14 Let planchet stand outside of the desiccator for 15 minutes. If the samples are not noticeably hygroscopic, they are ready for counting; (if they are hygroscopic, proceed with Step 8.3.15.

8.3.15 If the samples demonstrate hygroscopicity, cautiously flame planchet to dull redness over a Meeker burner. Avoid popping and spattering. Maintain heat for at least one minute. Cool in a desiccator. Reweigh to nearest 0.1mg and reenter the new mass in the electronic benchsheet. Submit the planchets and any necessary documentation to the Radiochemistry Instrument Group. The Radiochemistry Instrument Group will analyze and ultimately dispose of the planchets in a manner described in SOP 724.

8.3.16 Store the samples in a desiccator for at least 72 hours before counting. Where EPA methodologies are not required, such as for non-water matrices, etc., the samples should be desiccated overnight or until they are ready for counting.

8.4 PROCEDURE FOR SOLIDS

8.4.1 Analysis is routinely reported on a dry weight basis. The use of oven dried solid samples allow direct calculation of aliquot mass without the need to correct for sample moisture content. Rocky, coarse or non-homogeneous solids should be milled or ground to pass a No. 4 sieve before taking an aliquot for analysis. See SOP 721 for soil preparation procedure.

8.4.2 Weigh 3g of solid sample to the nearest 0.1g into a labeled 50mL centrifuge tube.

8.4.3 Add the appropriate spike and amount of spike per Section 10. Add 2mL of simulated river water reagent to the blank and LCS.

NOTE: It is important protocol to always add QC spikes *before* any chemical treatments applied during sample processing.

8.4.4 Slowly add 8N HNO_3 to give a total volume of 30mL. Be sure to account for the volume of salt solution and spiking solutions. (i.e., the LCS would receive only 26mL of nitric acid if it already contains 2mL of salt solution and 2mL of spiking solution). Some samples may react vigorously with the acid, so it may be necessary to add the acid in small increments.

8.4.5 Mix to break up clumps.

8.4.6 Heat on Hot Blocks with caps on loosely for (1) one hour. Allow samples to cool and mix by vortexing.

8.4.7 Centrifuge for 10 minutes and filter the supernatant using VWR Grade 313 pleated paper, or equivalent, into a new, labeled centrifuge tube.

8.4.8 Determine the mass of solids as in Section 8.3.3, except use 5mL instead of 10mL. **The planchet should be flamed for all solid samples unless otherwise indicated by applicable DQO's or the client.** Calculate and record the required aliquot volume of solution using Equation 2 shown below:

$$V(mL) = \frac{0.375}{W(g)}$$

EQUATION 2

8.4.8.1 If the calculated aliquot exceeds 20mL, use a 20mL aliquot. Aliquots should be in increments of 5 up to 20mL. Directly transfer the additional aliquot to the planchet used for the 5mL aliquot. Proceed with Step 8.4.9.

8.4.8.2 If the mass of the residue from the 5mL aliquot is more than 100mg, calculate the required amount less than 5mL. Aliquots should be calculated in increments of 1mL (unless an aliquot smaller than 1mL is appropriate). Directly transfer the calculated aliquot to a clean, labeled, and tared planchet.

8.4.9 Dry the sample on a hot plate set to 3. Once the sample is dry, turn the hot plate up to 10 for 20-30 minutes. After the sample has been heated for 20-30 minutes, cautiously flame the planchet to a dull redness over a Meeker burner. Avoid popping and spattering. Maintain heat for at least one minute.

8.4.10 When all planchets are dry, remove and cool in a desiccator for at least 30 minutes. Note the date and time of the desiccation in the Notes section on the benchsheet. Also, in the Notes section, note that all samples were flamed.

8.4.11 Remove the samples from the desiccator and weigh the planchets on an analytical balance. Record the mass to the nearest 0.1mg in the designated cell of the mass benchsheet.

8.4.12 Submit the planchets and any necessary documentation to the Radiochemistry Instrument Group. The Radiochemistry Instrument Group will analyze and ultimately dispose of the planchets in a manner described in SOP 724. Store the planchets in a desiccator at least overnight or until they are ready for counting. Be sure to note the date and time the samples were placed in the desiccator on the benchsheet.

8.5 PROCEDURE FOR SUSPENDED SOLIDS

8.5.1 Label a 2in stainless steel planchet for each sample. Tare each planchet with a 47mm glass fiber filter. Record the tare weights on a QASS.

8.5.2 Filter a known volume of aqueous sample through the tared glass fiber filter. Record the volume of sample filtered on the benchsheet. Return the filter to the labeled planchet.

8.5.3 Reweigh the planchet/filter and record on the QASS.

NOTE: If the samples that have been submitted are already filtered on a glass fiber filter, the analyst may omit Section 8.5.2 and 8.5.3 and enter the procedure at this point.

8.5.4 Subtract the tare weight in Section 8.5.1 from the gross weight in Section 8.5.3 to determine the mass of suspended solids. If results are requested on a dry weight basis, the filters must be dried overnight prior to re-weighing in Section 8.5.3. Samples yielding over 5 grams of suspended material should be scraped down gently with a spatula until the mass is approximately 5 grams. Record the final mass of suspended solids in the sample weight column of the soils benchsheet.

8.5.5 The sample preparation now proceeds as a solid in Section 8.4. The entire sample on the filter, including the filter, is transferred to the centrifuge tube in Section 8.4.1. Submit the QASS with the benchsheet and note on the benchsheet that the analysis is for suspended solids rather than solids.

9. CALCULATIONS

9.1 Calculate the mass of solid deposited by subtracting the tare weight (g) from the gross weight (g). This gives the solids deposit weight in grams. To convert to mg, multiply the grams by 1000.

9.2 Calculate the alpha and beta activity, counting uncertainty, TPU, MDC and crosstalk factors in activity units per aliquot unit following SOP 708.

9.2.1 TPU FACTORS. As defined in SOP 708, the following one-sigma preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty (TPU):

Water samples require a preparation uncertainty factor of 0.0565. This is based on one gross aliquoting (sample homogeneity), one quantitative transfer, one pipetting, two mass measurements and one volumetric measurement. See the following equation:

$$0.0565 = \sqrt{0.05^2 + 0.025^2 + 0.004^2 + 0.003^2 + 0.003^2 + 0.006^2}$$

Solid samples require a preparation uncertainty factor of 0.0567. This is based on one gross aliquoting (sample homogeneity), one quantitative transfer, two pipetting, two mass measurements, and one reagent addition. See the following equation:

$$0.0567 = \sqrt{0.05^2 + 0.025^2 + 0.004^2 + 0.004^2 + 0.003^2 + 0.003^2 + 0.006^2}$$

In practice, these two TPU factors are statistically equivalent. To simplify the data reporting procedure, the greater of the two (0.0567) may be used for both matrices.

9.2.2 Calculate the alpha and beta activity according to SOP 708, except for solids, the final sample aliquot is calculated as:

$$\text{Final Sample Aliquot} = \frac{\text{SampMass} * \%\text{Sol} * \text{AnalAliqVol}}{\text{DigTotVol}}$$

where:

SampMass = Initial Sample mass taken for digestion

%**Sol** = percent solids for sample

AnalAliqVol = Volume of digestate taken for analysis

DigTotVol = Total Volume of Digestate

10. QUALITY CONTROL

10.1 Method blanks will be run at a frequency of five-percent (i.e., one per 20 field samples) with a minimum of one per batch. Method blanks for water consist of deionized (DI) water and match the largest sample volume used. Nitric acid is added to the method blank, as it is to the samples, prior to evaporation. Method blanks for solids are 2mL of salt solution brought up to 30mL with 8N nitric acid.

10.2 Laboratory Control Samples (LCS) will be run at a frequency of five-percent with

a minimum of one per batch. Known quantities of NIST-traceable alpha (e.g., ^{230}Th for Drinking Water Compliance using Method EPA 900.0 and ^{241}Am for any others) and beta (^{90}Sr/Y) emitters are spiked into DI water at the start of the procedures. The spiking levels are determined according to specific data quality objectives for the work being performed, but will generally be 5-50 times the required minimum detectable concentration for the respective analyte or at an activity level roughly equivalent to levels expected to be observed in the samples. The volume for the LCS is as large as the largest sample volume. The LCS consists of deionized water at the correct volume and the appropriate spike and spike volume. The LCS for solids consists of 2mL of salt, the appropriate spikes and spike volume, brought up to 30mL with 8N nitric acid.

10.3 Duplicate samples will be run at a frequency of five percent with a minimum of one per batch, or according to client specifications. Client requested duplicate analyses shall be run as required and may count as the QC replicates for that batch.

10.4 Matrix Spike (MS) will be run at a frequency of five-percent with a minimum of one per batch. Known quantities of NIST-traceable alpha (i.e., ^{230}Th for Drinking Water Compliance using Method EPA 900.0 or ^{241}Am for any others) and beta (^{90}Sr/Y) emitters are spiked into a representative sample at the start of the procedures. The spiking levels are generally 5-50 times the analyte activity level expected to be observed in the samples.

10.5 The LIMS Standards Database should be consulted for the identification of the proper ^{241}Am or ^{230}Th, and ^{90}Sr working standards and spike activities.

10.6 Method blanks for air filter and suspended solids samples may be prepared to reflect the proper background contribution of the filter medium used for analysis. Method blanks for suspended solids consist of clean glass fiber filter medium from the same batch used for capturing the solids. Air filter blanks, if supplied by the client, may be used as a “reagent” blank. Otherwise, a blank planchet is usually the best representation of the sampling medium background.

10.7 LCS for filter-mounted samples consists of a planchet containing a known amount of standard ^{241}Am and ^{90}Sr.

11. DEVIATIONS FROM METHOD

This SOP is substantially compliant with SW-846 Method 9310 and EPA Method 900.0. The following information states deviations from and distinctions between the two reference methods as well as other regulatory issues that should be considered.

11.1 In this procedure, alpha and beta activities are determined simultaneously on the beta plateau. Crosstalk calibration of the proportional counter allows for correction of the contribution of “crosstalk” into respective opposing channels (beta-to-alpha and alpha-to-beta). Methods 9310 and 900.0 instruct the counting of alpha and beta at their respective plateaus. By setting the alpha/beta discriminators such that there is negligible contribution of beta events to the alpha

energy region, there is no advantage for counting on the respective voltage plateaus. However, there are significant disadvantages to counting on the two plateaus independently: (1) The count time required immediately doubles and (2) the alpha efficiency is lower at the alpha plateau such that analysis time may need to be increased more to reach the same required detection limit.

11.2 This procedure has been modified to accommodate matrices other than drinking waters. The procedure treats solubilized radioactive constituents in digestate or leachate solutions as a water sample.

11.3 Implementation Guidance for Radionuclides (December 2000) indicates that ^{230}Th is to be used for purposes of demonstrating compliance with the standard. Unless otherwise specified, all other results are completed using ^{241}Am as the reference nuclide for gross alpha.

11.4 SW-846 defines sampling and preservation protocols that may diverge from the requirements of Method 900.0. The sampling process is completed prior to receipt and processing of water samples by the laboratory and does not directly affect laboratory operations. SW-846 does specify a holding time of 180 days. The SOP references both protocols that are to be used to ensure compliance with applicable regulation.

11.5 A second deviation between the two methods is the Method 900.0 requirement that a minimum 10,000cts/detector and standard be accumulated during the absorption curve calibration. This SOP requires that 10,000 counts be accumulated, satisfying both methods.

11.6 Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of the laboratory's internally derived acceptance criteria.

11.7 Methods 9310 and 900.0 are otherwise substantially identical. This SOP meets or exceeds the requirements of the methods for the analysis of water samples.

12. SAFETY HAZARDS AND WASTE

12.1 SAFETY AND HAZARDS

All Safety and Hazards are managed in accordance with the current facility plans:

- Chemical Hygiene Plan (CHP)
- Radiation Protection Plan (RPP).
- Emergency and Contingency Plan (ECP)
- Respiratory Protection Plan (RESPP)

12.2 WASTE DISPOSAL

All Wastes are disposed of in accordance with the Waste Management Plan (WMP)

13. REFERENCES

13.1 Method 9310, EPA SW-846, Gross Alpha and Gross Beta, Revision 0, September 1986.

13.2 Method 900.0, Prescribed Procedures for Measurement of Radioactivity in Drinking Waters, EPA-600 4-80-032, August 1980.

13.3 Method 7110B, Standard Methods for the Examination of Water and Waste Water, 18th Edition, APHA, 1992.

13.4 EPA 816-D-00-002, Implementation Guidance for Radionuclides, December 2000.

13.5 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

APPENDIX A

QUALITY ASSURANCE SUMMARY SHEET

ALS W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

_____

_____

_____

_____

_____

_____

_____

TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

APPENDIX B

SAMPLE CONDITION FORM (LIQUID)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	pH	**COLOR**	**REMARKS**

Form 631r4a.doc (7/21/06)

SAMPLE CONDITION FORM (SOLIDS)

ANALYST: _____ ANALYSIS DATE: _____ METHOD: _____

WORK ORDER #	SAMPLE ID	DRY WEIGHT (g)	**TEXTURE**	**REMARKS**

Form 631r4b.doc (7/21/06)

ALS Standard Operating Procedure

DOCUMENT TITLE:	SAMPLE PRESCREENNG
REFERENCED METHOD:	N/A
SOP ID:	703
REV. NUMBER:	9
EFFECTIVE DATE:	DECEMBER 4, 2013

ALSSTANDARD OPERATING PROCEDURE 703 REVISION 9

TITLE: SAMPLE PRESCREENING

FORMS: Appendix A, B

APPROVED BY:

PRIMARY AUTHOR_____ DATE _____

QUALITY ASSURANCE MANAGER _____ DATE _____

LABORATORY MANAGER _____ DATE _____

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the semi-quantitative determination (i.e., prescreening) of non-volatile gross alpha and beta activity in samples. Prescreen results enable the Radiation Safety Officer (RSO) to determine what precautions are necessary in order to process the samples in the laboratory safely.

2. SUMMARY

2.1 The RSO develops protocols for deciding which samples need to be prescreened. Where sufficient prior knowledge regarding a client's samples exists, a determination of "always prescreen" or "prescreening not required" may be made in advance. Where previous knowledge about a client's samples is insufficient, the RSO uses prescreen results to determine what precautions are necessary for processing the samples in a manner that is safe to laboratory personnel.

If it is known in advance that incoming samples require prescreening, the Project Manager (PM) can use an Incoming Project Notice Form (Form 214, or equivalent) to inform Sample Control and other laboratory staff before the samples arrive. Samples that need to be prescreened may also be determined as a result of the sample login survey performed by Sample Control staff upon sample receipt (SOP 202).

Regardless of which mechanism triggers the prescreen test, Sample Control staff are responsible for notifying the RSO or designee when prescreening is required.

2.2 Liquid samples are prepared for prescreening by drying an aliquot of liquid on a planchet. The mass of solid residue is determined, and the planchet is counted in a proportional counter. Solid samples are prepared for prescreening by transferring a known mass (approximately 100mg) to a stainless steel planchet, adding nitric acid, then evaporating the planchet's contents to dryness on a hotplate. If a high degree of sample inhomogeneity is expected (consult RSO or Radiochemistry Supervisor), the samples may alternately be leached with nitric acid, and after the suspended solids are allowed to settle, an aliquot of the resulting leachate may be tested as previously described for liquids. The prescreening of other sample matrices, such as non-aqueous liquids, must be handled on a case-by-case basis.

2.3 Gross alpha prescreen measurements are referenced to ^{241}Am; gross beta prescreen measurements are referenced to ^{90}Sr/Y.

3. RESPONSIBILITIES

3.1 This procedure is to be performed only by personnel who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review or the successful completion of precision and accuracy tests performed.

3.2 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review. All personnel who work with samples involving this method are responsible for noting any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

Emitters that are volatile in hot acidic solution are not amenable to measurement by this method.

5. APPARATUS

5.1 Low-level gas flow proportional counter

5.2 Stainless steel planchets, two inch, ringed bottom

5.3 Beaker, 50 or 100 mL, Pyrex™

5.4 Pipettors, Eppendorf™ or equivalent, 1 and 5 mL, with disposable tips

5.5 Transfer pipets, disposable

5.6 Balance, analytical, 0.0001g sensitivity

5.7 Petri dishes

5.8 Hot plate and Hot Blocks

5.9 Infrared lamp

5.10 Tweezers

5.11 Tongue depressors

5.12 Centrifuge tube, 50mL

5.13 Rubber policeman

5.14 Centrifuge

6. REAGENTS

6.1 Deionized (DI) water, obtainable from the laboratory's deionized water system

6.2 Nitric acid (HNO_3), concentrated. TLV = 2ppm (TWA); irritant, corrosive

6.3 Nitric acid, 8N: Cautiously add 500mL conc. HNO_3 to approximately 400mL DI water, dilute to 1 L. TLV = 2ppm (TWA); irritant, corrosive

6.4 Nitric acid, 3N: Cautiously add 190mL conc. HNO_3 to approximately 700mL DI water, dilute to 1 L. TLV = 2ppm (TWA); irritant, corrosive

6.5 ^{241}Am spiking solution, NIST-traceable, independent second source

6.6 ^{90}Sr spiking solution, NIST-traceable, independent second source

Note: All spiking solutions are from a source that is different than that used for calibration.

6.7 Modified USGS Simulated River Water Reagent (salt solution): Dissolve 3.72g $MgSO_4$, 3.10g NaCl, and 3.24g $CaCl_2$ in 200mL 1N HNO_3.

6.8 Anhydrous calcium chloride ($CaCO_4$) or indicating Drierite^{TM}, for desiccator

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Store samples to be prescreened in the Sample Control walk-in cooler RU #20. Sample containers may be taken to the Prescreen Lab for aliquotting, but must be returned to the walk-in cooler as soon as the aliquots are obtained.

NOTE: Samples designated for prescreening are NOT to be prepared in normal sample preparation areas without specific permission from a Radiochemistry Supervisor.

8. PROCEDURE

8.1 GROSS SCREEN PREPARATION WORKSHEET

Initiate a Gross Screen Preparation Worksheet (Form 796) for each group of samples to be prescreened. Use the information on the chain of custody (COC) or workorder to fill out the Sample ID. Locate one of the containers for each sample and transfer them to the Prescreen Lab. Return these samples to the cooler as soon as the aliquots have been obtained.

8.2 PREPARATION OF LIQUIDS FOR PRESCREENING

8.2.1 Label and tare a clean, dry planchet for each sample to be prescreened. Record the weight on the worksheet (Form 796) to the nearest 0.0001g.

Prepare quality control (QC) samples per Section 9.

8.2.2 Use a calibrated pipettor (SOP 321) with a clean pipet tip to acquire a 10mL aliquot of sample from the container.

NOTE: A reduced aliquot may be taken for samples with expected activities above 5000cpm. The RSO will determine when a reduced aliquot is used. Also, aliquot sizes should be decreased for samples with significant quantities of suspended solids.

8.2.3 If the sample is unpreserved, or preserved with anything other than HCl, proceed to Step 8.2.5.

8.2.4 If the sample has been preserved with HCl, it will corrode the planchet. Convert to a nitrate system as follows:

8.2.4.1 Place the aliquot (Step 8.2.2 above), in a labeled 50mL beaker and add 5mL conc. HNO_3.

8.2.4.2 Slowly evaporate to near dryness on a hot plate, avoiding spattering.

8.2.4.3 Add 1mL of conc. HNO_3 to the residue and repeat evaporation.

8.2.4.4 Dissolve the residue in 1-2mL of 3N HNO_3, slurry any undissolved solids.

8.2.4.5 Quantitatively transfer the beaker's contents to a labeled, tared planchet using 3N HNO_3. Rinse the beaker 3 times with small portions (≈1mL) of 3N HNO_3. Transfer all rinses to the planchet. Use a rubber policeman to help transfer solids.

8.2.5 Add the sample to the planchet and dry the planchet on a hot plate.

8.2.6 Remove the planchet and allow to cool for about 15 minutes.

8.2.7 Weigh the planchet and record the weight on the worksheet. This weight will later be used in determining the solids present during counting.

NOTE: The amount of solids should be within the range of the instrument calibration, so as to reduce self-absorption losses in activity measurements. If the solids are greater than the range of the instrument calibration, a proportionately smaller aliquot will have to be processed as above per Steps 8.2.1.

The proportionate amount of reduced aliquot to use may be estimated using the following equation:

$$V\ (mL) = \frac{0.95}{W\ (g)}$$

where:

V (mL) = volume of reduced aliquot

W (g) = mass of solids present in the original 10mL aliquot

Note that if a 1mL aliquot was originally used, divide the V(mL) in the equation above by ten to get the correct new aliquot.

8.2.8 Transfer the planchets to a clean petri dish.

8.2.9 Proceed to Section 8.5.

NOTE: Prepare oils as described in section 8.3 for solids. Be aware to avoid spattering. Due to the nature of the matrix (oil), extra drying time may be required. Consult Supervisor with any questions.

8.3 PREPARATION OF SOLIDS FOR PRESCREENING (DIRECT DEPOSITION)

8.3.1 Label and tare a clean, dry planchet for each sample to be prescreened. Record the weight on the worksheet (Form 796) to the nearest 0.0001g. Prepare QC samples per Section 9.

8.3.2 Transfer approximately 100mg of sample directly to the tared planchet. Record the mass to the nearest 0.0001g on the benchsheet.

NOTE: Some samples may contain standing water at the top of the container. Homogenize these samples thoroughly (i.e., mix-in the water) before obtaining an aliquot.

8.3.3 Place the planchet on a hotplate. Set the heat to low-medium. Carefully add 5mL conc. HNO_3.

8.3.4 Slowly evaporate to dryness, avoiding spattering.

8.3.5 Remove the planchet from the hotplate and allow to cool for about 15 minutes, or until cool to touch.

8.3.6 Weigh the planchet and record the weight on the worksheet. This weight will later be used in determining the solids present during counting. **See NOTE, Step 8.2.7 above.**

8.3.7 Transfer the planchets to a clean petri dish.

8.3.8 Proceed to Section 8.5.

8.4 PREPARATION OF SOLIDS FOR PRESCREENING (LEACHING) - **Consult with a Radiochemistry Supervisor before preparing samples in this manner!**

8.4.1 Weigh 2 grams or 0.5 grams (see note below) of solid, on an analytical balance whose calibration has been previously verified (SOP 305), into a 50mL centrifuge tube. Record the weight on the worksheet (Form 796).

NOTE: Two (2) grams of sample should be aliquoted for samples with expected activities less than 5000cpm. An aliquot of 0.5 grams or less, may be used for samples with higher expected activities.

8.4.2 Add 8mL concentrated nitric acid to the centrifuge tube.

8.4.3 Leach the sample fifteen minutes on Hot Blocks.

8.4.4 Remove the sample from the Hot Blocks and allow to cool.

8.4.5 Add 17mL of 8N HNO_3 to bring the digest volume to 25mL. Swirl sample to mix completely.

8.4.6 Centrifuge the samples at 3500rpm for 15 minutes.

8.4.7 Prepare QC samples per Section 9.

8.4.8 Take a 2mL aliquot of the leachate and deposit this onto a labeled, tared planchet.

NOTE: The proportionate amount of solid aliquot used may be calculated using the following equation:

$$W_{aliquot}\,(g) = \frac{W_{total}\,(g) \times V_{aliquot}\,(mL)}{V_{total}\,(mL)}$$

where:

Valiquot (mL) = volume of aliquot used

Vtotal (mL) = total volume of leachate

Waliquot (g) = mass of solids present in the original 2 mL aliquot

Wtotal (g) = mass of sample recorded from step 8.4.1.

8.4.9 Follow Steps 8.2.1 to 8.2.7, as for liquids.

8.5 COUNTING OF PRESCREEN SAMPLES

8.5.1 Determine the mass of solids (i.e., residue), in mg, per Section 8.6 below.

8.5.2 Samples are counted in the Prescreen Lab per SOP 724.

8.5.3 Verify that all information has been recorded on the Gross Screen Preparation Worksheet where needed, and is legible. Sign your initials in the space at the top of the form provided for "Analyst".

8.5.4 Give a copy of the prescreen results, including the blank and LCS, to the appropriate PM or the RSO.

8.6 CALCULATIONS

Amount of solids (mg) = [Gross wt of planchet (g) - tare wt of planchet (g)] x 1000 mg/g

NOTE: Activity, uncertainty, and minimum detectable concentration (MDC) calculation formulae may be found in SOP 708.

9. QUALITY ASSURANCE/QUALITY CONTROL

9.1 One blank is to be prepared and analyzed each week. This one blank will be used for all matrices prepared that week. Prepare the blank by pipetting 5.0mL of concentrated nitric acid onto a labeled planchet; add 1mL of salt solution and dry on a hotplate. This blank is subject to the same acceptance criteria specified in the Gross α/β procedure (SOP 724), and review of Radioanalytical Data (SOP 715)..

9.2 One laboratory control sample (LCS) is to be prepared and analyzed each week. This one LCS will be used for all matrices prepared that week. The LCS consists of approximately 100dpm of ^{90}Sr and 100dpm of ^{241}Am spiked onto a tared planchet, containing approximately 5mL of conc. nitric acid. ***If the spike solution was made in HCl, the solution must be converted to a nitrate system prior to planchetting in order to prevent corrosion of the stainless steel planchet.*** One (1) mL of salt solution is added to the planchet prior to drying. The LCS is acceptable if the value yielded is +/-30 % of the expected value. If this criterion is not met, notify a Radiochemistry Supervisor immediately for possible corrective actions.

10. DEVIATIONS FROM METHOD

This is a proprietary method, developed by ALS. Therefore, there are no deviations from promulgated methods.

11. SAFETY, HAZARDS AND WASTE DISPOSAL

11.1 SAFETY AND HAZARDS

All Safety and Hazards are managed in accordance with the current facility plans:

- Chemical Hygiene Plan (CHP)
- Radiation Protection Plan (RPP).
- Emergency and Contingency Plan (ECP)
- Respiratory Protection Plan (RESPP)

11.2 WASTE DISPOSAL

All Wastes are disposed of in accordance with the Waste Management Plan (WMP)

12. REFERENCES

12.1 Eastern Environmental Radiation Facility Radiochemistry Procedure Manual, EPA 520/5-84-006, 00-01.

12.2 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

APPENDIX A

EXAMPLE

Kit: Y / N Rush? Y / N Prescreen? Y / N *ALS*

INCOMING PROJECT NOTICE

Date: _____ Copy to: Sample Control

Initiator: _____

Date(s) expected: _____

Client: _____ Assigned PM: _____

Address: _____ Client Contact: _____

_____ Phone: _____

Report to: _____ Fax: _____

Proj. Name/Number: _____

# Samp	Matrix	Analysis/Method	Price	Sub Lab	# x Cont. Type	Preserv.	Tot. Bottles
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		
					x		

QC Level: _____ Disposal or handling? $5 / $10 / $15 / $_____ / RTC

Report Level: _____ TAT (working days): 20 / 15 / 10 / 5 / 3 / 2 / 24hr /____

EDD: N / Y Format: Report: Wet Weight / Dry Weight / As Received

Kit to:

Date kit needed: _____ am / pm

Attention: _____

Company: _____

Address: _____

_____

Phone: _____

Potential Radioactivity:

Do the samples contain radioactive materials?	Y / N
Are any samples potentially mixed hazardous materials?	Y / N
Are any samples from a known RAM site?	Y / N

Additional Special Handling:

Include: COC(s) Bubble Wrap Labels Seals Blue Ice Temp. Blks

Comments: Rush Special Test Special Analyte Special Charge Detection Limits (see attached)

Kit Prepared by: _____ Date: _____ Picked up by: _____ Date: _____

I:\cprtns\misc\forms\IPN_Form214r5.xls (10/29/03)

APPENDIX B

EXAMPLE

SOP 703 Rev _____ **LB5100B** ***ALS***

Date	Sample ID	Group	Carrier	Count Duration (minutes)	Start Time	Analyt's Initials	Position Check Initials	Comments

Reviewed by / Date _____

Form 796r6.xls (3/26/08)

ALS Standard Operating Procedure

DOCUMENT TITLE:	CALCULATIONS FOR RADIOANALYTICAL RESULTS
REFERENCED METHOD:	N/A
SOP ID:	708
REV. NUMBER:	9
EFFECTIVE DATE:	APRIL 11, 2011

ALS Environmental

ALS
STANDARD OPERATING PROCEDURE 708 REVISION 9

TITLE: CALCULATIONS FOR RADIOANALYTICAL RESULTS

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE _____

QUALITY ASSURANCE MANAGER _____ DATE _____

LABORATORY MANAGER _____ DATE _____

1. SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) provides the basic calculations for Activity Concentration, Total Propagated Uncertainty (TPU), Decision Level (DL), and Minimum Detectable Concentration (MDC). The algorithms provided in this SOP accurately reflect the processes used in the ALS LIMS system for performing the same calculations.

Deviations from these calculations are special cases, requiring the approval of the Department Manager. These deviations are documented in the individual method SOPs. In addition, method-specific descriptions of uncertainty coefficients and calculational "switches" are also found in the individual method SOPs.

ALS standard (i.e., default) practices are discussed in this SOP. Client-specified calculations that deviate from ALS standard practices are defined in the LIMS program specification applicable to the samples being processed.

Where uncertainty calculations are concerned, this SOP describes the principles and practices taken to estimate the TPU in radioanalytical procedures. This procedure incorporates recommendations from the NIST Technical Note 1297, "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results", which is equivalent to ISO "Guide to the Expression of Uncertainty in Measurements".

DL and MDC calculations provide analytical values that respectively describe the limits of statistical probability for blank sample analyses and for analyses that are distinguishable from a blank sample.

2. SUMMARY

This SOP first describes the calculation of the various correction factors that are applied to all Activity, TPU, DL and MDC calculations.

2.1 CORRECTION FACTORS

Most correction factors are combined and applied as the denominator in the final calculations. The specific correction factors include the following:

- Crosstalk
- External Background
- Base Counting Efficiency
- Efficiency Correction (e.g. Mass Attenuation)
- Progeny Ingrowth
- Progeny Efficiency
- Decay
- Chemical Yield
- Sample Volume
- Emission Abundance
- Units Conversion

After the correction factors have been determined, this SOP describes the appropriate calculations for Activity, TPU, DL and MDC.

Due to the complexity of radioanalytical calculations, ALS has devised a system that employs a universal calculation format with a series of arithmetic "switches" that allow for the inclusion (or exclusion) of the various correction factors.

2.2 UNCERTAINTY

Radioanalytical data reporting convention includes the estimated analysis uncertainty. This procedure provides estimates of uncertainties throughout the radiochemical preparation and counting process, such that the reported uncertainty includes all known sources of potential error. Individual uncertainty estimates, determined at the one-sigma (1σ) level, are "summed in quadrature" to estimate the one-sigma Total Propagated Uncertainty. Total Propagated Uncertainties (TPU) may subsequently be reported at a multiplier of the sigma value (two- or three-sigma) or at a specific confidence interval (95%, 99%, etc.), as requested by a particular client or procedure. All uncertainties listed in this procedure are given as 1σ values.

Where possible, estimates of uncertainties in various significant steps of radioanalytical procedures are established, either by the collection of empirical data, or by reference to a reliable authority, such as the ANSI N42 standards. These include uncertainty estimates in volume and mass determinations, process reproducibility, instrument calibration and operation, and counting uncertainty.

Estimated uncertainties may be calculated either in activity units (e.g., pCi/g) or as a relative uncertainty (e.g., a percentage of the measured activity). By convention, any uncertainty calculated as a relative value must be multiplied by the sample activity, thereby converting the value to activity units, before using that uncertainty component in the final TPU calculation.

2.3 DLs and MDCs

On a practical basis, the MDC is the level of activity required to be present in a sample to be able to statistically distinguish that sample from one with no activity, at the 2σ confidence interval. More specifically, in a paired observation, in which sample results are background-corrected, the "Decision Level" (or "Critical Level") is the maximum expected result, at the 2σ confidence interval, for a sample with no activity. Therefore, in a sample with an activity concentration equal to the MDC, the minimum expected result at the 2σ confidence interval would be equal to the Decision Level.

Decision Level and MDC determinations are a priori calculations that are generally independent of the actual measured activity concentration in the sample. These calculations can be accurately performed prior to the analysis. Gamma spectroscopy is the exception to this statement, because spectral background is affected by sample activity in a gamma spectroscopy analysis.

As with Activity and TPU, DLs and MDCs for radioanalytical procedures are determined by mathematical formulae that take into account sample volume, chemical recovery, instrument detection efficiency and background, and sample counting duration. This calculation provides for analysis of actual samples to demonstrate the ability to meet desired or required detection limits. This calculation, or an alternative as specified by the client, shall be performed for each type of analysis as a verification of detection limit capabilities.

It is noted that the traditional formulae, described in Section 5.5.1 and 5.5.2 of this SOP, rely on the assumption that the sample count duration and the background calibration count duration are equal. In cases where this assumption does not hold, the refinement in the calculations shown in Section 5.5.3, is appropriate. It is also noted, however, that the use of the traditional formulae is well-entrenched among some clients, despite any differences in count times, and changing this formula may cause unacceptable discontinuity in historical monitoring programs and other scenarios. Consequently, ALS continues to provide the traditional formulae by default, and offers the revised formula upon request.

The analyst should note that improved detection limits may be obtained through use of larger sample volumes, longer counting times, or improved sample analysis geometries if the *a priori* calculation reveals an inadequate detection limit.

3. RESPONSIBILITIES

3.1 ALS's Project Managers (PM) serve as the primary interface with the client. To the extent possible, it is the PM's responsibility to understand the client's needs with regard to the manner in which radioanalytical results are calculated, and to inform the client of the option to request client-specified calculations, if necessary. The PM is responsible for creating/maintaining LIMS program specifications that satisfactorily address the clients needs, as applicable.

3.2 ALS's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specifications supercede ALS's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.3 It is the Department Manager's responsibility to ensure that any material changes to this SOP, which may affect the calculations performed in LIMS, are reflected in the LIMS program. These changes may include correction factors, uncertainty component factors, etc. Updates in LIMS may require the assistance of the IS Department, to make changes to the LIMS program. In all cases, it is also the Department Manager's responsibility to ensure that the calculational changes made in the LIMS program are properly verified.

3.4 It is the analyst's responsibility to be familiar with both the preparation SOP and the analysis SOP for the method results being reported. These SOPs will include calculation coefficients, as well as provide guidance in the fundamental concepts behind the analytical method.

3.5 Analysts must demonstrate the capability to generate acceptable results using the procedures described herein. This demonstration typically comes in the form of supervisory training and review, as well as periodic documentation of the validation of the LIMS program that generally performs these calculations.

3.6 It is the responsibility of all personnel to perform the tasks as described in this SOP. Any anomalies or out-of-control events must be noted, and corrective action taken and documented. For the purpose of this SOP, out-of-control events are defined as those calculations that cannot be validated, by manual calculation, to within 3% of the reported LIMS result. This criteria is defined in SOP 709.

4. APPARATUS AND MATERIALS

There are no apparatus or materials, including reagents and standards, used in this SOP. It is noted, however, that calibration factors and other calculation coefficients may be defined in the individual preparation and analysis SOPs used for a particular method.

5. CALCULATIONS

5.1 GENERAL CORRECTION FACTORS

These general correction factors are applicable to all calculated results for a given sample analysis. The calculation of Activity Concentration, TPU, DL and MDC require identical correction factors, such as chemical yield, etc., to ensure that the final reporting units are comparable, thereby allowing for a valid comparison of results.

5.1.1 Instrument Background (CalBCPM)

The basic instrument background count rate, in counts per minute (cpm), is described in the individual instrument SOPs. This value is subtracted from the gross sample count rate (GCPM) to determine the net sample count rate for the analysis.

This is the background count rate that is subtracted in all analytical methods performed on a given instrument. Additional background correction factors, such as filter contributions or quench curve adjustments, that are applicable to a single method are described below as “External Background (ExtBCPM)”.

5.1.2 External Background (ExtBCPM)

External background contributions, such as the additional contribution of paper filters to a beta analysis, which are not accounted for in the basic instrument background calibration, are described in the individual preparation and analysis SOPs.

Additional examples of external background contributions include the batch-specific adjustment of the background quench curve in liquid scintillation analyses, and the yield-dependent beta contribution from the Sm carrier in a Pm-147 analysis.

5.1.3 Crosstalk Count Rate (XTLK)

The Crosstalk Count Rate refers to the additional background contribution, in multi-channel analyses such as gross alpha/beta, in which the analyte results in a region of interest exhibit an interference from other analyte results in a different region of interest. The Crosstalk Count Rate is a function of the Crosstalk Calibration Ratio, which is determined during the base efficiency calibrations.

The primary region of interest is sometimes called the minor region (m) and the interfering region is sometimes called the major region (M). The presence of measurable activity in the major region contributes additional counts to the minor region of interest. These additional counts must be treated as additional background counts since they

interfere with the accurate quantification of activity in the minor region of interest.

For example, in gas-flow proportional counting there are alpha- and beta- regions of interest. The presence of measurable alpha activity primarily shows up in the alpha region. In addition, some alpha activity will also show up in the beta region. These counts are not attributable to beta activity and must be subtracted from the gross beta count rate in order to accurately quantify the true beta activity in the sample. See Figure 1 .

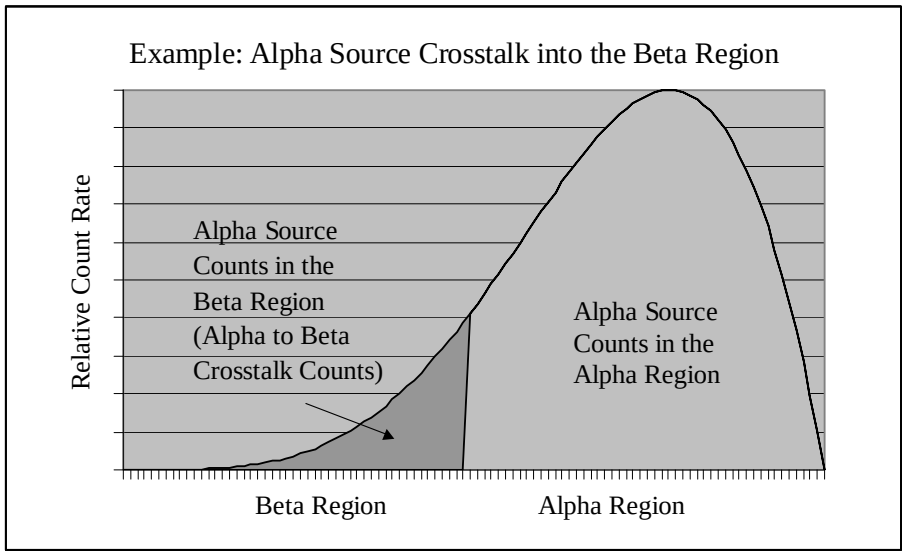


Figure 1

The Crosstalk Calibration Ratio is determined during the base efficiency calibration of the major region and is simply the ratio of net counts in the minor region to net counts in the major region;

$$XTLK_{M>m} = (NetEffCPM_m/NetEffCPM_M)$$

where:

$XTLK_{M>m}$ = Crosstalk Calibration Ratio

$NetEffCPM_m$ = Net count rate in the minor region of interest, during the efficiency calibration of the analyte primarily found in the major region.

$NetEffCPM_M$ = Net count rate in the major region of interest, during the efficiency calibration of the analyte primarily found in the major region.

In alpha/beta example given above, $XTLK_{M>m}$ would be the alpha to beta Crosstalk Calibration Ratio, determined during an alpha efficiency calibration. $NetEffCPM_m$ would be the net beta count rate observed during the alpha efficiency calibration process. $NetEffCPM_M$ would be the net alpha count rate observed during the same alpha efficiency calibration.

The Crosstalk Count Rate in a sample analysis is calculated as the additional count rate in the minor region and is a function of the net sample count rate in the major region;

$$XTLK = (XTLK_{M>m})(NetCPM_M)$$

where:

XTLK = Crosstalk Count Rate in the minor region during a sample analysis, to be treated as additional background.

$NetCPM_M$ = Net count rate in the major region, during a sample analysis.

In alpha/beta example given above, $NetCPM_M$ would be the net alpha count rate. XTLK would be the beta Crosstalk Count Rate, attributable to the sample alpha activity, to be subtracted from the gross beta count rate as additional background.

5.1.4 Base Counting Efficiency (BaseEFF)

The determination of the base counting efficiency is described in the individual preparation and instrument SOPs. The base counting efficiency factor gives the ideal instrument response, in the presence of a particular radionuclide. The units for counting efficiency are “counts per emission”.

5.1.5 Efficiency Correction (BaseMassAtt)

The determination of the base efficiency correction factor is described in the individual preparation and instrument SOPs. The correction factor is a unit-less multiplicative correction factor, less than one, that accounts for physical interferences that reduce the sample counting efficiency, such as mass attenuation in a gross alpha/beta analysis or a quench correction in a liquid scintillation analysis.

5.1.6 Progeny Ingrowth (ING)

In cases where the analyte that is isolated in the preparation method decays into a radioactive progeny that is observable in the analysis, the resulting ingrowth of progeny is taken into consideration.

The progeny ingrowth factor describes the relative activity of the ingrown daughter product, as compared to the parent. This special form of the equation assumes that the half-life of the daughter is much shorter than the half-life of the parent;

$$ING = 1 - e^{\lambda * t4}$$

where:

e = the base of the natural logarithm

λ = the decay factor for the progeny;

= ln(0.5) / (progeny half-life)

t4 = the elapsed time the isolation of the parent nuclide to the beginning of the sample count.

Note that in this calculation, as in any decay or ingrowth calculation, the units of time in which the half-life is expressed (e.g. years, days, etc.) must be the same units in which the elapsed time is expressed.

For example, Sr-90 undergoes beta decay, with a half-life of 28.5 years into a radioactive daughter Y-90, which also undergoes beta decay with a half-life of 64 hours. Upon chemical isolation of the Sr-90, the ingrowth of Y-90 immediately resumes. If the sample is held for 72 hours before analysis, the degree of ingrowth of the Y-90 daughter is;

$$1-e^{((\ln(0.5)/64h*72h)} = 0.5415$$

Consequently, for a given amount of Sr-90 activity present in the sample, 72 hours after chemical separation there will also be 54.15% of that amount, which will be present as Y-90 activity.

5.1.7 Progeny Efficiency (ProgEFF)

In some cases the progeny emissions are measured and the counting efficiency for the progeny emissions are sufficiently different from the counting efficiency of the parent emissions. In these cases, the counting efficiency of the progeny are determined separately, and are analogous to the base counting efficiency determination. As in any counting efficiency determination, the units are “counts per emission”.

5.1.8 Progeny Efficiency Correction (ProgMassAtt)

As with the determination of the base efficiency correction factor, the progeny counting efficiency may need to be corrected for physical interferences, such as mass attenuation in a gross alpha/beta analysis or

a quench correction in a liquid scintillation. This progeny efficiency correction is also a unit-less factor, less than one.

5.1.9 Decay to the Sampling Date (D)

The decay factor is a unit-less correction factor that describes the amount of radioactive parent material remaining after a given period of decay time. By convention, radioanalytical results are generally decay-corrected to the sampling date unless otherwise specified;

$$D = e^{\lambda * t0}$$

where:

λ = the decay factor for the parent;

= ln(0.5) / (parent half-life)

t0 = in the GENERAL CASE, the elapsed time from the field sampling or reference date to the beginning of the sample count (as in H-3).

in the case where INGROWN PROGENY are counted, the elapsed time from the reference date to the isolation/separation of the parent nuclide (as in Sr-90).

5.1.10 Decay During the Count (L)

Since radioactive decay is measured by observation of the radiation emissions over a period of time (usually between 1 and 1,000 minutes), and since the rate of decay changes over time, the change in the decay rate over the duration of the count must be accounted for. This is especially important during the measurement of radionuclides for which the half-life is less than ten times the count duration.

The decay during the count (L) is calculated as follows;

$$L = \left(\left(1 - \exp^{\lambda * t3}\right)/\left(-\lambda * t3\right)\right)$$

where:

λ = the decay factor for the first radionuclide in the chain of radionuclides that are present during the sample count.;

= ln(0.5) / (half-life)

For example, in a Sr-90 analysis in which Sr-90 and its Y-90 daughter are both present, use the half-life of the Sr-90 parent. In a Ra-228 analysis in which the only nuclide present is the Ac-228 daughter, use the half-life of the Ac-228 daughter.

5.1.11 Chemical Yield (yield)

The determination of chemical yield is described in the individual preparation SOPs. Chemical yield is generally determined by pre-separation and post-separation measurement of stable carriers or radioactive tracers added to the sample, and is expressed in decimal format. *For example, a chemical yield of 95.13% is expressed as 0.9513.*

5.1.12 Sample Volume (vol)

The sample volume is the equivalent amount of sample material actually presented for analysis. Described in the individual preparation SOPs, the sample volume for analysis is equal to the original volume of sample aliquotted, less any amounts removed for yield determinations, splits, etc.

5.1.13 Emission Abundance (abund)

Emission abundance values (like half-lives) are derived from published reference tables. These values describe the frequency with which a given emission of radiation occurs for each decay of a parent atom.

For example, the decay of Ba-137m results in a 662 keV gamma photon emission 89.98% of the time. The emission abundance is 0.8998.

In some cases, the analysis of a particular radionuclide may require the measurement of one or more progeny. The creation of these progeny may only occur during a fraction of the parent atom disintegrations. The "branching ratio" for a particular decay scheme describes the frequency of the resulting progeny. As a practical consideration in the ALS LIMS reporting software, the abundance values and branching ratios are multiplied into a single correction factor.

*For example, in the determination of Cs-137, 94.6% of decays result in the creation of Ba-137m. When measuring the resulting 662 keV gamma emissions, the rate of Cs-137 decay can be inferred by correcting the observation by both the gamma emission abundance and the branching ratio. See Figure 2. The effective correction factor is 0.8998 * 0.9460 = 0.8512.*

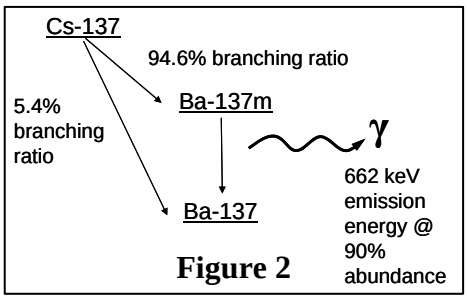


Figure 2

5.1.14 Units Conversion (actconv)
Results are converted into conventional activity reporting units through the application of an appropriate conversion factor. ALS default reporting units of picoCuries (pCi) are achieved through the application of the conversion factor 2.22 dpm/pCi.

5.2 "SWITCHES" and the STANDARD DENOMINATOR (k)
The application of the various correction factors described above is achieved with a series of arithmetic "switches" that allow for the inclusion (or exclusion) of those factors.

A table of values for the various switches described below, as they are applied to individual methods, is provided in Appendix A. These values may be superseded by subsequent revision of the analytical methods. Consult the individual preparation and analysis SOPs for the latest revisions to the methods.

The combination of selected correction factors and their related arithmetic switches create a standard denominator (k), to be applied in the calculation of Activity, TPU, DL, and MDC;

$$k = (A + B) * C * K * L$$

where:

$$A = \left(BaseEFF * BaseMassAtt^{\mathbf{c}} \right) * \left(1 + \left(1 - \exp^{\lambda * t4}\right) * \mathbf{d}\right)$$

and where:

BaseEFF = Base calibration efficiency (cpm/dpm).

Base MassAtt = Mass attenuation factor for the base efficiency (no units).

switch c = 0, if there is no mass attenuation correction in this method.

1, if there is a mass attenuation correction in this method.

switch d = 0, if there is no ingrowing daughter product present during the count that has the same counting efficiency as the parent (as in gross α/β).

1, if there is an ingrowing daughter product present during the count, and it has the same counting efficiency as the parent (as in Sr/Y-90).

exp = the base e of the natural logarithm (2.718).

λ = the decay constant [ln(.5)/(half-life of the nuclide of interest)].

Similarly,

$$B = \left(ProgEFF * ProgMassAtt^{\mathbf{e}} \right) * \left(1 - \exp^{\lambda * t4}\right) * \mathbf{f}$$

where:

ProgEFF = Progeny calibration efficiency (cpm/dpm), if applicable. See switch f below.

ProgMassAtt = Mass attenuation factor for the progeny efficiency (no units).

switch e = 0, if there is no mass attenuation correction for the progeny in this method.

1, if there is a mass attenuation correction for the progeny in this method.

switch f = 0, if there is no ingrowing daughter products present during the count that have a different counting efficiency from the parent (as in Sr/Y-90 and gross α/β).

1, 2, 3, etc., based on the number of ingrowing progeny present during the count, with a different counting efficiency from the parent (as in Total Radium, where f=3).

$$C = \left(\exp^{\lambda * t2} * \left(1 - \exp^{\lambda * t1}\right)\right)^{\mathbf{g}}$$

where:

switch g = 1, if the analyte to be counted is the ingrown daughter product of the parent target analyte and the parent target analyte is not present in the fraction for analysis (as in Ra-228).

0, Otherwise.

$$K = yield * vol * abund * actconv * \left(\exp^{\lambda * t0}\right)^{\mathbf{h}}$$

where:

yield = chemical yield (no units).

vol = sample size (grams, liters, m3, etc.).

abund = abundance correction, including branching ratios, from published reference data (no units).

actconv = activity units conversion factor, e.g. 2.22 dpm/pCi, to report data in pCi units.

switch h = 0, if the target analyte should not be decay corrected, usually because the specific nuclide is unknown (as in gross αβ, or Total Activity).

1, if the decay factor for the target analyte is known and is to applied (as in Sr-90, Th-228, H-3, etc.).

$$L = \left(\left(1 - \exp^{\lambda * t3}\right)/\left(-\lambda * t3\right)\right)^{\mathbf{h}}$$

where:

switch h = defined above.

IMPORTANT NOTE: In the L factor defined here,

if the g switch defined above is 0, then use the λ of the parent target analyte (as in Sr-90).

if the g switch defined above is 1, then use the λ of the ingrown progeny (as in Ra-228).

5.3 ACTIVITY CONCENTRATION

The determination of the activity concentration in a sample begins with the sample gross count rate measurement on a given instrument, such as a gas-flow proportional counter for gross α/β analyses. Various background count rate contributions, described in Sections 5.1.1 through 5.1.3 above, are subtracted from the gross count rate to yield a net count rate, which is attributable only to the actual sample activity. The standard denominator is then applied to convert the result into conventional reporting units. The final result expresses the radioactive decay rate per volume of sample material, decay corrected to the sampling date;

$$Activity = \frac{GCPM - \left[CalBCPM + \left(XTLK * a\right) + \left(ExtBCPM * b\right)\right]}{k}$$

where:

GCPM = Gross count rate (cpm)

CalBCPM = Calibrated instrument background count rate (cpm).

XTLK = Crosstalk contribution to the analyte background (cpm).

switch a = 0, if there is no crosstalk contribution in this method.

1, if there is a crosstalk contribution in this method.

ExtBCPM = External background contribution, such as the additional contribution of paper filters to a beta analysis, which is not accounted for in the base background calibration.

switch b = 0, if there is no external background contribution in this method.

1, if there is an external background contribution in this method.

5.4 UNCERTAINTY

In general, uncertainty refers to the estimated lack of accuracy and/or precision in a reported value. The uncertainty is first estimated for each individual process in the analytical method. The component uncertainties are then combined to give a Total Propagated Uncertainty (TPU) for the entire method. When accompanying the reported activity concentration, this TPU describes the range of values in which the laboratory believes that the true value of the sample lies, at the stated confidence interval.

Unless stated otherwise, the values and formulae provided below are stated at the one-sigma (1σ) confidence interval. These values, and the associate TPU, may be expressed at any other confidence interval by multiplying by the equivalent expansion factor, as described in Section 0.

5.4.1 PRIMARY COMPONENTS

Primary components of the TPU calculation are listed below, and are detailed in the Sections shown:

Analyte Count Rate Uncertainty	Section 5.4.2
Chemical Yield Determination Uncertainties:	
Radiometric Tracer Measurements	Section 5.4.3.1
ICP Mass Measurements	Section 5.4.3.2
Gravimetric Mass Measurements	Section 5.4.3.3
Analysis Uncertainties	Section 5.4.4
Preparation and Sample Handling Uncertainties	Section 5.4.5

5.4.2 ANALYTE COUNT RATE UNCERTAINTY (CU)

The analyte count rate uncertainty is the estimated deviation of the observed count rate from the true mean count rate of the analyte of interest. This component of TPU is due solely to the statistically random nature of radioactive decay.

The uncertainty of a single radiometric measurement is estimated as the square root of the total number of counts acquired. It is calculated as a count rate uncertainty, in units of counts per unit of time, as follows:

$$U_R = \sqrt{\frac{R_S}{T_S}}$$

where:

U_R = Count Rate Uncertainty

R_S = Gross Count Rate in the Sample

T_S = Duration of the Sample Count

In practice, however, a single radiometric measurement is rarely used to report activity concentrations. Instead, the gross sample count rate is background corrected by subtracting the background count rate to obtain a sample net count rate. This is known as a “paired observation”, and is calculated as a count rate uncertainty, in units of counts per unit of time, as follows:

$$U_R = \sqrt{\frac{R_S}{T_S} + \frac{R_B}{T_B}}$$

where:

R_B = Count Rate in the Instrument Background Determination

T_B = Duration of the Instrument Background Count

In some analytical techniques, multiple background corrections may be made. A routine instrument background correction will be made, based on the periodic background determination ordinarily performed on the instrument. Further background adjustments may be made in cases where the basic background determination is not representative of the specific analytical technique being employed. Some examples include batch-specific adjustments to the quench curve on the liquid scintillation counter, batch-specific adjustments for the filter contribution in I-129 analyses by gas-flow proportional counting, and

sample-specific contributions to the Compton continuum in gamma spectrometry analyses.

In these cases, the contribution of the additional background determination to the overall counting uncertainty is calculated as

$$U_R = \sqrt{\frac{R_S}{T_S} + \frac{R_B}{T_B} + \frac{R_A}{T_A}}$$

where:

R_A = Count Rate in the Additional Background Determination

T_A = Duration of the Additional Background Count

Where multiple, independent measurements contribute to the additional background determination, as in the case of quench curve adjustments or I-129 blank filter counts, conservatively use the count duration of a single measurement, rather than the combined duration of all measurements. The Count Rate should, however, be the average of the individual measurements.

After calculating the Count Rate Uncertainty in units of count per unit time, that number should be converted to activity concentration units, typically pCi/gram or pCi/liter, by dividing by the appropriate conversion factors, for example:

$$\text{Counting Uncertainty (pCi/g,l)} = \frac{\text{Count Rate Uncertainty (cts/min)}}{k}$$

where:

k = the standard denominator defined in section 5.2.

It is important to note that, in potentially zero (or near zero) background counting systems such as alpha spectrometry, the calculation should guard against the erroneous production of a calculated uncertainty that is at or near zero. Reporting a counting uncertainty of zero is unacceptable, since the count is duration is limited (not infinitely long) and the failure to observe an event during the count does not guarantee that an event will never be observed. Reporting zero activity with zero uncertainty (infinite precision) is not possible.

To guard against this possibility, counting uncertainties are re-calculated by substituting the values ($3/T_S$) for R_S, ($3/T_B$) for R_B, and ($3/T_A$) for R_A in the equations above, to calculate a “Zero Uncertainty”

value. If the Zero Uncertainty is greater than the calculated Counting Uncertainty, the value of the Zero Uncertainty replaces the calculated Counting Uncertainty.

The use of the constant 3 in these equations estimates a maximum true value for an observation that resulted in zero events.

5.4.3 CHEMICAL YIELD DETERMINATION UNCERTAINTIES (YU)
These will vary considerably, depending on the method used to quantify the chemical yield of a given separation procedure, as described below.

5.4.3.1 RADIOMETRIC TRACER MEASUREMENTS
Chemical yields may be determined by the analysis of a radioactive tracer added to the sample prior to chemical separation. The method for estimating the uncertainty associated with a radiometric tracer measurement is identical to the analyte count rate uncertainty described in Section 5.4.2 above, except that the tracer counts are used instead of the counts for the analyte of interest.

5.4.3.2 ICP MASS MEASUREMENTS
Chemical yields may be determined by Inductively Coupled Plasma (ICP) analysis of pre-separation vs. post-separation concentrations of a stable carrier element. The uncertainty in this yield determination is assumed to be 8.3% of the measured sample activity.

5.4.3.3 GRAVIMETRIC MASS MEASUREMENTS
Chemical yields may be determined by the measurement of the residual mass of prepared sample deposited onto a planchet or filter. In this case, the error in the yield determination may be significantly affected by interfering chemical constituents native to the sample, which the laboratory has no control over. The uncertainty in a gravimetric yield determination is conservatively estimated at 10% of the measured sample activity.

5.4.4 ESTIMATES OF INSTRUMENT ANALYSIS UNCERTAINTIES (IU)
5.4.4.1 Uncertainties associated with the instrumental analysis of radiochemical samples are assumed to be as follows:

Calibration (In-house prep. of standards): 5.0%

Calibration (Vendor-prepared standards): 2.0%

Counting Reproducibility:	1.0%
Sample Position Reproducibility:	1.5%
Counting Efficiency:	1.5%
Dead Time Estimates:	1.0%

These individual, independent uncertainty components are combined, or propagated, together by calculating the square root of the sum of the squares of the various components. This technique of combining independent uncertainties is also known as “summing in quadrature”, and is shown below. This will result in a single uncertainty estimate for a procedure with multiple uncertainty contributions. Note that the same propagation technique is used to combine preparation uncertainty factors in Section 5.4.5.

5.4.4.2 Instrumental Uncertainty (for calibration with a vendor-prepared standard):

Relative Uncertainty =

$$\sqrt{.020^2 + .01^2 + .015^2 + .015^2 + .01^2}$$

$$= 0.0324 = 3.2\%$$

5.4.4.3 Instrumental Uncertainty (for calibration with an in-house prepared standard):

Relative Uncertainty =

$$\sqrt{.05^2 + .01^2 + .015^2 + .015^2 + .01^2}$$

$$= 0.0561 = 5.6\%$$

5.4.5 ESTIMATES OF CHEMICAL PREPARATION UNCERTAINTIES (PU)

5.4.5.1 Uncertainties associated with the various steps in the chemical preparation of samples are estimated to be as follows:

Gross Aliquoting (Sample Homogeneity):	5%	
Quantitative Transfers:	2.5%	#
Spike or Tracer Standard:	2.5%	
Pipetting:	0.4%	*

Volumetric Measurements	
(non-volumetric labware):	0.6% *
Mass Measurements:	0.3% *
Reagent Addition (repipetting/dispensing):	0.6% *
Aliquoting and ICP Yield Determinations	
(Section 3.3):	8.3% *
Gravimetric Yield Determinations (Section 3.3):	10%

* these uncertainty factors have been empirically determined by ALS.

\# quantitative transfers need not be considered if a tracer or carrier used for yield determinations has already been added to the sample.

5.4.5.2 PROPAGATION OF PREPARATION UNCERTAINTIES

As described above, in Section 5.4.4.1, independent preparation uncertainties are summed in quadrature. Some generalized examples are given below, for clarification. ***Please note that these are examples only***. Specific preparation uncertainty factors are given in the individual preparation SOPs.

Example 1: Alpha or Beta Analyses by Gas Flow Proportional Counting (GFPC)

minimal preparation, error =

$$\sqrt{(.05^2 + .004^2 + .006^2 + .003^2 + .003^2 + .025^2)} = .0565 = 5.7\%$$

Based on sample homogeneity, a single pipetting, a single volumetric measurement, two mass measurements, and a quantitative transfer.

Example 2: Liquid Scintillation Analyses

minimal preparation, error =

$$\sqrt{(.05^2 + .006^2 + .006^2 + .003^2)} = .0508 = 5.1\%$$

Based on sample homogeneity, two volumetric measurements, and a single mass measurement.

Example 3: Gamma Spectroscopy

minimal preparation, error =

$$\sqrt{(.05^{2} + .003^{2})} = .0501 = 5.0\%$$

Based on sample homogeneity and a single mass measurement.

5.4.6 CALCULATION OF TOTAL PROPAGATED UNCERTAINTY

The individual uncertainties described above are combined, or propagated, together by calculating the square root of the sum of the squares of all the individual uncertainties.

Note that, in order to combine uncertainty factors, those factors must first be in the same units, such as pCi/g or Bq/L. Uncertainty factors that are expressed as a fraction of the sample activity, such as the instrument and preparation uncertainty factors described above, must be multiplied by the sample activity concentration before proceeding with the propagation calculation.

Be sure that all uncertainty factors are in activity concentration units before performing this last step.

$$TPU = \sqrt{\mathrm{CU}^{2} + Yield\mathrm{U}^{2} + \left(I\mathrm{U} * \mathrm{Activity}\right)^{2} + \left(P\mathrm{U} * \mathrm{Activity}\right)^{2}}$$

where:

$YieldU = YU$

in cases where a radioactive tracer is employed and the yield uncertainty has been expressed as a counting uncertainty, in activity concentration units.

And:

$YieldU = \left(YU * Activiy\right)$

in cases where a stable carrier is measured by ICP, gravimetrically, or other non-radioactive yield determinations, and the yield uncertainty is expressed as a relative uncertainty.

5.4.7 EXPANSION OF THE 1σ TOTAL PROPAGATED UNCERTAINTY
As previously mentioned, the TPU calculation above is expressed at the one sigma (1σ, or 68.3%) confidence interval.

The TPU may be expressed at any other confidence interval by multiplying the 1σ TPU by the appropriate expansion factor (z), shown below.

σ value	% confidence interval	Expansion factor (z)
1.00	68.3	1.00
1.96	**95.0**	1.96
2.00	95.4	2.00
2.56	**99.0**	2.56
3.00	99.7	3.00

Additional expansion factors may be determined by calculating the relative coverage area (% confidence interval) of the normal distribution curve.

5.5 Decision Level (DL) and Minimum Detectable Concentration (MDC)
In a background-corrected nuclear measurement, in which the background count rate is expected to randomly vary with a normal distribution, the analysis of a blank sample will naturally show activity that is not necessarily zero, depending on the pairing of these randomly fluctuating count rates. The DL refers to the maximum activity concentration (at the specified confidence interval) that would be expected to be reported in a blank sample analysis.

By extension, the MDC described that level of activity that would have to be in a contaminated sample in order to give a result that is sufficiently higher than the DL, so that the sample is statistically distinguishable from one with no activity.

By convention, the DL and the MDC are expressed at the 95% confidence interval.

As described above, in Section 2.3, ALS provides default DL and MDC calculations that follow industry convention. These default formulae assume that the background determination for the sample analysis was performed for the same duration as the sample analysis itself.

5.5.1 DL

Unless otherwise specified in documentation of specific analytical methods, instrumentation software, or client requirements, the DL shall be calculated as:

$$DL = \frac{2.33\sqrt{B}}{kT_s}$$

where:

B = the total counts in the background for the sample

T_s = the sample count duration

k = the standard denominator described in Section 5.2

5.5.2 MDC

Unless otherwise specified in documentation of specific analytical methods, instrumentation software, or client requirements, the MDC shall be calculated as:

$$MDC = \frac{4.65\sqrt{B} + 2.71}{kT_s}$$

5.5.3 REVISED DL AND MDC CALCULATIONS IN CASES WHERE THE SAMPLE COUNT DURATION DIFFERS FROM THE BACKGROUND COUNT DURATION

As described above, in Section 2.3, ALS recognizes that there may be technical refinements to the default DL and MDC calculation, in cases where the sample and background count times differ.

These refinements, while technically sound, are generally provided only at the client's request because many clients view these changes to the calculations as a source of discontinuity to the historical record for some monitoring data. Nonetheless, the analyst should be aware of, and versed in, the revised formulae;

$$MDC = \frac{3.29\sqrt{R_B * T_s * (1 + T_s / T_b)} + 2.71}{k * T_s}$$

$$DL = \frac{2.33\sqrt{R_B * T_s * (1 + T_s / T_b)}}{k * T_s}$$

where:

R_B, k, and T_s are defined as above

T_b = the background calibration count duration

6. QA/QC

All instruments shall be calibrated according to requirements described in SOPs 704, 713, 714, 724, and 783 prior to performing these calculations.

7. SAFETY, HAZARDS AND WASTE DISPOSAL

7.1 SAFETY AND HAZARDS

All Safety and Hazards are managed in accordance with the current facility plans:

- Chemical Hygiene Plan (CHP)
- Radiation Protection Plan (RPP).
- Emergency and Contingency Plan (ECP)
- Respiratory Protection Plan (RESPP)
-

7.2 WASTE DISPOSAL

All Wastes are disposed of in accordance with the Waste Management Plan (WMP)

8. REFERENCES

8.1 ANSI N42 Standards, National Committee on Radiation Instrumentation.

8.2 NIST Technical Note 1297, “Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results”, U.S. Dept. of Commerce, 9/94.

8.3 Knoll, Glenn F., Radiation Detection and Measurement, 3rd Ed., Wiley & Sons, 1999.

8.4 ALS Analytics, Inc Project ID 02-15-001, “Empirical Measurements for TPU Determinations”, 3/02.

8.5 Lloyd A. Curie, "Limits for Qualitative Detection and Quantitative Determination", Anal. Chem. 40, 586-93, March 1968.

8.6 National Council on Radiation Protection and Measurements, NCRP Report No. 58, 309, September 1984.

8.7 EPA 520/1-80-012, "Upgrading Environmental Radiation Data", Health Physics Society Committee Report HPSR-1, 6-26, August 1980.

8.8 Allen Brodsky, et al, “Statistical Considerations in Practical Contamination Monitoring”, Radiation Protection Management, Vol. 8, No. 4, (July/August 1991), pp. 64-78.

8.9 MARLAP Manual, July 2004, Section III, Section 20.4.

APPENDIX A

LIMS SWITCH SETTINGS FOR SPECIFIED METHODS

ClassCode	TLAnalyte	SwitchA	SwitchB	SwitchC	SwitchD	SwitchE	SwitchF	SwitchG	SwitchH	RptHC	AbundCrit
GAB	GROSS ALPHA	1	0	1	0	0	0	0	0	-1	1.0000
GAB	GROSS BETA	1	0	1	0	0	0	0	0	-1	1.0000
GROSS_ALPH	GROSS ALPHA	1	0	1	0	0	0	0	0	-1	1.0000
GROSS_BETA	GROSS BETA	1	0	1	0	0	0	0	0	-1	1.0000
I129	I-129	0	1	0	0	0	0	0	1	-1	1.0000
I129	I-129+	0	1	0	0	0	0	0	1	-1	1.0000
GR_ALPH_CO	GROSS ALPHA	1	1	1	0	0	0	0	0	-1	1.0000
RA228	RA-228	0	0	0	0	0	0	1	1	-1	1.0000
RA228	YTTRIUM	0	0	0	0	0	0	0	1	-1	1.0000
RaTOT	BARIUM	0	0	0	0	0	0	0	1	-1	1.0000
RaTOT	RA-226	0	0	1	0	1	3	0	1	-1	1.0000
RaTOT	TOTAL RADIUM	0	0	1	0	1	3	0	1	-1	1.0000
SR89	SR-89	0	0	0	1	0	0	0	1	-1	1.0000
H3	H-3	0	0	0	0	0	0	0	1	-1	1.0000
SR90	SR-90	0	0	0	1	0	0	0	1	-1	1.0000
C14	C-14	0	0	0	0	0	0	0	1	-1	1.0000
NI63	Ni-63	0	0	0	0	0	0	0	1	-1	1.0000
Tc99	Tc-99	0	0	0	0	0	0	0	1	-1	1.0000
Rn222	Rn-222	0	0	0	0	0	0	0	1	-1	1.0000
PuISO	PU-238	0	0	0	0	0	0	0	1	-1	1.0000
Am241	AM-241	0	0	0	0	0	0	0	1	-1	1.0000
Pu242	PU-242	0	0	0	0	0	0	0	1	-1	1.0000
Ra226_RnE	Ra-226	0	0	0	0	0	0	1	1	-1	1.0000
Np237	NP-237+	0	0	0	0	0	0	0	1	-1	1.0000
GAB_No_Att	GROSS ALPHA	1	0	0	0	0	0	0	0	-1	1.0000
GAB_No_Att	GROSS BETA	1	0	0	0	0	0	0	0	-1	1.0000
TotActivit	TOTAL BETA	0	0	0	0	0	0	0	0	-1	1.0000
Pb210_LiqS	Pb-210	0	0	0	0	0	1	0	1	-1	1.0000
Pb210	Pb-210	0	0	0	0	0	1	0	1	-1	1.0000
SR8990	SR-89	0	0	0	1	0	0	0	1	-1	1.0000

ClassCode	TLAnalyte	SwitchA	SwitchB	SwitchC	SwitchD	SwitchE	SwitchF	SwitchG	SwitchH	RptHC	AbundCrit
SR8990	SR-90	0	0	0	1	0	0	0	1	-1	1.0000
Pm147	Pm-147	0	0	1	0	0	0	0	1	-1	1.0000
Fe55	Fe-55	0	0	0	0	0	0	0	1	-1	1.0000
Ni59	Ni-59	0	0	0	0	0	0	0	1	-1	1.0000
Pu241	PU-241	0	0	0	0	0	0	0	1	-1	1.0000
TotActivit	TOTAL ACTIVITY	0	0	0	0	0	0	0	0	-1	1.0000
AmISO	CM-244	0	0	0	0	0	0	0	1	-1	1.0000
AmISO	AM-243	0	0	0	0	0	0	0	1	-1	1.0000
CmISO	CM-244	0	0	0	0	0	0	0	1	-1	1.0000
UISO	U-232	0	0	0	0	0	0	0	1	-1	1.0000
UISO	U-238	0	0	0	0	0	0	0	1	-1	1.0000
UISO	U-233/234	0	0	0	0	0	0	0	1	-1	1.0000
UTOT	U-232	0	0	0	0	0	0	0	1	-1	1.0000
UTOT	U-235	0	0	0	0	0	0	0	1	-1	0.8500
ThISO	TH-229	0	0	0	0	0	0	0	1	-1	1.0000
ThISO	TH-230	0	0	0	0	0	0	0	1	-1	1.0000
Th/Ac	TH-227	0	0	0	0	0	0	0	1	-1	0.5383
PuISO	PU-239	0	0	0	0	0	0	0	1	-1	1.0000
PuISO	PU-242	0	0	0	0	0	0	0	1	-1	1.0000
PuISO	PU-239/240	0	0	0	0	0	0	0	1	-1	1.0000
Am241	AM-243	0	0	0	0	0	0	0	1	-1	1.0000
AmISO	AM-241	0	0	0	0	0	0	0	1	-1	1.0000
CmISO	CM-242	0	0	0	0	0	0	0	1	-1	1.0000
CmISO	AM-243	0	0	0	0	0	0	0	1	-1	1.0000
UISO	U-234	0	0	0	0	0	0	0	1	-1	1.0000
UISO	U-235/236	0	0	0	0	0	0	0	1	-1	1.0000
UISO	U-235	0	0	0	0	0	0	0	1	-1	0.8500
UTOT	U-234	0	0	0	0	0	0	0	1	-1	1.0000
UTOT	U-238	0	0	0	0	0	0	0	1	-1	1.0000
ThISO	TH-228	0	0	0	0	0	0	0	1	-1	1.0000
ThISO	TH-232	0	0	0	0	0	0	0	1	-1	1.0000
Th/Ac	TH-228	0	0	0	0	0	0	0	1	-1	1.0000
Th/Ac	TH-230	0	0	0	0	0	0	0	1	-1	1.0000

ClassCode	TLAnalyte	SwitchA	SwitchB	SwitchC	SwitchD	SwitchE	SwitchF	SwitchG	SwitchH	RptHC	AbundCrit
Th/Ac	TH-232	0	0	0	0	0	0	0	1	-1	1.0000
Th/Ac	TH-229	0	0	0	0	0	0	0	1	-1	1.0000
Th/Ac	AC-227	0	0	0	0	0	0	1	1	-1	0.5383
Po210	PO-210	0	0	0	0	0	0	0	1	-1	1.0000
Po210	PO-209	0	0	0	0	0	0	0	1	-1	1.0000
Np237	NP-237	0	0	0	0	0	0	0	1	-1	1.0000
Pu242	PU-239	0	0	0	0	0	0	0	1	-1	1.0000
Ra226_RnE	BARIUM	0	0	0	0	0	0	0	1	-1	1.0000
Pm147_LiqS	Pm-147	0	0	0	0	0	0	0	1	-1	1.0000
UTOT	U-233/234	0	0	0	0	0	0	0	1	-1	1.0000
UTOT	U-235/236	0	0	0	0	0	0	0	1	-1	1.0000
CmISO	Cm-243/244	0	0	0	0	0	0	0	1	-1	1.0000
PuISO	Pu-244	0	0	0	0	0	0	0	1	-1	1.0000
ThISO	Th-231	0	0	0	0	0	0	0	1	-1	1.0000
ThISO	Th-234	0	0	0	0	0	0	0	1	-1	1.0000
CmAmISO	Am-242/243	0	0	0	0	0	0	0	1	-1	1.0000
CmAmISO	Am-241	0	0	0	0	0	0	0	1	-1	1.0000
CmAmISO	Cm-245/246	0	0	0	0	0	0	0	1	-1	1.0000
CmAmISO	Cm-247	0	0	0	0	0	0	0	1	-1	1.0000
CmAmISO	Cm-248	0	0	0	0	0	0	0	1	-1	1.0000
CmAmISO	Cm-244	0	0	0	0	0	0	0	1	-1	1.0000
U232TOT	U-232	0	0	0	0	0	0	0	1	-1	1.0000
U232TOT	U-238	0	0	0	0	0	0	0	1	-1	1.0000
GAB_BP	GROSS ALPHA	1	1	1	0	0	0	0	0	-1	1.0000
GAB_BP	GROSS BETA	1	1	1	0	0	0	0	0	-1	1.0000
GAB_BP_NoA	GROSS ALPHA	1	1	0	0	0	0	0	0	-1	1.0000
GAB_BP_NoA	GROSS BETA	1	1	0	0	0	0	0	0	-1	1.0000
CL36	Cl-36+	0	0	0	0	0	0	0	1	-1	1.0000
CL36	Cl-36	0	0	0	0	0	0	0	1	-1	1.0000
AmISO	Cm-242	0	0	0	0	0	0	0	1	-1	1.0000
ThISO	Th-227	0	0	0	0	0	0	0	1	-1	1.0000

ALS Standard Operating Procedure

DOCUMENT TITLE:	ANALYSIS OF ALPHA EMITTING RADIONUCLIES BY ALPHA SPECTROSCOPY
REFERENCED METHOD:	----------
SOP ID:	714
REV. NUMBER:	2
EFFECTIVE DATE:	APRIL 5, 2013

ALS Environmental

ALS
STANDARD OPERATING PROCEDURE 714 REVISION 12

TITLE: ANALYSIS OF ALPHA EMITTING RADIONUCLIDES BY ALPHA SPECTROMETRY

FORM: APPENDIX B, C

APPROVED BY:

TECHNICAL MANAGER _____ DATE _____

QUALITY ASSURANCE MANAGER _____ DATE _____

LABORATORY MANAGER _____ DATE _____

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the steps necessary to perform spectroscopic analysis of alpha emissions on samples of various media using high-resolution ion implanted silicon alpha spectrometry. This procedure is applicable to all alpha spectrometry analyses performed at ALS. The target analytes are routinely separated from liquids (primarily aqueous) and solid samples (primarily soils, wastes, filters) following equilibration of the sample with a suitable isotopic tracer, and mounted by micro-precipitation onto 25mm, 0.1 micron (μm) pore sized filters, fixed into 31mm stainless steel planchets. Analyte activity is derived from the relative count rates of analyte and tracer isotopes and the known activity of tracer added. When no suitable nuclide is available for use as an isotopic tracer (e.g., ^{237}Np), splits of each sample are prepared following addition of a known quantity of NIST-traceable tracer solution of the target analyte. The chemical yield data generated from split sample analysis is used for the calculation of sample results.

2. SUMMARY

Alpha emissions from radionuclides are detected by an ion-implanted semiconducting silicon wafer, which transfers the energy deposited into a small electronic pulse for each alpha interaction, where the pulse height is proportional to the incident alpha energy. The 600mm^2 ion implanted silicon detectors are mounted in vacuum chambers and operated at or below 500 milliTorr absolute pressure to minimize loss of alpha particle energy during the path from the sample to the detector. The data collection and processing is performed through the AlphaVision32©, V5.32.02 (Detectors 1-64) and V5.6.2 (Dectors 65-96) software package.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review. The Alpha Spectroscopist

is responsible for day-to-day operations, calibrations, troubleshooting, repair of the instrument, and related details

3.2 It the analyst's responsibility to ensure that the activity of the calibration sources are properly verified at least annually by comparison to an independent source. In addition, it is the analyst's responsibility to ensure that the independent source has been verified by a NIST-traceable laboratory within a year of use. In practice this means that the independent source can be sent off-site for re-verification at an interval of just less than two years.

3.3 It is the responsibility of the analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOP 715.

3.4 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.5 ALS's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede ALS's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.6 The Department Supervisor or designee performs final review and sign-off of the data. Initialing and dating the report components and review checklists indicate that reviews for precision, accuracy, completeness, and reasonableness are complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.7 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager or designee.

4. INTERFERENCES

4.1 The presence of excessive precipitate in the final source will lead to degradation of spectrum quality due to self-absorption effects. Excessive tailing, poor peak separation or visible evidence of unusual amounts of solids on the final source may necessitate cleanup of the sample (by dissolving LaF_3–analyte precipitate in

boric/nitric acid, co-precipitating as a ferric hydroxide, dissolving $FeOH_3$ in HCl and repeating the microprecipitation steps. Additional column separation may be necessary to remove various interfering constituents).

4.2 The levels of activity taken for analysis should be minimized to prevent contamination of the detection system and overwhelming the tracer. Aliquot size should be judged according to expected activities for the samples (refer to pre-screening data available in the work order folder) and should generally be held within the range of less than 30-50pCi.

4.3 For the alpha spectrometry system, a sample with elevated activity is defined as one that has more than 200 total disintegrations per minute (DPM) deposited on the planchet. This includes all requested analytes of interest as well as the tracer analyte. When such a sample is encountered, the Preparation Lab and Instrument Lab Supervisors must be notified so that they can investigate the possibility of equipment contamination. At the instrument, a background check of the detector used to count the sample must be performed before any subsequent samples may be counted by that detector. This is performed to ensure that detector contamination did not occur, which could bias subsequent analyses on that detector. Generally, a 1000-minute background calibration is run in order to fulfill the background check requirement. If the new background calibration passes quality control criteria, this calibration replaces the previous weekly background calibration until the next weekly background calibration is performed. If the new background calibration fails to meet quality control criteria, consult the Department Supervisor for corrective action. Please refer to Section 11 of this SOP for background quality control criteria.

4.4 The ALS default minimum detectable concentration (MDC) formula referenced in this SOP 708 conservatively assume that background count times equal or exceed sample count times. If extended count times are necessary to meet data quality objectives (DQOs), it is advisable that dedicated background counts be conducted immediately prior to the count to both ensure that count time parity is achieved, and to minimize the potential effect of detector contamination.

4.5 The presence of significant peak activity in a spectrum other than that expected (e.g., thorium peaks in a plutonium spectrum) is significant cause for concern. Re-preparation or appropriate sample cleanup may be indicated. Consult with the Department Manager for advice in such cases.

4.6 Detectors are segregated into U/Th/Np only and Am/Cm/Pu/Np/Po only due to the progeny resulting from U/Th samples. The U/Th progeny will cause an interference in Am/Cm/Pu measurements.

4.7 In some cases, the addition of normal tracer analytes will cause interference in other analytical regions of interest (ROIs). For example, ^{229}Th activity generally

"tails" into the ^{230Th} ROI, and ^{243}Am may have measurable ^{241}Am activity present. These potential interferences must be accounted for in the analytical procedure.

4.8 In some cases, two requested analytes may be indistinguishable by alpha spectrometry (e.g. ^{233}U and ^{234}U). In these cases, the combined ROI is reported as a single result for both analytes (e.g. $^{233/234}$U).

5. APPARATUS, MATERIALS AND REAGENTS

This procedure is conducted with the use of installed alpha detection and analysis equipment consisting of ion implanted silicon detectors mounted in combination vacuum chambers/spectrometers. These spectrometers are controlled by a personal computer based analysis system with multi-channel analyzer interface, integral multi-channel analyzers (MCAs), alpha analysis software, and associated cabling. Currently, the analysis software used to analyze samples is AlphaVision32©, Version 5.3, by EG&G Ortec Corporation. The alpha detectors used to count samples are Ortec "U-024-600-AS" 600mm^2 ULTRA_AS ion-implanted detectors, or equivalent. In addition, the following materials are used for routine maintenance of the detectors.

5.1 KimWipe™ lint-free wipes

5.2 cotton balls

5.3 Methanol, reagent grade
TLV=200ppm

5.4 canned (pressurized) air

6. SAMPLE HANDLING

6.1 All samples received by the radiochemistry Instrument Lab must be checked in within one business day, using the LIMS internal chain of custody (SOP 318).

6.2 Generally, samples with long count times (greater than 360 minutes) are loaded at the end of the day. Samples with shorter count times (less than 360 minutes) may be loaded throughout the day, as time allows

6.3 Generally, samples are prioritized for counting based on the client requested due date.

6.4 Polonium is generally volatile under the vacuum conditions used in this analysis. Samples for polonium analysis are sealed with a thin film covering to prevent detector contamination. The planchets should be carefully handled on the outside of the planchet, with a gloved hand rather than forceps, to prevent puncturing of the thin film.

6.5 In some cases, short-lived analytes or interfering progeny may require samples to be analyzed as quickly as possible. For example, ^{227}Th has an 18.72 day half-life and significant delays in counting will result in elevated detection limits. Also, the ^{232}U- progeny, ^{228}Th ingrows with a half-life of 1.9 years and significant delays in counting will result in ^{228}Th interference in the ^{232}U ROI.

6.6 Uranium and thorium analyses, particularly those in high activity samples, should be removed from the detector as soon as possible after the completion of the count to prevent recoil and progeny contamination of the detector.

6.7 Standard verifications and proficiency demonstrations should be analyzed and processed within 48 hours of receipt from the prep lab due to the pressing production needs of the Department.

6.8 Planchets will be stored in the Instrument Lab for a minimum of three months prior to disposal to allow for reanalysis if necessary.

7. PROCEDURES

Instructions are given for the AlphaVision32© program, Version 5.3. Throughout the text of this document, < > defines a computer keystroke, ___ defines a window header, and [ ] defines a menu option on the AlphaVision software. Basic technician-level access to AlphaVision can be obtained through the user name "user" and the password "user". See the Department Manager for administrator- and supervisory-level access.

7.1 OPERATING CONDITIONS

The alpha spectrometers are operated in a low vacuum system, less than 500milliTorr absolute pressure, at detector bias voltages of typically 30-50 volts DC. The operating conditions shall be verified weekly by running energy/efficiency and background calibrations on each detector. See Section 11 for quality control procedures.

7.2 SAMPLE PREPARATION

Samples are prepared by radiochemical separation applicable to the radionuclide(s) being evaluated. Samples are prepared in the Actinides Preparation laboratories using chemical separation and deposition processes (refer to the radiochemistry preparations procedural SOPs for specific information). The samples are received in the Instrument Lab in the form of a filter mounted on a labeled planchet or as in the case of ^{210}Po, as an electroplated disk to be counted.

7.3 DATA ACQUISITION AND ANALYSIS

7.3.1 Each alpha spec detector is separately contained in a metal housing with an o-ring sealed door hinged at the bottom of the housing. Forceps are used to handle planchets. Planchets are loaded into detectors that are calibrated and have passed all QC checks. Planchets for Uranium or Thorium analysis are loaded only into those detectors that are designated for U/Th. Detector numbers are recorded in the appropriate place on the benchsheet. To load the planchets into the detectors after the vacuum has been properly released from the chamber (see below): Open the door, slide out the tray, place the planchet on the tray, slide the tray back in. Make sure the filter paper on the planchet is centered under the detector. Close the door. *Note*

that the tray position within the chamber should always be in the position of the current calibration; currently that position is the default (top) position in the chamber.

7.3.2 Before the analysis can be started, the detector chambers must be evacuated. There is one vacuum line connected to each tower. To evacuate a chamber, turn the knob under the door to the 'PUMP' position. However, once the knob has been turned to apply vacuum to a chamber, all other chambers that are connected to the same vacuum line will temporarily lose vacuum and bias. *If bias to chambers is lost during active counting of samples, the data quality will be compromised!*

On the AlphaVision (AV) grid displayed on the computer, certain colors are set to indicate the status of the chambers:

- **Green** indicates an idle chamber.
- **Red** indicates a detector that is offline.
- **Yellow** indicates a chamber with an active count running.

Therefore, before applying vacuum, chambers where data is being acquired must have the vacuum put on hold by turning the knob under the door to the 'HOLD' position. For example, to start a count in a detector or group of detectors with other samples counting in the same tower (and thus sharing the same vacuum manifold), the vacuum must be put on 'HOLD' for detectors containing the samples that are already counting.

Now it is safe to turn the knobs to the right to 'PUMP' to evacuate all detectors that have been loaded. It is necessary to manually check that all detectors have been properly evacuated. This is done by selecting 'MCA VIEW' by right clicking on that detector with the mouse. Once the spectrum window has opened, select [ACQUIRE] and [ADJUST CONTROLS…]. The vacuum pressure, bias voltage, and current can now be viewed. Once it has been verified that all detectors are pumped down, the detectors that have been placed on 'HOLD' can now be turned to 'PUMP'.

7.3.3 Record the Detector Number, Analytical Run, Sample ID, Analyte Type/Matrix, Count Duration, and Analyst's Initials and in the Alpha Spectroscopy Run Log (Form 746).

7.3.4 After samples have been loaded, and the counting chambers evacuated,

start spectrum acquisition as follows:

7.3.4.1 From the AV menu bar select [PROCESS] then [BATCH].

7.3.4.2 Under General, enter the analytical run (i.e., UAS0608100-2_A) and select the correct template (i.e., iso U or U default) from the drop down menu. Select, [NEXT] which will move to the next screen.

7.3.4.3 In the Batch screen, select the current month and analyte type. Select [NEXT], which will move to the sample screen.

7.3.4.4 In the Sample screen, select [ADD]. A new small screen will open. Enter sample ID of first sample of analytical run only. Select [OK] to close the small screen. Enter the correct sample units (g, L) and sample aliquot size (This may be done in whole numbers instead of entering exact aliquot volumes. In order for LIMS to perform the final calculations, it queries aliquot volumes from the benchsheet, not from the aliquot entry in AV. Therefore, rounding of aliquot sizes in AV does not impact data quality). Select [NEXT], which will move to the Acquisition screen.

7.3.4.5 In the Acquisition screen, enter the run time in minutes. Select [NEXT], which will move to the Analysis Setup screen.

7.3.4.6 In the Analysis Setup screen, select the correct nuclide library, ROI set, and Tracer set from the drop down menus. Enter the Tracer amount from the benchsheet.

7.3.4.7 Select [PREVIOUS] to return to the Sample screen. Enter the remaining sample IDs from the analytical run. Select [FINISH], which will open a screen showing all sample IDs that have been entered.

7.3.4.8 To assign detectors, select a desired detector and drag over to the appropriate sample ID. When all detectors have been assigned, select [START NOW].

7.3.5 When unloading samples, release the vacuum as slowly as possible by turning the knob counterclockwise from ‘Pump’. Turn the knob slowly the rest of the way to vent. *Air should not be heard rushing into the detector to any appreciable extent as air current stirs up particles and*

potentially contaminates the detector and chamber.

7.3.6 When removing the samples from the detector chambers, verify the position by checking the sample removed from the detector against the detector # recorded on the benchsheet. Any discrepancy should be noted on a QASS and/or the benchsheet and the raw data printout. If a discrepancy is found, the sample may need to be re-analyzed.

7.4 SPECTRUM ANALYSIS

Each nuclide emits alpha particles at distinct energies characteristic of the decaying species (see attached Table 1 for a short list of energies). When an alpha particle is incident on the detector, an electrical pulse is generated, the signal produced is analyzed according to pulse height, and is stored as a count in the appropriate channel of the given MCA buffer. As the number of counts stored increases, peaks for each radionuclide begin to form. AV is programmed to conduct an ROI analysis of the spectrum from the data gathered during the count and information that was previously entered (i.e., tracer DPM, target nuclides and relative ROIs, recovery type, etc.). The results of the analysis are then summarized in a raw data results report and a graphical hardcopy printout of the spectrum is produced. The raw data results are also written to the AV database.

7.4.1 After sample acquisition has been started, it is possible to examine the spectrum “live” to make a real-time estimate of chemical yield expected for that sample (note that sufficient time must have elapsed for the spectrum to be discernible, 10-15 minutes is usually sufficient).

7.4.1.1 This may be accomplished by selecting the detector with the mouse, right clicking and choosing [MCA VIEW]. At this point, the chemical yield can be estimated from the net area of the peak. The detector may also be manually analyzed in order to get a printout to determine preliminary chemical yields. See Section 9 for the appropriate calculation.

7.4.1.2 Alternately, select the “spectrum” line in the sample entry in the upper right window, right-click the mouse and select [INTERIM ANALYSIS]. This will perform a normal analysis, as described in Section 7.4.2 below, using the data acquired thus far. The analysis report will show calculated yields, activities, etc. as well as a printout of the interim spectrum.

7.4.2 When the preset live time has elapsed, the detector icon turns solid green to indicate that the full count duration has elapsed. The spectrum and analysis data is then reviewed prior to printing the raw data and

saving the .pdf image.

7.4.2.1 In some cases the software fails to recognize the tracer peak in the spectrum and the analysis sequence is stopped before completion. In this case, at the analyst's discretion, the analytical sequence may be manually taken to completion. Select the analytical parameters by right-clicking the mouse on the spectrum entry in the upper right window. Select [ANALYZE]. In the Analysis window, uncheck the "Shift With Tracer" box, then select [OK]. ROIs may then be evaluated, as described below.

7.4.2.2 Select the "analysis" line in the sample entry in the upper right window. This displays the spectrum and ROIs in the "Spectrum" tab. Specific analytical considerations for evaluating and adjusting ROIs are discussed below. *NOTE – due to limitations in the AlphaVision software, if ROI adjustments need to be made, first select [INTERACTIVE ROI ANALYSIS]*. Adjust ROIs as necessary. ROIs can be adjusted by dragging the ROI boundaries left and right. Finally, select [INTERACTIVE ROI ANALYSIS] again.

7.4.2.3 Select the "Report" tab at the bottom left of the report window to display the raw data report. Select the printer icon at the top left, which will call up the default PDF Factory program. Save the image under the file name designated on the LIMS Instrument Worksheet (e.g., U81925D.PDF), then print a hard copy for further review.

7.4.3 After samples have finished counting, perform a cursory review of the raw data printouts to ensure that chemical yield, duplicate error ratio(s) (DER), minimum detectable activity (MDA), tracer counts, blank activity, and laboratory control sample (LCS) values all satisfy applicable data quality objectives. Check the spectra for peak shifts and peak resolution. Verify that a raw data printout and spectrum is present for all counted samples. Determine if there are samples to be recounted or re-prepared. This will give the Preparation Group adequate time to complete a re-extraction if any of these parameters fail to pass acceptance criteria.

7.4.4 In the absence of client-specific yield requirements, a sample that has between 15-30% yield recovery may be reported in some cases. In such cases, spectral quality must be acceptable in the analyst's judgment and all other QC criteria must be met. The sample is flagged with a "Y2" flag, a narrative comment is made, and the results are

reported, with Supervisory oversight.

Samples with chemical yields below 15%, those with yields below client-specific yield requirements, or those that do not meet the spectral quality requirements listed above require corrective action. An NCR will be initiated (see SOP 928) and sample re-extraction may be necessary. Samples with low yields may still be reported when a sample is of an uncommon matrix, if re-extraction would not be expected to produce improved chemical yield, or if a second extraction of a sample shows repeated poor chemical yield (generally an indication of matrix interference). Low yield is always documented in a case narrative, and an explanation is included if the sample was not re-analyzed. Consult with the Department Manager and the Project Manager before reporting results for a sample that has shown poor yield.

7.4.5 DER values are calculated using the formula found in SOP 715. Compare blank activities to established limits and, if applicable, to client/project-specific data quality objectives. Compare LCS results to the known values for a particular radionuclide for appropriate spikes. The known values are found on the benchsheet; crosscheck this against the standard verification worksheet.

7.4.6 Sample measurements are routinely determined by internal addition of isotopic tracer to each sample prior to separation. Samples are traced with adequate activity and counted for a sufficient period of time such that counting uncertainties of approximately 5% (1 sigma) are obtained for the tracer peak (approximately 400 net tracer counts). Samples that do not achieve approximately 400 tracer counts may be counted longer or are re-prepared to achieve the target uncertainty. However, if tracer counts fall below 400 and all other QC criteria are met and assuming that the additional uncertainty is clearly reflected in the reported TPU or clearly documented in the case narrative, then the samples may be reported, with Supervisory oversight.

7.4.7 ROIs are areas that encompass spectral peaks. Default values have been set based on the expected energies defining the channels between which specific nuclide peaks are expected to fall. Occasionally, slight adjustment of the ROI by a few channels may be necessary to ensure good fit with the acquired data before a final report can be generated. To adjust the ROI, the general guidelines used consist of:

7.4.7.1 For routine Isotopic Uranium, set the boundaries for ^{238}U and ^{234}U so that they are the same distance from the centroid as they are for the tracer, ^{232}U. The ^{235}U ROI will

encompass an energy range from approximately 4217keV to 4396keV. The count data for this ROI will be abundance corrected for 85.1% of the total alpha activity measured. This technique minimizes the high bias to the ^{235}U results due to tailing of the ^{234}U peak.

For Isotopic Uranium where $^{235/236}$U is requested, set the boundaries for ^{238}U and ^{234}U so that they are the same distance from the centroid as they are for the tracer, ^{232}U. The area between the right boundary of ^{238}U and the left boundary of ^{234}U represents $^{235/236}$U. The ^{238}U, $^{235/236}$U, and ^{234}U regions should be directly adjacent to each other with no space in between.

7.4.7.2 For Plutonium and Americium, when there are no peaks for the nuclides and the tracer peak resolution is good, ROIs are set to correspond to energies listed in Radioactive Decay Data Tables, David C. Kocher (reference available on ALS network). Set the ROI for the missing nuclide between the higher and lower energies.

7.4.7.3 Samples analyzed for Isotopic Thorium concentrations have a radioactive tracer, ^{229}Th, added to allow for chemical yield determinations in the separation process. A limitation of this method is that all client and QC samples demonstrate the presence of a small amount of characteristic activity in the ^{230}Th region of interest (ROI) that is attributable to ^{229}Th activity. Peak resolution at this level is inherently limited by methodology and software capabilities.

In order to avoid a high bias to the reported ^{230}Th activity concentrations, an arithmetic correction is made to the count rate in the ^{230}Th ROI. A population of method blank samples, which is assumed to be free of ^{230}Th contamination, is analyzed and the average net contribution to the ^{230}Th ROI is used to make the arithmetic correction. The current blank population (established in April 2006) showed the ^{230}Th correction to be 2.73% of the counts acquired in the ^{229}Th ROI. This value is re-evaluated yearly.

The adjusted number of ^{230}Th background counts is, therefore, calculated as (^{230}Th ROI Calibrated Background Counts) + (0.0273 * ^{229}Th ROI Net Counts). This adjusted

background count number is used in all the usual calculations for Net Activity, Counting Uncertainty, and Minimum Detectable Concentration.

This adjustment to the ^{230}Th background counts is made automatically by entering the correction value (2.73%) in the "Contaminated Tracer" box of the "Tracer Information" screen in AlphaVision. This information should only be entered under the supervision of the Department Manager.

For Thorium samples without ^{230}Th activity, set the ROI for the LCS first. This defines the shape of the peaks and gives an idea of the location and the size of the tracer peak. Note the channel for the middle of the tracer peak of the LCS. Additionally, note the channel for the lower energy end of the ROI for the tracer peak of the LCS. The difference in channel number will be used to set the ROI for samples without appreciable ^{230}Th activity. Samples with ^{230}Th activity will have enough peak resolution in order to accurately set ROI boundaries. For a sample without significant ^{230}Th activity, determine the channel number for the middle of the tracer peak, subtract the number of channels determined from the LCS, and set the lower energy ROI at the new channel.

7.4.8 The full width at half maximum (FWHM) is defined as the width of the peak distribution at a level that is half the maximum ordinate of the peak. Except for isotopic thorium analyses, in determining acceptable resolution, the tracer FWHM shall be between 40 and 100keV. Consult the Supervisor for samples that do not meet this criterion. If the deviation is minimal and all other criteria are met, results are reported with a narrative comment and supervisory approval.

7.4.8.1 Due to limitations in the AV software, the FWHM may need to be manually confirmed, if the reported value falls outside the 40–100 keV range.

7.4.8.2 Find the channel inside the peak with the greatest number of counts. Divide this number of counts by 2 to obtain the "half max" value.

7.4.8.3 Find the left-most channel of the peak that has counts less than the "half max" value. Move the cursor to the right, counting the number of channels, until the right-most channel of the peak that has counts less than the "half-max"

value is selected. Multiply this number of channels by the slope of the energy calibration (nominally 10.0 kev/CH) to obtain a conservative estimate of the FWHM value, in keV.

7.4.8.4 If greater precision in the FWHM estimation is necessary, calculate the partial channels associated with either side of the spectrum by fitting a straight line between the two channels that bound the "half-max" value, and interpolating the precise point at which the "half-max" value is obtained.

For example, suppose that the half-max value is 80 counts, and left-hand side of the peak includes channel 123 with 70 counts, and channel 124 with 95 counts. The slope of the number of counts per channel is 25 cts/CH (i.e., 95cts-70cts).

Determine the portion of the channel where the peak crosses the 80-count level. This point is calculated as (80 cts –70 cts)/(25 cts/CH) or 0.4 channel. Repeat this process for the right side of the peak.

To calculate the FWHM for this peak begin with an initial value of 0.4 CH, start at channel 124 and count to the right as described above, stopping at the channel that has counts greater than the "half-max" value, and add the fraction of a channel calculated for the right side of the peak. Convert this to keV units by multiplying by the slope of the energy equation.

7.4.9 Isotopic Thorium uses ^{229}Th as a tracer analyte. Because ^{229}Th occurs at emission energies from approximately 4800-5100keV at various branching ratios, this peak is expected to be much broader than other isotopic tracer peaks. Therefore, the calculated FWHM value is expected to be greater than that for other analyses, and spectral quality is still sufficient for accurate quantification. Inspection of thorium spectra from analyzed quality control samples (method blanks and laboratory control samples) indicates that a FWHM value equal to or less than 160keV still provides adequate spectral quality. Therefore, for thorium analyses, 160keV is used as the upper FWHM limit. As with the other analytes, if deviation from 160keV is minimal and all other criteria are met, results are reported with a narrative comment and Supervisory approval.

7.5 MAESTRO (MCA CONTROL OPTION IN ALPHAVISION)

Maestro is used to examine a live spectrum (one that is in the process of being acquired). Maestro can be accessed in AlphaVision by selecting the detector on

the grid, right click on the mouse, and select [MCA VIEW]. Data acquisition can be stopped and started, and the buffer cleared with the normal menu options. After viewing the spectrum, exit Maestro to return to AlphaVision.

7.6 DATA REPORTING

7.6.1 For the final data package, individual results forms, QA results forms, and results summaries are generated. These reports are created in LIMS after uploading data from the AV database in the R:\USER directory. The data is uploaded by double-clicking on the "LIMS DATA TRANSFER" icon, located on the desktop of the AV computer.
REVIEWING HARD COPY REPORT FORMS
Review all forms for completeness. Crosscheck raw data to the Raw Data Report form. Check yields, activity values, MDC values, and other data quality control parameters. Note any flags that require an explanation in the narrative.

7.6.2 NARRATIVES
For most clients, a general narrative template may be used.

The narrative template gives a summary of the samples included in the data package, including preparatory information, any anomalous situations encountered, any quality control deviations, or any other applicable information which may affect data quality. .

7.6.3 NARRATIVE COMMENTS

- Any time there is a Non-Conformance Report (NCR), a narrative comment and a copy of the NCR is required. Any time data quality objectives have not been met, but the deviation is not great enough to prohibit reporting (i.e., activity in the blank, but not greater than the requested MDC; 1.42 < DER < 2.13 (warning versus control limits, see SOP 715); requested MDCs not met as a result of small sample aliquot size), a narrative comment is required.
- Minor anomalous situations that have no effect on results usually do not require a narrative comment, but should have a Quality Assurance Summary Sheet (QASS, Form 302). If in doubt, ask the Department Manager regarding the proper way to narrate an anomalous situation.
- **Gross QC failures cannot be narrated without proper NCR documentation!** If any of these types of situations are discovered at the time of reporting, notify the Department Manager and Project Manager immediately. The following types of situations require an NCR and most likely will require

a re-extraction: LCS exceeds control limits; activity in blank greater than requested MDC; DER failure > 2.13; contamination of the sample; chemical yield outside the control limits.

8. CALCULATIONS

Alpha spectra are interpreted and analyzed by a sophisticated mathematical routine that provides for peak identification, peak area analysis, and peak energy determination. Details of calculations performed by the AlphaVision software can be found in the AlphaVision Software Reference Manual (see References Section below, 15.1). ALS's routine alpha spectroscopic analysis of samples employs an ROI approach to spectrum analysis.

The following raw data generated by the AV system are used for sample calculations: Analyte and Tracer Net Counts and Count Time; associated Background Counts for each ROI; Background Count Time and Detector Efficiency. Further data (including Sample Aliquot, Split and Dilution Data, Percent Solids Data, Tracer Concentration and Amount Added, and Estimates of Total Uncertainty as described in SOP 708) from the preparation and standards spiking process, is taken from the electronic benchsheet and merged with the count data during the data reduction step during reporting. Total Efficiency calculations assume that the nuclide used for the tracer is not native to the sample.

Total uranium (a modification of EPA 908.0 by alpha isotopic summation) is calculated using the isotopic uranium results. The net counts are summed and the background counts are summed for ^{234}U, ^{235}U and ^{238}U. The equations depicted in Sop 708 are then used, substituting the 'summed net counts' for 'net counts' and 'summed background counts' for 'background counts', to determine the total uranium (TU) results:

where:

$$\mathbf{SmplNtCts_{TOT}} = SmplNtCts_{234} + SmplNtCts_{235} + SmplNtCts_{238}$$

$$\mathbf{BkgCts_{TOT}} = BkgCts_{234} + BkgCts_{235} + BkgCts_{238}$$

9. RESULTS INTERPRETATION

9.1 It is essential that appropriate analysis volume and units, tracer information, efficiency files and library files be used to ensure accurate analyses. Results must be reviewed to ensure that the sample type used was appropriate to the analysis type (e.g., Pu, U, Th, etc.) and the report reflects proper sample volume and units.

9.2 All target analyte peaks in the spectrum must be matched to the appropriate radionuclide, and, where applicable, the presence of a given radionuclide should be supported by the presence of other significant alpha emissions from that radionuclide.

9.3 Although most of the analyses are routine, it is important to note that each radionuclide has a different peak shape. This is especially evident when dealing with high level samples, and radionuclides that do not exhibit clear and defined peak shapes.

9.4 Peak shape is most often negatively affected by an unusual sample matrix, which may contribute to the attenuation of alpha particles. This attenuation can cause the spectrum to be interspersed with small non-descript peaks, which must be accounted for when adjusting ROI's. If there is any question as to the placement of ROI's see the Alpha Spectoscopist or the Department Manager.

9.5 The radionuclide of interest can also effect the spectrum. For example, thorium spectra usually exhibit more non-descript peak shapes, especially in the ^{229}Th and ^{230}Th ROIs. A typical thorium spectrum is included in Appendix A of this SOP. The other radionuclides analyzed by alpha spectrometry exhibit defined and similarly shaped peaks (i.e., plutonium, uranium, americium, curium, and neptunium). Typical plutonium and uranium spectra are also included.

10. PERIODIC MAINTENANCE

10.1 VACUUM PUMP

The vacuum pump shall be checked weekly. The pressure of both vacuum pumps should be below 250 milliTorr. If the pressure is not below 100milliTorr, see the Department Manager. Note in the Alpha Spec Calibration Log Book, the date and pressure of both vacuum pumps. The pump oil level should be above the “MIN” level mark on the pump. Inform the Primary Alpha Spectroscopist if one or both of the vacuum pumps is above 250 milliTorr. Changing the oil in the vacuum pump usually will bring the vacuum pressure down to or below 250 milliTorr. The vacuum pump oil should be changed annually to prevent any unusual wear on the vacuum pump. Note the oil change date in the Alpha Spec Maintenance Log.

10.2 AIR FILTERS

Air filters are located at the bottom of the MCA NIMBIN. The air filters need to be cleaned annually or as needed by removing and vacuuming. Note the filter cleaning date in the Alpha Spec Maintenance Log Book.

10.3 DETECTOR AND CHAMBER CLEANING

The detector and chamber should be cleaned annually or as indicated by the results of periodic background measurements. Periodic cleaning to reduce background contamination may be performed at any time. To clean the detectors and chambers, always wear gloves to prevent contamination. Remove the detectors with a 5/16” open-end wrench. *Do not attempt to remove the detectors by hand. This can damage the microdot connection!* Clean the chamber using a clean cotton ball and alcohol. The connection between the detector and the chamber needs to be thoroughly cleaned. Using a clean cotton ball and alcohol, clean the detector window, then the top and sides of the detector. Clean the

connection on the top of the detector thoroughly. The detector calibrations (Energy, Efficiency, and Background) must be re-calibrated following cleaning of the chamber, sample tray, or detector.

11. QUALITY CONTROL

11.1 CALIBRATION PROCEDURES

Note that the procedure for acquiring any calibration spectrum is the same as that of a normal sample acquisition. All calibrations must be documented in the Alpha Spec Calibration Log. Calibrations for the alpha spec include energy, efficiency, and background calibrations, and are done every two weeks.

11.1.1 ENERGY AND EFFICIENCY CALIBRATION

Eight electroplated sources are used that consist of ^{241}Am and ^{234}U with a small amount of ^{235}U activity. The sources are counted for approximately 35 minutes. The naming convention for these sources is ALS source ID 97-19-103-XX, where XX is equal to source 01, 02, etc. The energy/efficiency calibrations are typically done first, before the background checks. When the count is finished, the program will compare the locations of the ^{241}Am, ^{234}U and ^{235}U peaks to the primary emissions energies and perform a linear fit of the energy per channel data. This data will then be stored in the appropriate detector file for reference by the analysis program during sample analyses.

11.1.1.1 Load calibration planchets into an octet

11.1.1.2 Pump down detectors

11.1.1.3 Open AlphaVision

11.1.1.4 Click on the black calibration button to the upper left on the AlphaVision screen

11.1.1.5 Right click on detector you are analyzing and select [MCA VIEW]

11.1.1.6 Click [CLEAR], then [GO] for all detectors you are analyzing in that octet

11.1.1.7 Go back to the first detector and press [CTRL]+[LEFT or RIGHT ARROW] to move the cursor to the ^{241}Am peak at channel 249, make sure the peak is at channel 249 +/- 1

11.1.1.8 If the peak is within range select [STOP], then [CLEAR]

11.1.1.9 If the peak is not within range use the small standard screwdriver to move the “e-cal” potentiometer slightly left

or right. Repeat Steps 11.1.1.7 and 11.1.1.8 until the ^{241}Am peak is within range.

11.1.1.10 Exit “MCA view”

11.1.1.11 Click [PROCESS] and then [CALIBRATION]

11.1.1.12 In the General screen enter calibration name (Cymmddxx) and template number (the number on the planchet loaded into the detector)

where:

C = Calibration

y = last digit of the year

mm = month

dd = day

xx = detector number

11.1.1.13 Click on finish

11.1.1.14 After 35 minutes, a small window will appear. Select [CALIBRATION] from drop down menu, then select [CALIBRATE], [SAVE], then [CLOSE]. Repeat for each detector. This saves preliminary calibration data to the database.

11.1.1.15 To analyze the calibration, select detector and click on [SPECTRUM] tab on lower left of report window.

11.1.1.16 Zoom in on each peak by clicking and dragging a box around the peak, then right click and select [ZOOM IN].

11.1.1.17 Move the peak identifier of each peak to the top point of the peak by clicking and dragging the identifier.

11.1.1.18 Due to limitations in the AV software, both the peak identifier and the ROI must be adjusted in order for both the energy and efficiency coefficients to be properly saved. Consequently, move any ROI edge over and then back to its original position.

11.1.1.19 Right click and select [INTERACTIVE ROI ANALYSIS].

11.1.1.20 Repeat Steps 11.1.1.15 through 11.1.1.19 for all detectors in the octet.

11.1.1.21 Go back to first detector in the octet and select the [REPORT] tab at the bottom left of the report window.

11.1.1.22 Select [PRINT] icon in upper left of the report window.

11.1.1.23 In the screen that appears, save under calibration name Cymmddxx in the calibration folder.

11.1.1.24 Repeat Steps 11.1.1.21 through 11.1.1.23 for remaining detectors in the octet.

11.1.2 QA TEST FOR ENERGY/EFFICIENCY CALIBRATIONS

The QA test must be completed before reporting any samples through LIMS, otherwise the calibration report page will not show the correct calibration date.

11.1.2.1 Select [QA/QC] button to the upper left on the AV screen.

11.1.2.2 Select the detector number from list on the upper left and select [CALIBRATION ENERGY].

11.1.2.3 Select [CHART] tab from lower left of the report window.

11.1.2.4 Select [QA] from the menu options, then [CALIBRATION].

11.1.2.5 Select [QA], [DISPLAY], [CUSTOM], then [QUARTER]. Make sure that a dot appears on the chart in correct date.

11.1.2.6 Select [REPORT] tab at bottom left of window, then [PRINT] and minimize PDF factory screen.

11.1.2.7 Select [CALIBRATION EFFICIENCY].

11.1.2.8 Select [CHART] tab from lower left of the report window.

11.1.2.9 Repeat Step 11.1.2.5 and select [REPORT] tab at bottom left of window, then [PRINT]. Save as CCymmddxx. Where the “CC” indicates a calibration control chart and all other factors are as defined above.

11.1.2.10 Repeat Steps 11.1.2.2 through 11.1.2.9 for remaining detectors in octet.

11.1.2.11 Record the results of the calibration in the Alpha Spec Calibration Logbook.

11.1.3 BACKGROUND CALIBRATIONS

A blank filter paper is placed on a numbered planchet, one for every detector. The filter paper is counted for 1000 minutes, typically following the energy/efficiency calibrations. Filter papers and planchets are replaced at least annually.

11.1.3.1 Place the numbered, detector specific, blank filters into the detector chambers. Close the doors and apply vacuum to the chambers.

11.1.3.2 Open AlphaVision. Using the mouse, select the detector(s) that will be started. From the menu bar, choose [PROCESS] then [BACKGROUND].

11.1.3.3 Under General screen, Enter the batch filename as follows: Bymmddxx

where:

B = Background

y = last digit of the year

mm = month

dd = day

xx = M1, M2, M3, etc...for MCB number

11.1.3.4 Select the proper template from the drop-down menu, depending on whether the Octete is designated for U/Th analysis or Am/Pu analysis.

11.1.3.5 Under General screen, Select [NEXT].

11.1.3.6 Under Sample screen select [ADD] and enter sample ID of samples as Bymmddxx, where xx = detector number.

11.1.3.7 Click on [FINISH].

11.1.3.8 A new window will appear with all samples on it. Click and drag desired detector to sample ID. Select [START NOW].

11.1.3.9 After 1000 minutes, a window will appear for each detector.

11.1.3.10 Select [SAVE]. Save as Bymmddxx in calibration folder, where xx = detector number.

11.1.4 QA TEST FOR BACKGROUND CALIBRATIONS

The QA test must be completed before reporting any samples through LIMS, otherwise the calibration report page will not show the correct calibration date.

11.1.4.1 Select [QA/QC] button to the upper left on the AV screen.

11.1.4.2 Select the detector number from list on the upper left and select [BACKGROUND].

11.1.4.3 Select [CHART] tab from lower left of the report window.

11.1.4.4 Select [QA] from the menu options, then [BACKGROUND].

11.1.4.5 Select [QA], [DISPLAY], [CUSTOM], then [QUARTER]. Make sure that a dot appears on the chart in correct date.

11.1.4.6 Select [REPORT] tab at bottom left of window, then [PRINT]. Save as BCmmddxx, where BC = Background Control Chart.

11.1.4.7 Record the results of the calibration in the Alpha Spec Calibration Logbook.

11.2 CALIBRATION ACCEPTANCE CRITERIA

Because calibrations are performed every other week, and the accumulation of 30 data points would be impracticable, acceptance criteria for alpha spec calibrations are based on an initial calibration set rather than a mean and standard deviation of a historical population. Acceptance criteria are updated, at a minimum, when detectors are replaced, or when major service to the Octete is performed.

11.2.1 BACKGROUND ACCEPTANCE CRITERIA

For U/Th detectors, the warning limit is set at 500 counts, and the control limit at 750 counts, over the entire spectrum. Since the background calibration is evaluated over the entire spectrum, elevated counts due to ^{228}Th daughter products (expected progeny) will therefore elevate the entire count. Since these progeny occur at energies higher than most analytes of interest, they do not interfere with data quality, with the exception of ^{228}Th. However, as an additional quality assurance measure, any detectors that exceed the warning limit will be evaluated by the instrument operator to assure that all standard ALS data quality objectives will still be achieved under normal operating conditions.

For all other detectors, the warning limit is 100 counts and the control

limit is 150 counts.

11.2.2 BACKGROUND CALIBRATION CORRECTIVE ACTIONS
If the background determination does not pass acceptance criteria, clean the detectors thoroughly. Most frequently, short-lived decay products are responsible for the failure. Cleaning a detector will often help expedite the process of returning the backgrounds to normal levels. Repeat the background determination. In some cases, the department manager may OK a detector for use if the background counts are elevated as long as the background peaks do not interfere with the analysis performed on that detector. This decision should be clearly documented in the Instrument Calibration Logbook.

11.2.3 ENERGY CALIBRATION ACCEPTANCE CRITERIA
For energy calibrations, the energy calibration equation is used to calculate the energy in keV of the middle channel of the spectrum (256). The initial calibration is used as baseline and the warning limits are set ±40 keV from the initial value. Control limits are set ±50 keV from the initial value.

11.2.4 CORRECTIVE ACTION FOR ENERGY CALIBRATION
With the calibration source in place, manually adjust the E-cal pot. on the front of the chamber until the ^{241}Am peak centroid lies in channel 249. At this point the energy calibration must be repeated.

11.2.5 EFFICIENCY CALIBRATION ACCEPTANCE CRITERIA
The initial calibration is used as baseline and the warning limits are set at 3.33% of the initial value. Control limits are set 5% of the initial value.

11.2.6 CORRECTIVE ACTION FOR EFFICIENCY CALIBRATION
If it is determined that the instrument response has drifted relative to the point of initial calibration, the weekly operating limits and specific method calibrations will be re-established prior to analysis of further samples.

11.3 QC MONITORING
Please refer to SOP 715 for further details regarding preparation and monitoring of method blanks, laboratory control samples, duplicates, and chemical recoveries in samples.

12. DEVIATIONS FROM METHOD

This SOP describes a confidential, proprietary procedure developed by ALS Therefore, there are no deviations from a promulgated method.

13. SAFETY, HAZARDS AND WASTE DISPOSAL

13.1 SAFETY

All Safety and Hazards are managed in accordance with the current facility plans:

- Chemical Hygiene Plan (CHP)
- Radiation Protection Plan (RPP).
- Emergency and Contingency Plan (ECP)
- Respiratory Protection Plan (RESPP)

13.2 HAZARDS

There are no special hazards associated with the conduct of this procedure.

13.3 WASTE DISPOSAL

All Wastes are disposed of in accordance with the Waste Management Plan (WMP)

14. REFERENCES

14.1 AlphaVision Software Reference Manual, Model A-36-BI, Version 5.3.

14.2 ANSI Standard P-N42.23-D2, Measurement and Associated Instrumentation Quality Assurance for Radioassay Laboratories, Final, February 10, 1995.

14.3 ALS SOPs 708 and 715.

TABLE 1

COMMON ENERGIES AND APPROXIMATE CHANNEL LOCATIONS
(to assist the user during calibrations, QA checks and initial spectral interpretation)

Nuclide	***Energy (keV)**	**Target Channel**
Am-241	5485	249
Am-243	5275	228
Cm-242	6112	311
Cm-244	5805	281
Pu-242	4900	190
Pu-238	5499	250
Pu-239	5155	216
Th-228	5423	242
Th-229	4845	184
Th-230	4687	169
Th-232	4010	101
U-232	5320	232
U-234	4775	178
U-235	4396	140
U-238	4196	120

*** The nuclide navigator software that is supplied by alpha vision is the source used to determine the specified library energies. NUDAT (National Nuclear Data Center) of Brookhaven National Laboratory is the database chosen in nuclide navigator.**

NOTE: Actual Target Channels will vary slightly for each detector; peak energy and channel matching is done weekly with the energy calibration process in AlphaVision.

TABLE 2

SUMMARY OF INTERNAL QUALITY CONTROL (QC) PROCEDURES AND CORRECTIVE ACTION

QC Check	Frequency	Acceptance Criteria	Corrective Action
Energy Calibration	Weekly	The initial calibration is used as baseline Warning limits are set ±40keV from the initial value Control limits are set ±50keV from the initial value	Record failure in the Alpha Spectroscopy Maintenance Log. Check source integrity, detector configuration, recount and reprocess: Tag detector off-line; Determine and correct problem; or Narrate why condition is acceptable
Efficiency Calibration	Weekly	The initial calibration is used as baseline Warning limits are set at 3.33% of the initial value Control limits are set 5% of the initial value	Record failure in the Alpha Spectroscopy Maintenance Log. Check source position and integrity, detector configuration, recount and reprocess; Tag detector off-line; Determine and correct problem; or Narrate why condition is acceptable
Background Calibration	Weekly long background	U/Th detectors - the warning limit is set at 500 counts & the control limit is set at 750 counts, both over the entire spectrum. All other detectors - the warning limit is 100 counts and the control limit is 150 counts.	Clean chamber and detector, repeat check; Tag detector off-line; Determine and correct problem, re-establish limits; or Narrate why condition is acceptable
Vacuum check	Weekly	<100 milliTorr	Check/replace seals; locate and repair leak; or call service
Chemical Yield	Each sample	Each sample meets current control limits for analysis	Re-prep; or Qualify or Narrate why condition is acceptable
Regions of Interest (ROI)	Adjust ROI as needed	ROI is properly set, tailing does not compromise quantitiation	Adjust ROI's to fit identified peaks; For tailing, cleanup or re-prep and recount affected samples, consult with Supervisor; Qualify or Narrate why condition is acceptable
Spectral Interferences	Evaluate each spectrum for spectral interferences	Interfering activity does not compromise quantitation	Recount; Clean-up, re-prep/ recount affected samples; Consult with Supervisor or Department Manager; Determine and correct problem; or Qualify or Narrate why condition is acceptable

NOTE: SOP 715 contains acceptance criteria and corrective action for method blank, laboratory control samples, duplicate samples and matrix spike/matrix spike duplicates.

APPENDIX A

SAMPLE SPECTRA

The following three spectra examples demonstrate a typical uranium, thorium and plutonium spectra. Note that americium, curium, and neptunium spectra are somewhat similar to the plutonium spectrum, in relation to their peak shapes.

The thorium spectrum contains four analytes. The difficulty with the placement of the ROI's for ^{229}Th and ^{230}Th is due to close proximity of the two peaks. The small peaks to the right of the ^{228}Th peak are ^{228}Th daughter products, which are expected progeny.

The plutonium spectrum contains three analytes, with no other obvious peaks present. Note that uranium, americium, curium, and neptunium spectra should also contain no other peaks, other than those accounted for by existing ROIs.

In detectors used for Uranium and Thorium analyses, persistent background peaks are typically seen in the higher energy regions of the spectra. These peaks are associated with natural decay progeny and do not interfere with U and Th analyses except in the case of ^{228}Th, where the increased detector background is unavoidable and typically results in elevated ^{228}Th MDC values.

APPENDIX B

ALS

Alpha Spectrometer Instrument Run Log

Date:_____

Detector	Batch ID	Sample ID	Iso/Matrix	Duration	Initial

Detector	Batch ID	Sample ID	Iso/Matrix	Duration	Initial

Notes:

Reviewed
By

APPENDIX C

QUALITY ASSURANCE SUMMARY SHEET

ALS W.O. # / BATCH _____
TEST _____
METHOD _____
SOP/REV (PREP) _____
SOP/REV (ANAL) _____

Briefly document any QA or other problems or deviations associated with the analysis of samples. Problems could result from: log-in, color, odor, dilution, consistency, scheduling, equipment, or instrumentation, or may include documentation of minor deviations necessary due to unique DQO's or sample characteristics.

TECHNICIAN/ANALYST _____ DATE _____

DEPARTMENT MANAGER _____ DATE _____

ALS Standard Operating Procedure

DOCUMENT TITLE:	ANALYSIS OF ALPHA AND BETA EMITTING RADIONUCLIDES BY GAS FLOW PROPORTIONAL COUNTER
REFERENCED METHOD:	EPA 900.0
SOP ID:	724
REV. NUMBER:	11
EFFECTIVE DATE:	10/15/2013

ALS Environmental

ALS
STANDARD OPERATING PROCEDURE 724 REVISION 11

TITLE: ANALYSIS OF ALPHA AND BETA EMITTING RADIONUCLIDES BY GAS FLOW PROPORTIONAL COUNTER -- METHOD EPA 900.0

FORMS: APPENDIX A

APPROVED BY:

TECHNICAL MANAGER _____ DATE _____

QUALITY ASSURANCE MANAGER _____ DATE _____

LABORATORY MANAGER _____ DATE _____

1. SCOPE AND APPLICATION

This procedure describes the steps necessary to perform alpha and beta emissions analysis of samples of various media using the Tennelec LB 4100-W and Tennelec LB5100-W gas flow proportional counting (GFPC) systems. Samples will normally be liquids (primarily water) and solids (primarily soil or sand) evaporated onto planchets or precipitated onto filters. This procedure is applicable to all gross alpha/beta analyses, alpha analyses (such as Total Radium) and certain specific beta analyses (such as ^{90}Sr) performed on the Tennelec LB4100-W and LB5100-W by ALS.

2. SUMMARY OF METHOD

Alpha and beta particle emissions from the sample produce ionizations in a gas-filled chamber, generating a small electronic pulse for each interaction. The pulse height is dependent upon the incident energy of the particle. Since alpha and beta particles are normally emitted at widely separated energies, the instrument is able to discriminate between the alpha and beta particle interactions. The instrument provides raw counting information to a computer and spreadsheet-based analysis program. This information is then transferred to ALS's Laboratory Information Management System (LIMS) for further data reduction and reporting. This procedure provides the calibration, data collection, and analysis portions of EPA Method 900.0.

Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of ALS's internally derived acceptance criteria. In addition, gross alpha analysis of EPA drinking water samples is limited to a residual mass of 100mg on the planchet.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform these procedures according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review,

precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.2 It is the responsibility of the instrument operator to coordinate counting activities with preparation lab activities to ensure timely analysis of samples with short-lived radionuclides or other time-sensitive concerns.

3.3 It is the responsibility of the instrument analyst to ensure optimum instrument capacity through the timely performance and documentation of calibrations, daily performance checks, routine maintenance, etc., as described in Table 1.

3.4 ALS's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede ALS's standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.5 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.6 It is the responsibility of all personnel who work with samples utilizing this method to note any anomalous or out-of-control events associated with the preparation and analysis of the samples. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager.

4. INTERFERENCES / DISCUSSION / COMMENTS

4.1 Low background gas proportional counters generally monitor both alpha and beta activity simultaneously. In beta-specific analyses, such as ^{90}Sr, the alpha channel must be monitored for evidence of interfering radionuclides that might cause a bias to the analyte of interest. A count rate in the alpha channel greater than 10 times the crosstalk-corrected background count rate is cause for concern and must be further evaluated by the Department Manager for potential impact on the data quality. Further, these beta-specific analyses should not be performed on detectors that do not meet both the alpha and beta normal performance criteria, except with the approval of the Department Manager (as in cases where the data quality is not affected).

4.2 Instrument response is greatly affected by the residual mass of the sample on the planchet. This residual mass is generally recorded on the LIMS benchsheet, and

must be maintained at a constant weight to allow for the proper mass-attenuation correction. Some samples may absorb moisture from the air (hygroscopicity), making the residual mass unstable. All planchets must be stored in a desiccator to prevent hygroscopicity. The residual mass of planchets that are stored outside a desiccator, awaiting disposal, must be re-verified prior to any requested re-analysis.

4.3 Instrument response is also greatly affected by the distribution of sample residue on the planchet. Planchets must be inspected upon receipt to ensure even deposition of material, generally equivalent to the calibration planchets for that method.

4.4 On gas proportional counters with active guard detectors, the guard detector count rate must be monitored to ensure that that count rate is below established control limits. Elevated guard count rates are potentially indicative of other electronic problems that may bias the final results.

4.5 For samples analyzed by the gas flow proportional counter, an elevated level sample is defined by either a beta count rate of over 5,000 counts per minute (cpm) or an alpha count rate of over 1,000cpm. If a particular sample exceeds either of these parameters, the detector used to count that sample must be evaluated to ensure that no contamination of the detector has occurred. This evaluation is performed by analyzing a blank sample on the detector for a count duration that equals or exceeds the expected count duration for subsequent sample counts. If this blank analysis generates a result that is below the minimum detectable concentration (MDC) for the analysis in question, it may be assumed that no significant contamination of the detector has occurred and samples may be counted on that detector. If the results of the blank analysis are above the calculated MDC, contamination of the detector should be suspected. A Supervisor must then be notified so that proper corrective action procedures may be implemented. The detector in question must be shown to be free of contamination before any sample analysis may proceed.

5. APPARATUS AND MATERIALS

5.1 Gas Flow Proportional Counter; LB5100-W, LB4100-W, or equivalent

5.2 Forceps, stainless steel -- keep separate set for background and source/sample handling

5.3 Stainless steel planchets, 47mm diameter, for background calibration and daily performance checks

5.4 Desiccator

5.5 Kimwipes™

6. REAGENTS

6.1 Methanol, reagent grade

6.2 Color-indicating Dri-Rite™

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 All planchets must be stored in a desiccator to prevent hygroscopicity. The residual mass of planchets that are stored outside a desiccator, awaiting disposal, must be re-verified prior to any requested re-analysis.

7.2 Always handle the sample planchets with forceps or tweezers to minimize sample exposure to the operator and contamination in the laboratory.

8. PROCEDURES

Instructions given below are for the Oxford Systems Unit Manager (OSUM) Version 1.10. Throughout the text of this document, < > defines a computer keystroke, and [ ] defines a menu option in the OSUM software.

8.1 OPERATING CONDITIONS

Each alpha/beta counting system shall be operating with detector bias as determined during the installation and calibration of the system. The proper setting is determined by the generation of a voltage plateau, as described below. The amplifier settings for the instrument shall be determined during instrument installation and calibration to maximize detector efficiency and minimize alpha/beta crosstalk. The operating conditions shall be verified daily by performance of the daily instrument performance checks as described below.

8.2 SAMPLE PREPARATION

Samples to be analyzed by this method will have been prepared by radiochemical procedures applicable to the radionuclide(s) being evaluated. Sample preparation may be limited to quantitative distribution onto a planchet or may be as complex as a complete digestion and chemical separation. See appropriate radiochemical procedure(s).

8.3 SAMPLE ANALYSIS PROCEDURE

The applications software for these instruments is a Windows™ product. It is assumed that the operator of the software is familiar with the basic operation of Windows™.

8.3.1 LOADING SAMPLES

8.3.1.1 To load the LB4100, open one of the four sample drawers in the front of the instrument. Place the sample planchet in one of the four planchet holders. Note the position of the sample on the sample benchsheet and in the instrument run log (Form 780). Close and lock the drawer.

8.3.1.2 To load the LB5100, planchets are placed in individual, numbered carriers in the sample rack. Samples to be counted are identified by one of several group markers, labeled A through L, which must be placed in front of the first numbered planchet holder in a count batch. The count batch is properly ended by placing another group marker or the "END" marker behind the last sample in the count batch. Note the carrier number of the sample on the sample benchsheet and in the instrument run log (Form 780).

8.3.2 SETTING COUNT PARAMETERS

8.3.2.1 Prior to starting the sample analysis, the count parameters must be set properly for each batch. The count parameters may include the α and β counting efficiency files and the required count duration.

8.3.2.2 On the LB4100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Edit Parameters]. Select the [LIMS Data] application. At this point, enter the desired count duration and select the efficiency files that correspond to the analysis to be run. Close this screen when the proper information is entered.

8.3.2.3 The LB5100 uses a typical pull down menu in the main screen. Select [Edit Parameters], choose the appropriate application, and continue as described in the preceding paragraph.

8.3.3 STARTING THE SAMPLE COUNT

8.3.3.1 On the LB4100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Create Batch]. Select the detectors to be started. Type in the proposed file name in the format XXImmdd where XX is the analysis type, I is the instrument used, mm is the month and dd is the day. The following Table specifies the appropriate XX designation:

Analysis Type	**XX Designation**
Gross α/β	AB
Radiostrontium	SR
Radium-228	RA
Radium-226	RD
Total Radium	TR
Chlorine-36	CL
Iodine-129	IO

Additional count batches on a given day requiring the same file name may be appended with an A, B, C, etc.

Type in the batch ID as shown on the laboratory benchsheet. Select [Run]. The instrument will proceed to prompt for sample IDs for each detector. Enter the sample IDs as they appear on the benchsheet. Select [Done]. For each sample entered, the instrument will now prompt for analysis volume (in grams or liters) and residual mass (in milligrams). Leave the analysis volume blank and enter the residual mass, where appropriate, when it appears on the benchsheet. Select [Next] to proceed to the next sample. Select [Done] when all sample masses have been entered. The detector icons will now turn from green to yellow to indicate that the count is in progress. Enter the file name, detector ID, date and time, type of analysis, etc. as indicated in the instrument run log (Form 780) and on the LIMS benchsheet.

8.3.3.2 On the LB5100, select [Start Count] from the pull down menu. Select the application to be run. Enter the filename in the format listed above and select the group letter that corresponds to the group marker that was placed in front of the samples to be counted. Select [Done]. At this time the instrument will prompt for carrier ID, sample ID, analysis volume, and residual mass. After entering this information for all the samples to be analyzed, select [Done]. Enter the file name, group and carrier ID, date and time, type of analysis, etc. as indicated in the instrument run log (Form 780) and on the LIMS benchsheet.

8.3.4 UNLOADING SAMPLES

8.3.4.1 After the analysis is complete, the samples will be unloaded. In all cases the operator will check the positions of the samples and verify that the position matches the entries in the run log and on the benchsheet.

8.3.4.2 On the LB4100, the sample analysis must be “freed” before the samples are unloaded. The detector icons on the screen will flash alternately green and yellow to indicate that the desired count time has elapsed and that data acquisition has been completed. Select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Unit Status]. Select the batch ID or file name corresponding to the completed count batch. Select [Free]. At this point the detector icons will stay green. Unlock and open the drawer. Remove the sample planchets, verifying the position

against the run log and benchsheet entries. Close and lock the drawer. Initial the "Position Checked" column on the benchsheet.

8.3.4.3 On the LB5100, the sample batch is automatically completed and the carriers are restacked upon completion of the data acquisition. All that remains is to remove the samples, verifying the positions as described in the preceding paragraph.

8.4 DATA OUTPUT

8.4.1 Some tests require a file modification to properly use laboratory-determined base and progeny efficiencies, as well as crosstalk and attenuation factors.

8.4.1.1 Select [File] and [Run Excel].

8.4.1.2 Select [File], [Open…] to open the correct file located in C:\osum\lb4100\aqua\data*.xld, where * is the filename.

8.4.1.3 The library of efficiencies and calibration factors is found starting at cell Q110.

8.4.1.4 Select the appropriate box, including the header line, containing the necessary calibration information.

8.4.1.5 Depress <Ctrl> and <C> to copy the data range.

8.4.1.6 For base efficiencies, paste (<Ctrl> and <V>) the range in the appropriate cells beginning in column A.

8.4.1.7 For progeny efficiency, crosstalk, and attenuation factors, paste the range in the appropriate cells, beginning in column I.

8.4.1.8 Select [File], [Save], then [File], [Exit] to return to the OSUM program.

8.4.2 On both instruments, select [Data Output] from the main instrument menu. Select the correct filename from the displayed list. Data will be output in two forms -- a hard copy will be output from the printer, and a comma-delimited ASCII file will be created on the local drive. It is the ASCII file that will be used in the data reduction and reporting process.

Instrument A automatically creates the ASCII file during data output, but the ASCII file must be manually created on instrument B. To create the ASCII file manually on instrument B:

8.4.2.1 Select [File] and [Run Excel].

8.4.2.2 Select [File], [Open…] to open the correct file located in C:\osum\lb4100\aqua\data*.xld, where * is the filename.

8.4.2.3 Highlight the range from BU16 to CN16 and down to the bottom of the sample data.

8.4.2.4 Depress <Ctrl> and <C> to copy the data range.

8.4.2.5 Open a new Excel spreadsheet and paste the data into the sheet by selecting [Edit], [Paste Special], [Values].

8.4.2.6 Select [File], [Save as…].

8.4.2.7 Save new file under file type "CSV delimited" and name the file "*.ASC", where * is the same as the filename denoted above.

8.4.3 At this time, a preliminary review of the data should be performed to evaluate the quality of the data. Any analytical data quality problems should be identified. Calibration factors, achieved MDCs, Duplicate Error Ratios (DERs), spike recoveries, etc. should be evaluated. These items are formally checked in the data review process, but a preliminary review at this point will give any early warning of potential problems.

NOTE: Acceptance limits for quality control parameters may vary per client specifications (typically controlled via test code nicknames), consult applicable LIMS program specification.

9. CALIBRATION

The operator is referred to the instrument-specific operation manuals, cited in Section 13, for specific instructions on performing periodic calibrations. This Section contains those considerations that are specific to ALS.

9.1 PLATEAU APPLICATION

Plateau measurements are performed to optimize detector operating voltage. A plateau will be run at least on a quarterly basis to verify that the slope at the operating voltage is less than 3.5 % / 100 volts. If the plateau shows a slope at the current operating voltage greater than 3.5%, all other parameters for the instrument will need to be recalibrated, as described below.

9.2 DISCRIMINATOR SETTINGS (CHANNEL CROSSTALK)

Discriminator will be set at the same level for each detector to consistently optimize beta to alpha crosstalk to a maximum of 1%.

Discriminator settings will be verified quarterly, during the plateau verification, by comparing the alpha source efficiency in both the alpha and beta Regions of Interest (ROIs) to those originally observed during the existing plateau calibration count. The observed verification values will be within 5% of the original value. Otherwise, the instrument may be recalibrated or other corrective action taken, with the radiochemistry Manager's approval.

9.3 EFFICIENCY CALIBRATIONS

9.3.1 Standards for calibration shall be traceable to the National Institute for Standards and Technology (NIST) and shall be an independent source from the current spiking standard. Standards for Gross Alpha/Beta analysis will normally be of ^{241}Am for alpha and ^{90}Sr for beta. EPA Drinking Water methodology requires a ^{230}Th alpha source. Project-specific instructions may require a ^{137}Cs beta source. Standards used for efficiency calibrations for analyses counted on the gas flow proportional counter will use standards specific for that analysis. The analysis systems shall be calibrated for each physical form of sample to be analyzed (e.g., sample evaporated on planchet, filter, etc.) at least annually. .

9.3.2 OUTLIER TEST

9.3.2.1 Calibration standards are generally prepared in sets of at least five, to facilitate the efficient calibration of the instrument. Prior to using a set of calibration standards, a "gross outlier" test will be performed to eliminate the potential use of a calibration planchet that may have been improperly prepared, or suffer from non-uniform deposition of the standard.

9.3.2.2 Count the set of planchets sequentially on the same detector, either on the LB4100 or the LB5100, to achieve a maximum 2% counting uncertainty, at the 1σ confidence interval.

9.3.2.3 Calculate the mean and standard deviation of the set.

9.3.2.4 Any planchets that fall outside a ±2 standard-deviation acceptance limit and fall greater than 5% from the mean value, will be rejected and will not be used for calibrating the instrument.

9.3.3 To initiate efficiency calibrations, fill out a new line in the source table located at C:\OSUM\SOURCES.XLS in excel. Enter in the ID number, emission type (alpha or beta), the half-life (in days), DPM of source, reference date of standard used for source, and new archive filename.

9.3.3.1 On the LB4100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Edit Parameters]. Select the [Efficiency] application. At this point, enter the desired count duration that will ensure that 10,000 counts are acquired. Close this screen when the proper information is entered.

9.3.3.2 On the LB5100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Efficiency]. Select the detectors to be started. Type in the proposed file name in the format EXXmmddY, where XX is the test, mm is the month, dd is the day, and Y is the drawer. Type in the efficiency test name in place of a batch ID. Select [Done]. The instrument will proceed to prompt for sample IDs for each detector. Enter the source ID number in place of the sample ID. Select [Done]. The detector icons will now turn from green to yellow to indicate that the count is in progress. Enter the file name, detector ID, date and time, type of analysis, etc. as indicated in the instrument run log and on the benchsheet. Also make a notation in the instrument maintenance log book.

9.3.3.3 Select [Data Output] from the main instrument menu. Select the correct filename from the displayed list and [Print]. Compare the detector's efficiency with the previously calibrated efficiency. New efficiency should be within 5% of the previous efficiency. If all efficiencies are acceptable, then [Archive] the efficiencies as "Official Values". If the efficiencies are unacceptable, consult with the Department Manager for instructions.

9.4 MASS ATTENUATION CALIBRATION

9.4.1 Alpha and beta emitting samples that contain any measurable mass deposited on the planchet must be corrected for particle attenuation. This correction is then applied to the sample during the analysis phase. Multiple acquisitions of attenuation data are required. This data is obtained by creating multiple attenuation standards of the same activity and varying masses, normally 0 to 200mg. Each sample is counted in every detector, long enough to acquire approximately 10,000 counts. A fitted curve for the attenuation factor is then generated.

9.4.2 On the LB4100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Edit Parameters]. Select the [LIMS Data] application. At this point, enter the desired count duration that will ensure that 10,000 counts are acquired. Close this screen when the proper information is entered.

9.4.3 On the LB5100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [LIMS Data]. Select the detectors to be started. Type in the proposed file name in the format AXXmmdd where XX is the test, mm is the month, and dd is the day. Additional count batches on a given day requiring the same file name may be appended with an A, B, C, etc. Indicate the type of curve being preformed in place of a batch ID. Select [Done]. The instrument will proceed to prompt for sample IDs for each detector. Select [Done]. The detector icons will now turn from green to yellow to indicate that the count is in progress. Enter the file name, detector ID, date and time, type of analysis, etc. as indicated in the instrument run log and on the benchsheet. Also make a notation in the instrument maintenance log book.

9.4.4 The detector icons on the screen will flash alternately green and yellow to indicate that the desired count time has elapsed and that data acquisition has been completed. Select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Free]. At this point, the detector icons will stay green.

9.4.5 Select [Data Output] from the main instrument menu. Select the correct filename from the displayed list and [Close].

9.4.6 Repeat this process until all the attenuation planchets have been counted in every detector.

9.4.7 Use the data from the files to generate a curve, with the equation taking the general form bmx, where x is the residual mass of the sample planchet, in mg. The estimated target value for the m coefficient is 0.993 for an alpha attenuation curve, and 0.999 for a beta curve. The estimated target value for the b coefficient is 1.00. The template can be found at r:\inst\gfp\calibration\MassAtten_Template.xls.

9.5 INGROWTH CURVE FOR RADIUM-226

9.5.1 Assume that the total efficiency has two distinct components: (1) the base Ra-226 efficiency, that is always used at its full value, and (2) the aggregate efficiency of the three ingrown alpha-emitting daughter products, which is used in proportion to the degree of ingrowth.

9.5.2 Acquisitions of the efficiency at different stages of ingrowth are required in order to determine both the base efficiency and the progeny efficiency. Follow the steps outlined in Section 9.3 and count the efficiency planchets immediately after separation. Then count the planchets again after approximately 4 days, and then count after 21 days, as well as the mass alterntive calibration.

9.5.3 Use the data from the files to generate a curve, as described below. The template can be found at r:\secured spreadsheets\ Inst\GFPC\ Calibration\Tot-Ra_Calib_Template and Tot-Ra ATTN Calib_Template. .

9.5.4 By adjusting the estimated base efficiency for Ra-226, the residual (progeny) efficiency for each calibration count is calculated as the arithmetic difference between the observed total efficiency and the estimated base efficiency. Theoretically, if the estimated base efficiency is correct, the residual (progeny) efficiency will be the same for all stages of ingrowth. In practice, set the base efficiency such that the variance in the individual residual efficiencies over the ingrowth period is minimized.

9.5.5 Since the base efficiencies are determined with planchets that have residual mass, it is necessary to adjust the mass attenuation correction curve accordingly. The mass attenuation curve is generated in the manner stated in Section 9.4 with the final mass attenuation equation in the form bmx-x°, where x° is the average residual mass of the base efficiency calibration planchets.

9.6 BACKGROUND CALIBRATIONS

9.6.1 1000-minute background determinations are performed weekly with a clean planchet.

9.6.2 Planchets, pucks, and inserts will be cleaned with RadiacWash^{TM}, rinsed with DI water, and dried thoroughly at least monthly. The drawer stage will be cleaned with methanol weekly.

9.6.3 Control limits for weekly background checks are based on historical control limits established from the first 10 data points in the population (+/- 3 sigma). Prior to establishing historical control limits, interim limits are set at <0.50cpm alpha and <3.00cpm beta.

9.6.4 On the LB4100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Background, Weekly]. Select the detectors to be started. Type in the proposed file name in the format BKXmmddW where X is the instrument used, mm is the month and dd is the day. Select [Done]. The instrument will proceed to prompt for sample IDs for each detector -- leave as the detector IDs. Select [Done]. The detector icons will now turn from green to yellow to indicate that the count is in progress. Enter the file name, detector ID, date and time, type of analysis, etc. as indicated in the instrument run log and on the benchsheet. Also complete the appropriate spots on the chart at the top of the instrument run log.

9.6.5 Upon completion, select [Data Output] from the main instrument menu. Select the correct filename from the displayed list and [Archive] as "Official Values". Select [Yes] to replace the existing official values. Close this screen when completed. Open Excel, and print a hard copy of the calibration. If a detector is out of control, the background calibration should be repeated. If it is still out of control, the detector is tagged off-line for the week. If a detector continues to be off-line for the weeks to follow, consult with the Department Manager on how to proceed.

9.6.6 Finally, the weekly calibration values must be copied to the daily background check template to provide weekly control limits for the daily background checks that follow.

9.6.6.1 In the weekly calibration file, copy the range BI7..BJ27 to the clipboard.

9.6.6.2 Open the daily background check template file, BKGAB.XLP, and paste the contents of the clipboard into the same range, BI7..BJ27, by selecting the menu commands [Edit], [Paste Special], [Values], [OK]. See Step 10.2.2 for a more detailed explanation.

9.6.6.3 If weekly background calibrations are recounted on only selected detectors, paste only those values into the existing BKGAB.XLP file, so as not to overwrite the previous, acceptable values for the other detectors.

9.6.7 On the LB5100, begin the count by selecting the following menu options; [LB5100], [Start Count], [Background_Weekly]. Enter the filename as described above, the group ID, and the analyst's initials. Upon completion of the count, select [LB5100], and [Data Output], enter the file name and print.

10. QUALITY CONTROL

10.1 DAILY INSTRUMENT PERFORMANCE CHECKS

10.1.1 Daily Instrument Performance Checks include both efficiency checks and background checks. Sample analyses must not only be preceeded by acceptable performance checks, but also must be followed by acceptable checks, usually the following day (i.e., all sample analyses will be bracketed with acceptable performance checks).

10.1.2 In the event that the performance checks <u>following</u> the sample analyses do not meet normal acceptance criteria, the impact on the data quality will be evaluated to determine whether the sample analyses should be

redone. The sample analysis data may be used, with proper qualification, upon the Department Manager's approval.

10.2 DAILY BACKGROUND CHECKS

10.2.1 Daily background checks consist of a single 60 minute count of a clean planchet.

10.2.2 Control limits for the daily background check are derived from the weekly background calibration. The 1000 minute count rate is scaled to a 60 minute count rate and the Poisson uncertainty is calculated for that result. The final limits for the daily checks are calculated as the mean count rate for that detector ± three times the Poisson uncertainty.

10.2.3 On the LB4100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Background]. Select the detectors to be started. Type in the proposed file name in the format BKXmmdd where X is the instrument used, mm is the month and dd is the day. Additional count batches on a given day requiring the same file name may be appended with an A, B, C, etc. Select [Done]. The instrument will proceed to prompt for sample IDs for each detector -- leave as the detector IDs. Select [Done]. The detector icons will now turn from green to yellow to indicate that the count is in progress. Enter the file name, detector ID, date and time, type of analysis, etc. as indicated in the instrument run log and on the benchsheet. Also complete the appropriate spots on the chart at the top of the instrument run log.

10.2.4 Select [Data Output] from the main instrument menu. Select the correct filename from the displayed list and [Archive] as "Daily Check". Close this screen when completed. Open Excel, and print a hard copy of the check. If a detector is out of control, the background check should be repeated. If it is still out of control, the detector is tagged off-line for the day and the effect on the samples that were counted on the previous day is evaluated. If a detector continues to be off-line for consecutive days, consult with a primary GFPC operator or the Department Manager on how to proceed.

10.2.5 On the LB5100, begin the count by selecting the following menu options: [LB5100], [Start Count], [Background_Daily]. Enter the filename as described above, the group ID, and the analyst's initials. Upon completion of the count, select [LB5100], and [Data Output], enter the file name and print

10.3 DAILY EFFICIENCY CHECKS

10.3.1 Standards for Daily Efficiency Checks shall be traceable to the National Institute for Standards and Technology (NIST).

10.3.2 Daily Efficiency checks are run for gross alpha and gross beta. Count durations may be automatically terminated after the acquisition of 10,000 counts, if desired. Control limits are established from the first 30 data points in the population (± 3 sigma). Prior to the collection of 30 data points, interim control limits of ±10% of the initial measurement are used.

10.3.3 On the LB4100, select the instrument menu by right-clicking the instrument icon in the upper left corner. Select [Efficiency]. Select the detectors to be started. Type in the proposed file name in the format EFXmmdd where X is the instrument used, mm is the month and dd is the day. Additional count batches on a given day requiring the same file name may be appended with an A, B, C, etc. Select [Done]. The instrument will proceed to prompt for sample IDs for each detector-enter in source ID. Select [Done]. The detector icons will now turn from green to yellow to indicate that the count is in progress. Enter the file name, detector ID, date and time, type of analysis, etc. as indicated in the instrument run log and on the bench sheet. Also complete the appropriate spots on the chart at the top of the instrument run log.

10.3.4 Select [Data Output] from the main instrument menu. Select the correct filename from the displayed list and [Archive] as "Daily Check". Close this screen when completed. Open Excel, and print a hard copy of the check. If a detector result is outside of normal acceptance criteria, the check should be repeated. If it is still out of control, the detector is tagged off-line for the day and the effect on the samples that were counted on the previous day is evaluated. If a detector continues to be off-line for consecutive days, consult with the Department Manager for corrective action instructions.

10.3.5 On the LB5100, begin the count by selecting the following menu options: [LB5100], [Start Count], [Efficiency_Daily]. Enter the filename as described above, the group ID, and the analyst's initials. Upon completion of the count, select [LB5100], and [Data Output], enter the file name and print.

11. PERIODIC MAINTENANCE

11.1 CONTROL CHARTS

Control charts of the Daily Efficiency checks and the Backgrounds are printed out monthly using the [Control Chart] application from the main instrument menu. Control charts are to be used for trending analysis.

11.2 To facilitate the convenient management of sample data files, the following files

can be relocated after the ASCII files are transferred to LIMS. Calibration files can be relocated anytime after the data is output.

11.2.1 Move sample files from:

C:\OSUM\LB4100\Orange (or Aqua)\DATA*.XLD and *.ASC

to

C:\OSUM\LB4100\Orange (or Aqua)\DATA\OLD*.XLD and *.ASC

11.2.2 Move calibration and performance check files from:

C:\OSUM\LB4100\Orange (or Aqua)\CAL*.XLD and *.ASC

to

C:\OSUM\LB4100\Orange (or Aqua)\CAL\OLD*.XLD and *.ASC

11.3 COMPUTER BACK-UP

The computer files are backed-up monthly using an external tape drive. Prior to performing the back-up, scandisk is run and the hard drive is defragmented. No samples can be counted during the back-up procedure, as OSUM needs to be closed.

After a successful backup of the instrument data, individual data files created since the last backup can be deleted from the following locations:

C:\OSUM\LB4100\Orange (or Aqua)\DATA\OLD*.XLD and *.ASC

C:\OSUM\LB4100\Orange (or Aqua)\CAL\OLD*.XLD and *.ASC

11.4 Specific instrument components will be cleaned periodically, as described in Section 9.

12. SAFETY, HAZARDS, AND WASTE DISPOSAL

12.1 SAFETY

All Safety and Hazards are managed in accordance with the current facility plans:

- Chemical Hygiene Plan (CHP)
- Radiation Protection Plan (RPP).
- Emergency and Contingency Plan (ECP)
- Respiratory Protection Plan (RESPP)

12.2 HAZARDS

Bias applied to detectors is typically in the range of 1500 volts DC. This can result in electric shock if bias cables are disconnected while bias is applied. To minimize the possibility of electric shock, bias will be turned off to any detector before any cabling is disconnected.

12.3 WASTE DISPOSAL

All Wastes are disposed of in accordance with the Waste Management Plan (WMP)

13. REFERENCES

13.1 LB4100 Instruction Manual, Oxford Instruments, Inc., Rev. 9/90.

13.2 LB5100-W Operation Manual, Oxford Instruments, Inc., Version 1.0 (1992).

TABLE 1

SUMMARY OF INTERNAL QUALITY CONTROL (QC) PROCEDURES AND CORRECTIVE ACTION

QC Check	Frequency	Acceptance Criteria	Corrective Action
Efficiency and Background Checks	Daily	Within derived control limits.	Recount, re-evaluate, service instrument, if necessary or document why condition is acceptable.
Background Calibration	Weekly	Within derived control limits.	Tag method off-line. Determine and correct problem, re-establish limits; or document why condition is acceptable
Operating Voltage Plateau Check	Quarterly	Slope <= 3.5% per 100 volts	Recalibrate Plateau.
Discriminator Settings	Yearly, or when operating voltage is changed.	Beta to alpha crosstalk is <= 1%.	Adjust Discriminators.
Efficiency and Mass-Attenuation Calibrations	Yearly, or when operating voltage is changed.	For single point efficiency calibrations, the value will be within 5% of the previous calibration value. For mass attenuation curves, the fitted values shall be within 10% of the observed value for each point on the curve. Fitted values within 15% of the mass attenuation curve will be acceptable, with the department manager's approval. Initial Calibration Verifications (ICVs) will be within 10% of the expected value.	Tag method off-line. Determine and correct problem; verify source activity; recount and/or recalibrate or document why condition is acceptable.
Chemical Yield	Each sample, where method allows.	Each sample meets current control limits for analysis.	Re-prep; or Qualify or narrate why condition is acceptable

Note: This SOP and SOP 715 contain acceptance criteria and corrective action for method blank, laboratory control samples, duplicate samples and matrix spike/matrix spike duplicates.

APPENDIX A
Example
Daily QC

Daily QC entries are entered in the LB4100 run log as either "Daily Eff" or "Daily Bkg". The following is a description of each:

Daily Efficiency (Daily Eff) checks are counted using planchets that are specific to each detector. The checks are counted until 10,000 counts are reached, or for a maximum of 30 minutes. Control limits are listed on the 'Daily Efficiency' printout with 'PASS / FAIL' flags. If a detector is listed as outside control limits, it is recounted. If the detector is outside control limits for the second count, it is tagged offline for the day.

Daily Background (Daily Bkg) checks are counted for 60 minutes using clean flat planchets specific to each detector. Control limits are listed on the 'Daily Background' printout with 'PASS / FAIL' flags. If a detector is listed as outside control limits, it is recounted. If the detector is outside control limits for the second count, it is tagged offline for the day.

Weekly Background calibrations are counted for 1,000 minutes using clean flat planchets specific to each detector. Values from these counts are saved as official values and are used to determine the control limits for the 'Daily Background' checks. Control limits are listed on the 'Weekly Background' calibration printout with 'PASS / FAIL' flags. If a detector is listed as outside control limits, it is recounted. If the detector is outside control limits for the second count, it is tagged offline for the week or corrective measures are taken and the calibrations are re-performed.

Date _____ **SOP 724r____**

ALS
Low Background Gas Flow Proportional Counter Log
Instrument: LB4100B

Instrument Daily Response and Background Checks

Det.	Daily Response Check Start 1	Status	Start 2	Status	Background Check Start 1	Status	Start 2	Status	Det. Status
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									

Det = Detector; α = Alpha; β = Beta; P = Pass; H = High; L = Low; OL = Offline; R = Recount; W = Weekly; NP = Not Processed

Weekly Background Calibration

	Current Calib. File ID	Weekly Calib.	Status	File ID
Dr A				
Dr B				
Dr C				
Dr D				

Dr = Drawer

Gas Supply

P-10 Supply		P-10 Flow	
Tank 1		Dr A	
		Dr B	
Tank 2		Dr C	
		Dr D	

Comments:

Date _____ **SOP 724r____**

ALS

Low Background Gas Flow Proportional Counter Log
Instrument: LB4100B

Det.	Sample ID	Batch	Test	Count Dur. (min)	Start Time	Analyst Initials	File ID	Output Initial

Comments:

Page No.: _____ **B** Form 780r8.doc (6/23/06 Reviewed By / Date _____

(cont. from page _____ B)

ALS Standard Operating Procedure

DOCUMENT TITLE:	DETERMINATION OF RADIUM-228 VIA CHEMICAL SEPARATION OF RADIUM AND ACTINIUM
REFERENCED METHOD:	EPA 9320
SOP ID:	749
REV. NUMBER:	3
EFFECTIVE DATE:	3/24/14

ALS
STANDARD OPERATING PROCEDURE 749 REVISION 3
TITLE: DETERMINATION OF RADIUM-228 VIA CHEMICAL SEPARATION OF RADIUM AND ACTINIUM.

FORMS: NA

APPROVED BY:

PRIMARY AUTHOR _____ DATE _____
QUALITY ASSURANCE MANAGER _____ DATE _____
LABORATORY MANAGER _____ DATE _____

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes the measurement of radium-228 in waters, ground waters, soils, and waste samples. The procedure is devised so that the beta activity from actinium-228, which is produced by decay of radium-228, can be determined and related to the activity concentration of radium-228 present in the sample. Gas flow proportional counting of Ac-228 beta activity and radiochemical separation techniques found in EPA method 9320.

This SOP includes instruction for the digestion and separation of soil matrices. Where the use of this method is required for solid matrices, the default sample size is 1 gram, to achieve an MDC of approximately 5pCi/g. This allows for commonly encountered matrix interference issues, including low chemical recoveries.

If desired, the determination of Ra-226 by radon emanation may be conducted on the purified radium solution produced during this procedure.

2. SUMMARY

2.1 The radium isotopes in a water sample are collected by co-precipitation of barium and lead sulfate and purified by re-precipitation out of a basic EDTA solution. After a 36-hour period to allow for the ingrowth of actinium-228, actinium is carried on yttrium (Y) as the hydroxide and then carried with and mounted as barium sulfate, and quickly beta counted to minimize decay of the short-lived Ac-228 (~6 hours).

2.2 In solids, radium-228 is liberated from the solid matrix by a total digestion of the solid. The sample is muffled, transferred to a polypropylene specimen cup and digested in the presence of strong acids. After digestion, Ba in the sample digestate is precipitated as $BaSO_4$ and the samples are then processed following the same steps used for preparing water samples.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst performing the method to notify the Instrument Lab Gas-Flow Proportional Counter analyst in advance of the number of samples arriving and the expected delivery date and time. This allows the analyst to schedule adequate instrument time to analyze the short-lived Ac-228 analyte.

3.2 It is the responsibility of the analyst to perform the analysis according to this SOP and to complete all documentation required for review.

3.3 It is the responsibility of the analyst to be familiar with the acceptance criteria for the QC samples and other quality indicating parameters, as specified in SOPs 715 and 724 as well as the LIMS program specifications related to the client, project, and test method being performed.

3.4 Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.5 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the file indicates that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.6 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events associated with the analysis of the samples. Any discrepancies must be noted and corrective action taken and documented.

4. INTERFERENCES

4.1 The presence of significant quantities of dissolved constituents that may form insoluble sulfate precipitates interferes with the proper separation of radium and the subsequent quantification of Ra-228. In this case, reduced sample volumes may be required to minimize the matrix interference effects.

4.2 The presence of sediments in the preserved sample is a significant interference to this method. The client should field-filter the samples prior to preserving with HNO_3 and prior to sending them to ALS Laboratory Group – Fort Collins. Concerns arise since the ‘preservation’ recommended by the EPA (adding acid to samples which may also contain barium and or sulfates), will potentially lead to analyte loss due to precipitation. If sediments are removed following ‘preservation’, significant analyte loss is possible. Likewise, if sediments are left

in a sample, which is subsequently nitric acid preserved, radium leaching from the sediments may lead to a very significant high bias in measured radium concentrations.

4.2.1 The presence of significant quantities (>500mg) of suspended solids in a sample will interfere with collection of the barium sulfate precipitate. Any sample having visible sediments will be filtered prior to sample preparation.

5. EQUIPMENT AND MATERIALS

5.1 Stirring hot plate

5.2 Hot Blocks

5.3 Magnetic stir bars

5.4 Centrifuge

5.5 Polypropylene centrifuge tubes, 50mL

5.6 Stainless steel counting planchets, 2", flat

5.7 Graduated cylinders, 100mL and 1 or 2L

5.8 Pyrex™ beakers, or equivalent, 2L

5.9 Forceps

5.10 Eppendorf™ pipettors, or equivalent (reference ALS SOP 321 "Calibration Verification of Pipettes and Pipettors")

5.11 Test tubes, 15mL polypropylene, disposable

5.12 Polyethylene test tube caps

5.13 Re-pipettor, Eppendorf™, Model 4780 or equivalent. ALS SOP 321 "Calibration Verification of Pipettes and Pipettors"

5.14 Desiccator

5.15 Orbital shaker

5.16 Vortex mixer

5.17 Transfer pipettes

5.18 Qualitative fluted filter paper

5.19 Beakers, 100mL, Pyrex™, or equivalent

5.20 Analytical balance, Mettler™ AE 200, or equivalent. ALS SOP 305 "Balance Calibration, Verifications and Utilization"

5.21 Environmental Express™ 0.1 micron micro precipitation filter and funnel assembly, or equivalent

5.22 Vacuum manifold for performing vacuum filtrations

5.23 100 mL digestion cups

5.24 Watch Glass

5.25 Polypropylene watch cover

6. REAGENTS

NOTE: TLV and other hazard information may be given here. Any chemical with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is non-hazardous. The employee should be familiar with all pertinent MSDSs before proceeding. 3.1.6

NOTE: Chemicals, Reagents and Standards: Chemicals, reagents and standards used for testing shall be prepared and documented as per ALS SOP 300 "Standards, Solvents, Acid, Bases and Reagents Management in the Laboratory".

6.1 Deionized (DI) water

6.2 Acetic acid, 17.4M, Glacial CH_3COOH, reagent grade, concentrated
TLV = 10ppm (TWA); Irritant

6.3 Ammonium hydroxide, 15M, NH_4OH, reagent grade, concentrated
TLV = 25ppm (TWA for NH_3)

6.4 Ammonium sulfate, reagent grade.

6.5 Ammonium sulfate, 200mg/mL: Dissolve 200g $(NH_4)_2SO_4$ in DI water and dilute to 1000mL.

6.6 50% collodion, 50% amyl acetate: made by diluting equal volumes of collodion and amyl acetate.

6.7 Standardized Barium Carrier, 16mg/mL: Dissolve 28.5g $BaCl_2 \cdot 2H_2O$ in a 1000 ml volumetric flask with~ 500ml of DI water, then add 5mL 16M HNO_3. Dilute to 1000mL with DI water. Transfer to a clean, labeled 1L poly container. Document the preparation of this carrier in the LIMS Standards and Solutions

Database.
TLV = 0.5mg Ba/m^3 = 0.06ppm (TWA). Irritant

STANDARDIZATION OF Ba CARRIER BY ICP ANALYSIS
Prepare in triplicate a 1000-fold dilution of the Ba carrier using the ICP solution described in Section 16.6 below. Submit to the Metals Lab for analysis. Average the results and record in the reagent prep logbook. Additionally, record the Instrument ID, Analytical Sequence and date analyzed for the ICP.

6.8 Barium Carrier, 2mg/mL: Dissolve 3.56g $BaCl_2 \cdot 2H_2O$ in ~ 500ml of DI water, then add 5mL 16M HNO_3. Dilute to 1000mL with DI water. Transfer to a clean, labeled 1L poly container.

6.9 Citric acid, 2M: Dissolve 420.28g of $C_6H_8O_7 \cdot H_2O$ in DI water and dilute to 1000mL.

6.10 EDTA basic reagent, 0.25M: Dissolve 80g NaOH in ~3L of DI water. Slowly add 372g of (ethylenedinitrilo)tetraacetic acid, disodium salt, dihydrate - EDTA ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$), while stirring. After the salt is in solution dilute to 4L. If necessary, adjust the pH to ≥10 using a minimal volume of 10M NaOH.

6.11 Hydrochloric acid (HCl) 12M, reagent grade
TLV = 5ppm (ceiling). Irritant, corrosive

6.12 Hydrochloric acid, 2M: Slowly and carefully add 167mL of concentrated hydrochloric acid (reagent 6.11) to DI water and dilute to 1000mL.

6.13 Hydrofluoric acid (HF), 48.0-51.0%, concentrated
TLV = 3ppm (ceiling). Irritant, burns, bone, teeth, fluorosis

6.14 Isopropyl alcohol, concentrated
TLV = 100ppm (ceiling). Irritant, flammable.

6.15 Isopropyl alcohol, 20%: Add 200mL of concentrated isopropyl alcohol to DI water and dilute to 1000mL.

6.16 Methyl Red Indicator Solution: Dissolve 0.100g methyl red sodium salt powder in 100 mL of DI water

6.17 ICP diluting solution (1% HNO_3 / 5% HCl): Carefully add 10mL of concentrated HNO_3 and 50mL of concentrated HCl to 940mL of DI water. Mix thoroughly.
TLV = 2ppm for conc. HNO_3 (TWA), and 5ppm for conc. HCl (ceiling). Both irritants, corrosive

6.18 Lead carrier, 75mg/mL: Dissolve 119.9g $Pb(NO_3)_2$ in DI water. Add 5mL 16M HNO_3 and dilute to 1000mL with DI water.
TLV = 0.05mg/m^3 (=0.004ppm)

6.19 Nitric acid reagent concentrated (16M HNO_3)
TLV = 2ppm (TWA). Irritant, corrosive

6.20 Sodium hydroxide, 18M: Place about 500mL of DI water in a beaker in a water bath. Very slowly and carefully dissolve 720g of NaOH; work in the hood. The solution will boil if the NaOH is added to quickly. After the solution is cool, dilute to 1L with DI water. Store in a plastic container.
TLV = $2mg/m^3$ = 1.2ppm (ceiling). Irritant

6.21 Sodium hydroxide, 1M: Dissolve 40g of NaOH in 1L of DI Water

6.22 Methanol, reagent grade. TLV=200 ppm. Neuropathy, vision, central nervous system.

6.23 Sulfuric acid, 18N, H_2SO_4: Very carefully and gradually, add 500mL of reagent grade concentrated sulfuric acid, while stirring, to 500mL DI water.

CAUTION: The solution will boil if the reagent is added too quickly.
TLV = $1mg/m^3$ (=0.25ppm) (TWA). Irritant

6.24 Sulfuric acid, 0.1N H_2SO_4: Add 5.6mL of 18N H_2SO_4 to ~900mL of DI water. Mix well and dilute to 1L with DI water. Alternately, add 120mL of 18N H_2SO_4 to ~2L of DI water mix well and dilute to 22L.
TLV = $1mg/m^3$ (=0.25ppm) (TWA). Irritant

6.25 Triton X-100™ non-ionic surfactant solution, VWR #3929-2, or equivalent

6.26 Yttrium carrier, 9mg /mL: Dissolve 11.43g Y_2O_3 in ~100mL DI water. Heat to boiling and, while stirring with a magnetic stirring hot plate, carefully add small portions of conc. HNO_3. (About 60mL is necessary to dissolve the Y_2O_3. Additions of deionized water also may be needed to replace the water lost by evaporation). After total dissolution, add 40mL conc. HNO_3 and dilute to 1000mL with DI water.

7. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 It is recommended that samples be preserved at the time of collection by adding enough 1M HNO_3 per liter of sample to bring the pH to 2 (15mL 1M HNO_3 per liter of sample is usually sufficient). If samples are to be collected without preservation, they should be brought to the laboratory within 5 days, then preserved, and held in the original container for a minimum of 24 hours before analysis or transfer of the sample.

7.2 The container choice should be plastic (rather than glass) to prevent loss due to breakage during transportation and handling.

8 PROCEDURE

8.1 AQUEOUS SAMPLE PREPARATION

8.1.1 Verify and record (on Form 631) the pH of the sample according to SOP 733.

8.1.2 1.5L is a typical sample aliquot size for this method. However, this volume may need to be reduced if matrix interference is suspected. Use a graduated cylinder to measure the sample and pour into a clean, labeled 2L beaker. If less than 1.5L is used, record volume, then dilute to 1.5L with DI water.

8.1.3 Prepare quality control (QC) samples per Section 9.

8.1.4 Place the beakers on stirring hot plates. Add a stir bar to each and begin stirring.

8.1.5 How to take "initial" ICP aliquot

8.1.5.1 Using a calibrated pipette, aliquot 1.0mL of the raw sample into a clean test tube labeled with the sample ID and "I", and dilute to an appropriate volume to minimize interferences with metals analysis. This is typically accomplished by adding 9.0 of ICP dilution solution. Document the total dilution volume on the Radiochemistry ICP Worksheet. Cover with a test tube cap and mix well. Set aside until "final" ICP aliquot has been taken.

8.1.6 To each sample, add 4mL of 2M citric acid, 8-10 drops of methyl red indicator, 2 drops of non-ionic surfactant. The solution should be pink. If the solution does not turn pink, add a few more drops of methyl red indicator. If the sample has not yet become pink, consult the lab supervisor or technical manager.

8.1.7 Add 2ml of lead carrier (75mg/ml) to the beakers.

8.1.8 Spike the samples with 2 ML standardized barium carrier (16 mg/mL) and the appropriate amount of Ra-228 spiking solution to samples that require it per Section 9.

8.1.9 At this time prepare an ICP "reference carrier" (RC) sample by adding 2.0 mL of standardized barium carrier (16 mg/mL) to 23 ml of EDTA basic reagent. Set aside. This RC sample will be diluted similarly to the samples during "final" ICP. The reference carrier will be submitted with the samples prepared in this batch for ICP analysis to provide a reference concentration for the yield calculations..

8.1.10 Add 5mL to 15 mL 15M NH_4OH to obtain a definite yellow color. If, after 15 mL of 15 M NH_40H, a yellow color is not present, ensure that

the sample is basic (pH of ~10) by checking with a pH strip. At this time, if a sample is not basic, consult a supervisor.

8.1.11 Heat to incipient boiling (approximately 350 ^{o}C with digital hotplate) and maintain at this temperature for 30 min. while stirring.

8.1.12 Precipitate lead and barium sulfates by slowly adding 18N H_2SO_4 drop-wise until the pink color reappears; then add ~ 5 drops in excess. Add 8ml of 200mg/ml $(NH_4)_2SO_4$. Stir constantly and maintain temperature for 30 minutes.

8.1.13 Remove stir bars, rinsing with 0.1N sulfuric acid, and allow the solution to cool. Let precipitate settle for at least 4 hours or preferably overnight.

8.1.14 Aspirate supernatant. Transfer precipitate to a 50mL poly centrifuge tube, rinsing the last particles out of the beaker with 0.1N H_2SO_4. Centrifuge at 3,500 rpm for 10 minutes and discard the supernatant into the laboratory sink followed by plenty of cold tap water. **NOTE – For the remainder of this procedure any reference to centrifuging means centrifuge at 3,500 rpm for 10 minutes.**

8.1.15 Wash the precipitate with 15mL 16N HNO_3, vortex, centrifuge, and discard the supernatant into the laboratory sink or into the back of a fume hood, followed with plenty of cold tap water. At the analyst's discretion, additional washes may be performed to thoroughly remove interfering constituents.

8.1.16 Add 40 mL EDTA and vortex well. Heat in a 100 ^{o}C hot block for about 10 min., mixing occasionally to aid in dissolution. If the precipitate does not dissolve after heating on the hot block, add an additional 10 mL of EDTA and 1 mL of 18M NaOH. If solids persist, consult your Supervisor.

8.1.17 Add 1mLof 200mg/ml $(NH_4)_2SO_4$. Add 2 mL of 17.4M acetic acid. A barium sulfate precipitate should form. If a precipitate does not form, add additional acetic acid drop wise. Shake well, but do not vortex. Heat in a 100 deg C hot block (about 10 min.) until precipitate settles. Centrifuge and discard supernatant into the Ba/Pb waste carboy, per Section 12.2 of this SOP.

8.1.18 Add 25mL EDTA basic reagent, vortex and heat in a hot block until precipitate dissolves. If the precipitate does not dissolve after heating on the hot block after 15 minutes, add additional EDTA in 5 mL increments until the precipitate dissolves completely then repeat step 8.1.17 and 8.1.18. High concentrations of Ca are often the reason for the need to repeat these steps. Each time the steps are carried out Ca is removed when the supernatant is discarded. Continue repeating these

steps until the precipitate dissolves in 25ml of EDTA reagent. Record the volume of EDTA used to dissolve the precipitate on the bench sheet (usual volume is 25ml).

8.1.19 Prepare dilutions for the determination of "final" Ba yield by removing 0.05ml of the EDTA solution from the previous step, placing it into a "final" ICP tube and diluting to an appropriate volume to minimize interferences with metals analysis. This is typically accomplished by adding 10.0 mL of ICP dilution solution for a final volume of 10.05 mL. Document the total dilution volume on the Radiochemistry ICP worksheet. Dilute the reference carrier solution from step 8.1.19 similarly.

Note: It is important that the sample EDTA solutions and the reference carrier solution from step 8.1.5.2 be the same volume and mixed well prior to making the dilution described above. Compare the weights of the sample tubes and the reference carrier tube and if necessary bring all tubes to the weight of the heaviest tube by adding small amounts of EDTA reagent (0.1g tolerance).

8.1.20 Submit the diluted solutions to the metals department for the "final" Ba determination. Also submit the "initial" Ba dilutions from step 8.1.5.1 and the diluted "reference carrier" from step 8.1.19.

8.1.21 Add 16mL of thoroughly mixed 18M NaOH to each sample. In the centrifuge tube.

8.1.22 Add 1ml of yttrium carrier (9 mg/mL)and shake gently on an orbital shaker at a speed of 95 RPM for at least one hour to allow precipitation of $Y(OH)_3$ to be complete**. NOTE – for the remainder of this procedure, any reference to an orbital shaker means shaking at 110 RPM.**

8.1.23 Centrifuge and decant the supernatant into a new 50ml centrifuge tube. **Note the time and date on bench sheet – this is the time of beginning of Ac ingrowth. The old centrifuge tube containing the precipitate can be disposed by drying the plug and then disposing of the plug in the appropriate hazardous waste drum. The old centrifuge tube can then be soaked in radiac wash, rinsed in tap water, and discarded in the sanitary trash.**

8.1.24 Add 1ml of yttrium carrier (9 mg/ml) and 0.1ml of Pb carrier(15mg/ml) to the new 50 mL centrifuge tube,, and shake gently on an orbital shaker for enough time to allow adequate Ac-228 ingrowth, normally 24-36 hours. Consult your supervisor if a shorter Ac-228 ingrowth will be used. (Note: After 24 hours Ac-228 ingrowth is greater than 90%).

During this time Ac-228 will be retained on the $Y(OH)_3$ precipitate and Ra will remain in solution

8.1.25 Remove the centrifuge tubes from the orbital shaker after Ac-228 has ingrown for a sufficient time. Centrifuge and decant the supernatant into a clean 40 mL VOA vial if Ra-226 is to be determined by radon emanation or decant the supernatant into a 100 mL digestion cup. Save for possible re-extraction of ingrown Ac-228. After the data has been reviewed and all DQOs have been met, the supernatant may be discarded into the Ba/Pb waste carboy, per Section 12.2 of this SOP. **Note the time and date of the beginning of centrifuging on bench sheet – this is the beginning of Ac-228 decay.**

NoteComplete the following steps (8.1.25 through 8.1.34) as quickly as possible to minimize Ac-228 decay. Ensure that the Counting Lab has been informed on the number of samples and the approximate time the samples are to be analyzed. The samples should begin counting no later than 4 hours from the time of separation.

8.1.26 Add ~40ml of 1M NaOH to the $Y(OH)_3$ precipitate and mix well. The precipitate will not dissolve, the solution will be cloudy. Centrifuge and discard the supernatant into the laboratory sink.

8.1.27 Add 20mL 2M HCl to the centrifuge tube..

8.1.28 Add 1mL barium carrier (2mg/mL) and mix well to dissolve.

8.1.29 Add ~ 3.0g of $(NH_4)_2SO_4$ (this may be done using a calibrated scoop).

8.1.30 Add 5.0mL of concentrated isopropyl alcohol and mix well to dissolve the $(NH_4)_2\ SO_4$. Place on orbital shaker and allow about 10 minutes for complete formation of the $Ac/BaSO_4$ co-precipitate before proceeding to 8.1.31.

8.1.31 Place an Environmental Express™ 0.1micron micro precipitation filter/funnel assembly in a vacuum filtration manifold. Turn on the vacuum and pre-wet the filter to slightly above the filter funnel connection using methanol. Observe the flow rate of the methanol for evidence of a poorly seated filter. If there is any indication of a poorly seated filter, replace the filter assembly with a new one.

8.1.32 Filter the sample suspension from step 8.1.30 through the filter apparatus.

8.1.33 Rinse the centrifuge tube and cap with a few milliliters of 20% isopropyl alcohol; pour rinse onto the filter. Used centrifuge tubes may be soaked in Radiacwash™, rinsed in tap water, and discarded in the sanitary trash

8.1.34 After the suspension has been filtered, rinse the filter assembly with two approximately 2.0 ml volumes of 20% isopropyl alcohol . Follow the 20% isopropyl alcohol rinses with a single methanol rinse of ~2.5 mL.

8.1.35 After filtration, keep the vacuum on and remove the funnel. Spread a thin layer of the 50% collodion/ 50% amyl acetate in the center of a labeled 2"stainless steel flat planchet using a cotton swab. The area covered by the thin layer should be larger than the filter diameter. Carefully remove the filter membrane with a pair of forceps and fix it FACE UP on the 50% collodion/ 50% amyl acetate layer. NOTE: Double sided tape cannot be used as a substitute for the 50% collodin/50% amyl acetate. Tape can create false positive results during the analysis.

8.1.36 Dry on a digital hot plate at a 90 ^{o}C for a few minutes to affix the filter to the planchet. Submit planchets and necessary paperwork to the Counting Lab immediately for analysis. .

8.2 SOLID SAMPLE PREPARATION

8.2.1 Verify and record (on Form 631) the condition of the sample.

8.2.2 For samples that do not require muffling, weigh 1 g of dried pulverized soil into a clean, labeled 100 mL digestion cup and record the sample weight on the bench sheet. Proceed to Step 8.2.4

8.2.3 If muffling is required due to the presence of potentially interfering organic matter, weigh 1 g of dried, pulverized soil into a permanently labeled glass beaker. Record the sample weight and beaker number on the bench sheet. Proceed to Step 8.2.4. .

8.2.4 Prepare QC samples according to Section 9. Spike the samples with 2mL of standardized barium carrier (16 mg/mL) and the appropriate amount of Ra-228 spiking solution to samples that require it. At this time, prepare an ICP "reference carrier" (RC) as described in step 8.1.9. .

8.2.5 For samples to be muffled, dry the beakers on a hotplate set at 2 (Samples must be completely dry prior to muffling.). Cover the beakers with a watch glass and muffle at 600°C for at least 4 hours.

8.2.6 Transfer the muffled sample to a 100mL digestion cup, using at least 10 mL 16N HNO_3 to rinse the beaker. Scraping with a plastic spatula may be necessary to remove all of the soil from the beaker. Slowly add 10 mL 12N HCI and 10 mL conc. HFto the digestion cup. Cover with a polypropylene watch cover, and heat for 4 hours on a 100 ^{o}C hot block. Proceed to step 8.2.8.

8.2.7 For samples that were not muffled, to the digestion cup slowly add 10mL

of 16N HNO_3, 10mL 12N HCl, and 10 mL conc. HF. Cover with a polypropylene watch cover, and heat for 4 hours on a 110 ^oC hot block. Proceed to step 8.2.8.

8.2.8 Remove polypropylene watch cover and evaporate to dryness. Add 10mL concentrated HC1 and 10 ml DI water. Return the samples to the hot block for several minutes to facilitate dissolution.

8.2.9 Transfer the samples quantitatively to 50ml centrifuge tubes (using a DI water squirt bottle and a minimum of 3 rinses) and bring to 40ml with DI water (bring volume to the 40ml markings on the centrifuge tubes) . It is important that the 40ml volume be accurate. It may be useful to prepare a tube containing 40ml by weighing 40g of water into a centrifuge tube and using the tube to visually verify the 40ml sample volumes. After bringing the volume to 40ml mix the sample digestates thoroughly.

8.2.10 To the 50 mL centrifuge tube, add 8ml of 200mg/ml $(NH_4)_2SO_4$ and heat the samples in a 100 ^oC hot block for about 30 minutes to precipitate $Ra/BaSO_4$.

8.2.11 Centrifuge and discard supernatant into the Ba/Pb waste carboy, per section 12.2 of this SOP. Wash the precipitate with 15mL 16N HNO_3, vortex, centrifuge, and discard the supernatant into the laboratory sink or into the back of a fume hood, followed with plenty of cold tap water. At the analyst's discretion, additional washes may be performed to thoroughly remove interfering constituents. Add 40mL of EDTA reagent to the tube containing the precipitate.

8.2.12 Mix well and heat the samples in a 100 ^oC hot block for about 30 minutes to dissolve the $Ra/BaSO_4$ precipitate. Mix a few times during the heating time to ensure complete dissolution. If the precipitate does not dissolve after heating on the hot block, add an additional 10mL of EDTA and 1mL 18M NaOH. If solids persist, consult your Supervisor.Centrifuge and decant supernatant into a new 50ml centrifuge tube. The old centrifuge tube containing the precipitate can be disposed by drying the plug and then disposing of the plug in the appropriate hazardous waste drum. The old centrifuge tube can then be soaked in radiac wash, rinsed in tap water, and discarded in the sanitary trash.

8.2.13 Using a calibrated pipette, aliquot 0.05 mL of the solution from step 8.2.9 into a clean test tube labeled with the sample ID and "I", and dilute to an appropriate volume to minimize interferences with metals analysis. This is typically accomplished by adding 10.0 mL of ICP dilution

solution for a final volume of 10.05mL. Document the total dilution volume on the Radiochemistry ICP Worksheet. Cover with a test tube cap and mix well. Set aside until "final" ICP aliquot has been taken.

8.2.14 Follow steps 8.1.17 through 8.1.36 (aqueous sample preparation steps). In step 8.1.20 submit the "initial" Ba dilutions prepared in step 8.2.10 rather than the aqueous sample "initial" Ba dilutions described in step 8.1.5.1.

8.3 PREPARATION OF CALIBRATION STANDARDS

8.3.1 Prepare as many working calibration sources as the number of detectors to be calibrated. Calibration may be done using high energy beta emitter such as Ac-228, Y-90 or Sr-89. The following procedure is for calibration using Ac-228.

8.3.2 Spike 2ml of 16mg/ml standardized barium carrier into each centrifuge tube and bring to 25ml volume with EDTA reagent.

8.3.3 Spike between 1,000 and 10,000 dpm of NIST-traceable Ra-228 into each tube.

NOTE: The spiking solution should be a "second source" independent of the solution used for spiking batch QC samples.

8.3.4 Add 1mL $(NH_4)_2SO_4$, and 2 ML 17.4M acetic acid and mix thoroughly so that barium sulfate precipitates.

8.3.5 Heat in a 100 ^oC hot block (about 10 min.) until precipitate settles. Centrifuge and discard supernatant in the laboratory sink.

8.3.6 Add 25mL EDTA basic reagent, vortex and heat in a hot block until precipitate dissolves.

8.3.7 Follow steps 8.1.21 through 88.1.36 (aqueous sample preparation steps) to prepare working calibration sources.

8.3.8 Submit the working calibration sources to the counting lab with all necessary documentation.

8.3.9 Rotate the working calibration sources through the detectors to provide 4 counts from 4 different sources for each detector to give better instrument precision..

8.3.10 The calibration should be verified by preparing and analyzing (following this SOP) a minimum of three method blanks and three Ra-228 LCSs, spiked at an appropriate spiking level using a Ra-228 source different

from the source used for preparing the calibration sources.

9 QUALITY CONTROL

9.1 One method blank, prepared with 1500mL of DI water for aqueous samples or an empty 100ml digestion cup or a beaker with Whatman™ filter paper (when muffling) for soils is prepared for each batch of twenty or fewer samples. To be acceptable, the method blank activity shall be less than the MDA (or, if higher, less than the contract required MDC). Samples associated with an elevated method blank are acceptable if the sample activity is greater than five times the blank activity.

9.2 One LCS, prepared with 1500mL of DI water for aqueous samples or an empty 100ml digestion cup or a beaker with Whatman™ filter paper (when muffling) for soils is prepared for each batch of twenty or fewer samples. The LCS activity should fall within the general range of 5-10 times the requested detection limit (default = 1pCi/L). The LCS sample accuracy (measured activity/added activity) will fall within currently established control limits, as described in the LIMS program specifications.

9.3 A duplicate is prepared at a frequency of one per twenty or fewer samples. The duplicate sample DER will be within the established control limits, as described in the LIMS program specifications. Some clients may require use of RPD as a measure of precision. The duplicate sample RPD will be within specified control limits. Duplicate samples with activity levels less than 5 times the MDC will not be assessed using RPD.

10 CALCULATIONS

ALS SOPs 708, 715, and 724 give detailed information on calculations, data review and instrument performance criteria to be used in conjunction with this SOP.

10.1 The estimated sample preparation uncertainty, PU, is 0.10. This is based on SOP 708 guidelines for one gross aliquoting, two volumetric measurements, one spike/carrier addition, and one ICP yield determination:

$$0.10 = \sqrt{(0.05)^2 + (0.006)^2 + (0.006)^2 + (0.025)^2 + (0.083)^2}$$

10.2 For aqueous samples Ba chemical yield (Ba is used as a yield monitor for Ra) is calculated as follows:

$Ba_i = V_i * ICP_i * DF$
$Ba_f = V_f * ICP_f * DF$
$Ba_{RC} = V_{RC} * ICP_{RC} * DF$

% Ba recovery = Ba_f / (Ba_i + Ba_{RC}) * 100

Where:

Ba_i = initial mass of Ba in unspiked sample (µg)

Vi = final volume (from step 8.1.5.1) of diluted "initial" ICP sample (ml).

ICPi = Ba concentration in diluted "initial" ICP sample (µg/ml)

DF = dilution factor (amount solution was diluted prior to ICP analysis)

Ba_f = final mass of Ba after completion of Ra purification (µg)

V_f = final sample dilution volume, usually 25 mL as described in Step 8.1.18.

ICP_f = Ba concentration in diluted "final" ICP sample (µg/ml)

Ba_{RC} = Ba mass spiked into sample aliquot prior to performing separation/purification procedure (µg)

V_{RC} = reference carrier final volume – usually 25ml as described in step 8.1.9 (ml)

ICP_{RC} = Ba concentration in diluted reference carrier (µg/ml)

10.3 For solid samples Ba chemical yield (Ba is used as a yield monitor for Ra) is calculated as follows:

$Ba_i = V_i * ICP_i * DF$
$Ba_f = V_f * ICP_f * DF$
$Ba_{RC} = V_{RC} * ICP_{RC} * DF$

% Ba recovery = Ba_f / (Ba_i) * 100

If Ba_i is < Ba_{RC} then Ba_{RC} is used in place of Ba_i and a "low bias" flag is noted on the data report

Where:

Ba_i = initial mass of Ba in sample determined by analysis of diluted solution prepared in step 8.2.10 (µg)

V_i = final volume (from step 8.2.10) of diluted "initial" ICP sample (ml).

ICP_i = Ba concentration in diluted "initial" ICP sample (µg/ml)

DF = dilution factor (amount solution was diluted prior to ICP analysis)

Ba_f = final mass of Ba after completion of Ra purification (µg)

V_f = final sample dilution volume usually 25 mL as described in Step 8.1.18.
ICP_f = Ba concentration in diluted "final" ICP sample (µg/ml)

Ba_{RC} = Ba mass spiked into sample aliquot prior to performing separation/purification procedure (µg)

V_{RC} = reference carrier final volume – usually 25ml as described in step 8.1.9 (ml)

ICP_{RC} = Ba concentration in diluted reference carrier (µg/ml)

10.4 Calculate the actual volume, V_A, sample analyzed (accounting for volumes of sample removed) as follows:

$$V_A = V * ((V_i - ICP_i) / V_i) * ((V_f - ICP_f)/V_f)$$

Where:

V = sample aliquot (ml,g)

V_i (aqueous samples) = initial sample dilution volume. For samples not requiring a reduced aliquot V_i = V. (ml)

V_i (solid samples) = volume of diluted digestate from step 8.2.9 (ml)

ICP_i = volume taken for "initial" ICP analysis (ml)

V_f = final sample dilution volume , usually 25 mL as described in step 8.1.18.
ICP_f = volume taken for "final" ICP analysis (ml)

11 DEVIATIONS FROM METHOD

11.1 In addition to describing a procedure for aqueous samples, this SOP describes a procedure for determining Ra-228 in soil, which the laboratory employs at a client's request. Also, this SOP provides procedures for determining the chemical yield by the determination of Ba by ICP analysis. This measurement increases the accuracy of the method.

11.2 ALS routinely monitors Ba yields by ICP analysis.

11.3 Where drinking water methodologies are required by the client, the method QC recovery acceptance criteria shall be ±20%, irrespective of ALS's internally

derived acceptance criteria.

12 SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

12.1.1 All Safety and Hazards are managed in accordance with the current facility plans:

- Chemical Hygiene Plan (CHP)
- Radiation Protection Plan (RPP).
- Emergency and Contingency Plan (ECP)
- Respiratory Protection Plan (RESPP)

12.2 WASTE DISPOSAL

12.2.1 All Wastes are disposed of in accordance with the Waste Management Plan (WMP).

12.2.2 The analytical process effluent has been determined to not be hazardous in other than corrosivity except the Ba and Pb containing supernatants. These supernatants must be segregated into the Ba and Pb waste containers supplied by the Waste Disposal Coordinator.

13 REFERENCES

13.1 EPA Method 904.0, EPA 600/4-80-032, August 1980.

13.2 EPA Method 9320, EPA SW846, September 1986.

13.3 Ra-226 in Water, EPA 402-R-10-001, February 2010.

13.4 Definitions are listed in LQAP section 14.

13.5 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

13.6 ISO/IEC 17025:2005

13.7 MARLAP, July 2004, NUREG-1576 Volume 3, section 19.3.2

13.8 JCGM 100:2008. Evaluation of measurement data - Guide to the expression of uncertainty in measurement, Joint Committee for Guides in Metrology. (GUM)

ALS Standard Operating Procedure

DOCUMENT TITLE:	PREPARATION OF WATER SAMPLES FOR ACTINIDES
REFERENCED METHOD:	EPA 908.0
SOP ID:	776
REV. NUMBER:	14
EFFECTIVE DATE:	APRIL 8, 2013

ALS
STANDARD OPERATING PROCEDURE 776 REVISION 14

TITLE: PREPARATION OF WATER SAMPLES FOR ACTINIDES

FORMS: NONE
APPROVED BY:

PRIMARY AUTHOR Tamara Elliott DATE 4/2/13

QUALITY ASSURANCE MANAGER [signature] DATE 4/8/13

LABORATORY MANAGER Greg Frank DATE 4/2/2013

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) describes procedures for preparation of environmental and drinking waters for analysis of actinides. The SOP is based on EPA Method 908.0 for the preparation of waters for the separation of uranium. This SOP addresses only the initial concentration steps and is applicable to uranium, plutonium, thorium, americium, curium, and neptunium.

2. SUMMARY

The actinides are co-precipitated with ferric hydroxide and separated from the sample. Once the hydroxide precipitate is centrifuged and the supernatant decanted as waste, further steps are performed per the appropriate actinide separation and purification SOPs 765, 777, or 778. Please note that procedures for tracing and spiking samples are found in SOP 766.

3. RESPONSIBILITIES

3.1 It is the responsibility of the laboratory staff to perform these procedures according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, performance of precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.2 ALS's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supersede ALS's standard criteria. It is the responsibility of all personnel who work with samples or data

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the workorder file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken, documented, and approved by the Supervisor.

4. INTERFERENCES

4.1 The presence of significant quantities of suspended solids is a physical interference. Samples containing perceptible quantities of suspended solids are filtered prior to initiation of preparation and analysis, unless otherwise stated in the program specification. If the sample needs to be analyzed including a large amount of sediments, a modified procedure can be followed. This modified procedure will involve a soil digestion procedure to accommodate the sediment portion of the liquid.

5. APPARATUS AND MATERIALS

5.1 Pyrex™ beakers or equivalent, 400mL and 1500mL - 2000mL or other appropriate size

5.2 Watch glasses

5.3 Stirring hot plates

5.4 Graduated cylinder, 1.0L, or other appropriate size

5.5 Stir bars

5.6 Centrifuge bottles, 250mL

5.7 Wash bottles

5.8 Repeator Eppendorf™ pipet or equivalent and disposable pipet tips

5.9 pH paper, acidic

5.10 Muffle furnace

6. REAGENTS

NOTE: Any chemicals with a Threshold Limit Value (TLV) of less than 50ppm shall be worked with in a laboratory fume hood (e.g., solvents and acids).

6.1 Deionized (DI) water, obtained from the laboratory's deionized water system.

6.2 Nitric Acid (HNO_3), conc., reagent grade.

6.3 Ammonium hydroxide (NH_4OH), 15N, (conc.). TLV = 25ppm (for NH_3)

6.4 Ferric chloride carrier, 20mg Fe^{+3}/mL HCl. Made in-house by dissolving 96g $FeCl_3 \bullet 6H_2O$ per 1000mL of 0.5N

6.5 Actinides Tracer and Spike Solutions. High purity, NIST-traceable or equivalent, approximately 10-30dpm/mL activity (unless otherwise specified). A second source for tracer and/or spiking solutions should be used, independent of the source used for calibration (*required* for DOD samples per LIMS program specification). Tracer and spiking nuclide defaults are as follows:

6.5.1 For Pu-239/240, Pu-238 Tracer = Pu-242, Spike = Pu-239

6.5.2 For U-238, U-235/236, U-233/234, Tracer = U232, Spike = Nat-U

6.5.3 For Am-241, Tracer = Am-243 or Cm-244, Spike = Am-241

6.5.4 For Th-232, Th-230, Th-228, Tracer = Th-229 Spike = Th-230

6.5.5 For Cm-244, Tracer = Am-243, spike = Cm-244.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

It is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 to adjust the pH of the sample to less than 2. Addition of 5mL conc. HNO_3 per liter of sample is usually sufficient. If samples are to be collected without preservation, they should be brought to the laboratory within 5 days of collection and then preserved and held in the original container for a minimum of 24hrs before analysis or transfer of the sample from the original container (SOP 733). The container should preferably be plastic rather than glass. This prevents loss due to breakage during transport and handling and minimizes any possible losses due to analyte plate out on container walls.

8. PROCEDURE

8.1 DISSOLVED ANALYSIS

8.1.1 Before starting the procedure, check the pH of the sample. If the sample is unpreserved, add 5mL concentrated HNO_3 or enough to make the sample pH<2 unless otherwise noted in program specifications or work order instructions.

If the sample was not preserved, hold sample for 24 hours before aliquotting (refer to SOP 733 for sample preservation procedure).

If significant solids are present, filter the sample through a fluted qualitative filter paper (refer to SOP 736) unless otherwise noted.

8.1.2 Aliquot 1.0L of sample (or appropriate volume adjusted to reach MDA or account for sample activity) into a glass beaker. Record the volume of each sample on the benchsheet. If the sample aliquot is 200mL or less, the sample may be aliquotted directly into a 250mL centrifuge bottle. QC (MB and LCS) are created at this time using DI water.

8.1.3 Acidify the QC by adding a minimal amount of HNO_3 acid. **Note:** If samples were not preserved prior to aliquotting, enough HNO_3 must be added at this time to ensure the pH is less than 2. Otherwise, samples will not form a ferric hydroxide precipitate.

8.1.4 Using a repeater pipet, add 2mL of ferric chloride carrier. Spike and trace samples by consulting the benchsheet for information about the volume, activity and standard identification to be used for tracing and spiking. Add calibrated volumes of tracer and spike solutions to the samples, blank and blank spike per SOP 766.

8.1.5 For samples aliquotted into beakers, place a stir bar in each beaker, and set each sample on a hotplate. Stir the water sample. .

8.1.6 Slowly add concentrated NH_4OH (~60-75mL) to the sample. Add NH_4OH until the Fe $(OH)_3$ precipitate forms and turbidity persists while stirring continues. .Turn the stir mechanism off and remove stir bar. Allow precipitate to settle to the bottom of the beaker for a minimum of 30-45 minutes.

8.1.7 After the precipitate has settled, decant the aqueous portion away from the precipitate. Reduce the volume to approximately 200mL or less with **minimal** loss of precipitate. If this cannot be accomplished without significant loss of precipitate, the option is to perform multiple centrifugations to separate the supernatant from the precipitate. The aqueous portion of the sample can be discharged to ALS's wastewater system (i.e., disposed down the drain in the fume hood with large amounts of water).

8.1.8 Transfer the remaining solution containing the precipitate to a labeled 250mL centrifuge bottle. Rinse the sample beaker with a **minimum**

amount of deionized water and add the rinse to the centrifuge bottle.

8.1.9 For samples that were directly aliquotted into 250mL centrifuge bottles, add NH_4OH (25-30mL) until a precipitate forms.

8.1.10 Centrifuge the samples at approximately 3500rpm for 10 minutes. Discard the supernatant down the drain with large amounts of cold water unless otherwise specified due to hazardous or radioactive waste concerns.

8.1.11 Proceed to the appropriate separation and purification procedure, SOP 765, 777, or 778.

8.2 TOTAL ANALYSIS

8.2.1 Before starting the procedure, check the pH of the sample. If the sample is unpreserved, add 5mL concentrated HNO_3 or enough to make the sample pH<2 and hold for 16 hours. Refer to SOP 733 for sample preservation procedure.

8.2.2 Shake the sample container to homogenize and mix the sediment and measure a volume of one liter (or other appropriate volume to reach requested detection limits) of the water sample to be analyzed. Record the volume on the benchsheet. Pour the sample into an appropriately sized glass beaker.

8.2.3 Consult the benchsheet for information about the volume, activity and standard identification to be used for tracing and spiking. Add calibrated volumes of tracer and spike solutions to the samples, blank and blank spike as per SOP 766.

8.2.4 Heat the sample on a hot plate at a low temperature and take it to near dryness. Add ~25mL of 8N HNO_3 to the samples as to prevent plating of radioactivity onto the glass beaker. Heat the sample to dryness, but do not bake.

8.2.5 If the sediment portion contains any organic material, the samples should be muffled. If muffling is required, cover the sample with a ribbed watch glass and muffle the sample at approximately 600°C for at least 4 hours. NOTE: If gamma analysis is required, the maximum muffle temperature is 450-500 ^oC due to volatility of Cs-137.

8.2.6 From this point, follow the soil digestion procedure outlined in SOP 773. Following solid digestion, refer to the appropriate actinides separation SOPs (765, 777, or 778,) for further separation.

9. CALCULATIONS

TPU FACTORS. As defined in SOP 708, the 1σ preparation uncertainty factors should be applied during the final reporting stage of the analysis as a component of the Total Propagated Uncertainty (TPU). Refer to individual SOPs 765, 777, or 778 for applicable 1σ preparation uncertainty factors.

10. CALIBRATION STANDARDS

Calibration standards are not required for this procedure.

11. QUALITY CONTROL

11.1 A method blank of DI water is prepared with each batch of up to 20 field samples (i.e., at a five-percent frequency).

11.2 One laboratory control sample (LCS or blank spike), in DI water, is prepared with each batch of up to 20 field samples (i.e., at a five-percent frequency).

11.3 Duplicate sample analyses are prepared at a minimum frequency of five-percent, with at least one duplicate for each batch, or according to client specifications. If there is insufficient sample volume for this frequency of duplicates, a blank spike duplicate may serve as a measure of batch reproducibility.

12. DEVIATIONS FROM METHOD

12.1 This method has been modified from EPA Method 908.0 to enable determination of total uranium concentration of the sample by alpha spectroscopy. A known quantity of Uranium-232 tracer is equilibrated with the sample prior to separation. The tracer activity is used to calculate the concentration of uranium isotopes in the sample. The total uranium concentration is calculated as the sum of the U-234/235/238 activities.

12.2 Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of the lab's internally derived acceptance criteria.

13. SAFETY, HAZARDS AND WASTE DISPOSAL

13.1 SAFETY AND HAZARDS

All Safety and Hazards are managed in accordance with the current facility plans:

- Chemical Hygiene Plan (CHP)
- Radiation Protection Plan (RPP).
- Emergency and Contingency Plan (ECP)
- Respiratory Protection Plan (RESPP)

13.2 WASTE DISPOSAL

All Wastes are disposed of in accordance with the Waste Management Plan (WMP)

14. REFERENCES

14.1 EPA Method 908.0, "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," EPA-600/4-80-032, August, 1980.

14.2 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

ALS Standard Operating Procedure

DOCUMENT TITLE:	RADIUM-226 IN AQUEOUS AND SOIL MATRICES – RADON EMANATION TECHNIQUE
REFERENCED METHOD:	EPA 903.1, HASL 300 Ra-03, SM7500-Ra C
SOP ID:	783
REV. NUMBER:	10
EFFECTIVE DATE:	12/23/2013

ALS
STANDARD OPERATING PROCEDURE 783 REVISION 10

TITLE: RADIUM-226 IN AQUEOUS AND SOIL MATRICES -- RADON EMANATION TECHNIQUE -- METHOD EPA 903.1

FORMS: NONE

APPROVED BY:

TECHNICAL MANAGER _____ DATE _____

QUALITY ASSURANCE MANAGER _____ DATE _____

LABORATORY MANAGER _____ DATE _____

1. SCOPE AND APPLICATION

This standard operating procedure (SOP) and the method it references, EPA Method 903.1, describes a procedure to determine ^{226}Ra in soil and aqueous matrices. The method is based on the emanation and scintillation counting of ^{222}Rn and progeny produced by the decay of ^{226}Ra.

Due to the potential difficulty in obtaining a complete dissolution of some solid matrices, it is recommended that ^{226}Ra in soils and solids be routinely analyzed directly by gamma spectroscopic determination of ^{214}Pb and ^{214}Bi progeny. Radon emanation in soils should be performed only at the specific request of the client.

2. SUMMARY

2.1 The ^{226}Ra in aqueous samples is concentrated and separated by coprecipitation with barium sulfate. Prior to separation, a portion of the sample is removed for inductively coupled plasma atomic emission spectrometry (ICP-AES) determination of the preparation concentration of barium in the sample. The Ba[Ra]SO_4 precipitate is dissolved in basic EDTA solution, placed in a 40mL VOA vial, purged of any existing ^{222}Rn, and stored to allow quantitative in-growth of ^{222}Rn. After in-growth, the radon is purged into an alpha scintillation cell. The short-lived ^{222}Rn progeny are allowed to come to equilibrium with the parent radon (~4hrs) before the scintillation cell is counted for alpha activity. The 4hr in-growth period also allows for the decay of other radon isotopes.

2.2 In solids, ^{226}Ra is liberated from the solid matrix by a total digestion of the solid. The sample is muffled, transferred to a polypropylene beaker and digested in the presence of strong acids. After digestion, the sample is transferred to a VOA vial, purged, and counted, as stated in Section 8.1.

2.3 The absolute measurement of ^{226}Ra is effected by calibrating the scintillation cell (and emanation system) with a solution of NIST-traceable ^{226}Ra. Each alpha detector/cell combination must be calibrated individually and the cell constants applied to the specific detector/cell pairs when calculating results.

2.4 The detection limit for this method is dependent upon sample aliquot, sample count time, length of the in-growth period, the scintillation system background activity, and detection efficiency. The routine minimum detectable activity (MDA) is 1.0pCi/L for aqueous samples, and 1.0pCi/g for solid samples.

2.5 As a result of fluctuation of the background due to build-up and decay of Rn and its progeny, dedicated backgrounds must be counted for each detector/cell combination prior to emanation of each sample.

2.6 The emanation apparatus is set up as shown in Figure 1.

3. RESPONSIBILITIES

3.1 It is the responsibility of the analyst to perform these procedures according to this SOP and to complete all documentation required for review. Analysis and interpretation of the results are performed by personnel in the laboratory who have demonstrated the ability to generate acceptable results utilizing this method. This demonstration may come in the form of Supervisory/training review, performance of precision and accuracy tests, or the successful completion of an unknown proficiency test sample.

3.2 ALS's LIMS program specification system and associated project analyte nicknames are the means by which client-specific requirements for sample preparation, analysis, data evaluation and reporting are communicated to the laboratory. This system includes automated electronic controls where possible. The criteria defined in the program specification supercede ALS’s standard criteria. It is the responsibility of all personnel who work with samples or data involving this method, to consult the applicable LIMS program specification for client-specific requirements prior to initiating handling of samples or data.

3.3 Final review and sign-off of the data are performed by the Department Supervisor or designee. Initialing and dating the workorder file indicate that this review for precision, accuracy, completeness, and reasonableness is complete and satisfactory. Any errors that are found require corrective action, which includes notification to the technician/analyst who performed the work and documentation of measures taken to remediate the data.

3.4 It is the responsibility of all personnel who work with samples involving this method to note any anomalies or out-of-control events. Any discrepancies must be noted and corrective action taken, documented, and approved by the Department Manager.

4. INTERFERENCES

4.1 There are no known radiometric interferences to this method. Samples such as heavily sedimented samples and high brine content samples may require special treatment or a reduced aliquot prior to initiation of chemical separation procedures, as they might require more than 30mL of solvent to dissolve.

4.2 Water samples with high concentrations of sulfate-forming cations may present barium chemical recovery problems, but do not interfere with radiometric recovery in samples.

4.3 Soil samples in which visible precipitate accumulates in the bubbler during the ingrowth period may cause a low bias in the final results, as Ra-226 and the associated Rn-222 progeny may be sequestered in the precipitate and consequently be unavailable for radon emanation. Samples with visible sediment at the time of emanation require that the client be informed of the potential bias in the analytical results. Corrective action may involve either of the following options:

4.3.1 Disclose the potential bias to the analytical results in the case narrative and submit the results with that qualification.

4.3.2 Re-prepare the sample at a reduced aliquot, with a corresponding increase in detection limits. The reduced aliquot should be estimated at the sample mass that is unlikely to form precipitate in the bubbler.

4.4 Scintillation cells should be stored for at least four hours after purging with helium before background counts can be obtained. If cells are not stored for at least four hours before background counting, radon and its progeny that are not completely purged from the cell will not be in secular equilibrium and the background may be biased high, resulting in a low bias to the final analytical results.

5. APPARATUS AND MATERIALS

5.1 scalar, Ludlum Model 1000, or equivalent

5.2 photo multiplier tube, Ludlum Model 182, or equivalent

5.3 Tygon^{TM} tubing, various sizes

5.4 glass wool

5.5 gas regulator valve, 3000 PSIG, max

5.6 VOA vials, with septum lids, 40mL

5.7 scintillation cells

5.8 stirring hotplate

5.9 laboratory balance, resolution 0.01g

5.10 centrifuge tubes

5.11 graduated cylinder, 1L

5.12 beakers, Pyrex™, 100mL and 1.5 or 2L sizes, or similar

5.13 specimen cups, polypropylene, 100mL and 250mL sizes

5.14 spatulas, plastic

5.15 test tubes, disposable, with polyethylene test tube caps, 15mL

5.16 BD™ syringe, with luer-lock tip, or equivalent, 3mL

5.17 Deflected-point septum penetration needles (4 inch and 1 inch lengths)

5.18 stopcocks

5.19 5-channel Cole-Palmer Masterflex peristaltic pump equipped with Cat. No. 7014 – 20 pump heads.

5.20 Pipette, 1.0mL and 0.1mL sizes, with disposable pipette tips

5.21 Whatman™ filter paper, #42 (90mm), or similar

5.22 Parafilm™

5.23 stir bars

5.24 watch glasses

5.25 vortex mixer

5.26 Drierite™, or indicating desiccant, 10-20 mesh

6. REAGENTS

NOTE: TLV and other hazard information may also be given here. Any chemical with a TLV below 50ppm must be worked with in a laboratory fume hood. The absence of this information does not imply that the substance is non-hazardous. The employee should be familiar with all pertinent MSDSs before proceeding.

6.1 Distilled or deionized (DI) water, ASTM Type-II, or equivalent

6.2 Ascarite, drying reagent, 8-20 mesh.
TLV = 2mg/m3 = 1.22ppm (NaOH, ceiling)

6.3 Barium carrier, 16mg/mL, standardized: Dissolve 28.46g $BaCl_2 \cdot 2H_2O$ in DI water. Add 5mL 16N HNO_3 and dilute to 1000mL with DI water. See ALS SOP 712 for standardization procedure.
TLV = 0.5mg Ba/m3 = 0.06ppm (TWA). Irritant.

6.4 EDTA reagent, basic 0.25M: Dissolve 20g NaOH in 750mL water and slowly add 93g Na2EDTA· 2H2O. Heat and stir until dissolved, filter through coarse filter paper and dilute to 1L in DI water. Adjust pH to 10 with sodium hydroxide. Irritant.

6.5 Helium, gas. Ultra high purity, 99.999%.

6.6 Hydrochloric acid (HCl), 12N, conc.
TLV = 5ppm (ceiling).

6.7 Nitric Acid (HNO_3), 16N, conc.
TLV = 2ppm (TWA). Irritant, corrosive.

6.8 ^{226}Ra standard solution, Traceable to NIST, or equivalent: Prepare stock dilution of approximately 50pCi/mL. Prepare one source for calibration purposes, and a different independent source for spiking purposes.

6.9 Sulfuric acid, 18N: Carefully add 500mL 36N H_2SO_4 to approximately 450mL of DI water. Dilute to 1L with DI water.

NOTE: A rubber apron and face shield must be worn when handling concentrated H_2SO_4. Add H_2SO_4 slowly with stirring to prevent boiling due to liberation of heat during mixing.
TLV = 1mg/m3 = 0.25ppm (TWA). Irritant.

6.10 Sulfuric acid, 0.1N: Dilute 120mL 18N H_2SO_4 to 22L with DI water.
TLV = 1 mg/m3 = 0.25ppm (TWA). Irritant.

6.11 Nitric Acid, 8N: Carefully add 500mL of concentrated HNO_3 to approximately 400mL of DI water. Then bring to 1 liter with DI water.
TLV = 2ppm (TWA). Irritant, corrosive.

6.12 ICP diluting solution: Add 10mL 16N HNO_3 and 50mL 12N HCl to approximately 500mL of DI water. Bring to 1 liter with DI water.
TLV = See Sections 6.6 and 6.7.

6.13 Hydrofluoric acid (HF), 48.0-51.0%, conc.
TLV = 3ppm (ceiling). Irritant, burns, bone, teeth, fluorosis.

NOTE: Employees must be familiar with the HF burn kit location and use before performing this procedure.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Liquids: A sample should be collected in a manner that will provide the most representative sample. Collect a 2 liter sample in a plastic container, from a free-flowing source when possible.

7.1.1 For a total sample analysis, preserve the sample with nitric acid to a pH<2.0 upon collection (15mL 1N HNO_3 / 1L H_2O). If not preserved upon collection, then the sample should be preserved within 5 days. For a total sample analysis, preserve the sample with nitric acid to a pH<2.0 upon collection (15mL 1N HNO_3 / 1L H_2O). If not preserved upon collection, then the sample should be preserved within 5 days. If preservation is delayed, hold samples for a minimum of 24 hours after preservation.

7.1.2 For a "dissolved" sample analysis, use a 0.45µm membrane filter to remove the solids from the sample. After filtering, acidify the sample with nitric acid to a pH<2.0.

7.2 Solids: Preservation is not required. A representative sample of 25-50 grams should be submitted for analysis.

8. PROCEDURE

8.1 CALIBRATION

8.1.1 BACKGROUND CALIBRATION

Prior to each sample analysis, the cell is purged with helium and stored for at least four hours. The number of background counts associated with the alpha scintillation cell is then obtained by counting the cell in the detector to be used. The background calibration must be counted for a duration equal to or longer than the planned sample count. If the sample and background count times differ (e.g. if the sample count is shorter than the background count), the number of background counts should be adjusted to match the sample count time. Record this adjustment on a Quality Assurance Summary Sheet (QASS), Form 302. The count rate of the empty cell is employed as the background count rate in calculated results.

8.1.2 PLATEAU CALIBRATION (OPERATING VOLTAGE DETERMINATION)

The purpose of the plateau calibration is to determine the optimum operating voltage for the photomultiplier tube. This optimized operating voltage minimizes the detector background, while stabilizing the counting efficiency, under normal operating conditions. Plateau calibrations must be performed prior to initial use of the instrument and at least annually, prior to the efficiency calibrations.

8.1.2.1 Adjust the voltage setting on the scalar to a low voltage of approximately 500 volts.

8.1.2.2 Count the daily check source for one minute and record the number of counts in the maintenance logbook.

8.1.2.3 Increase the voltage by 100 volt increments, repeating the previous Step each time.

8.1.2.4 Continue to increase the operating voltage past 1,000 volts until the count rate significantly increases, indicating that the voltage is no longer on the plateau. Do not exceed 1,500 volts.

8.1.2.5 Plot the voltage against the gross counts on a scatter plot.

8.1.2.6 Repeat the process described above, removing the daily check source and counting an empty detector instead. Count times should be increased to five minutes and the range of voltages need only encompass the "flat" part of the plateau.

8.1.2.7 Select an operating voltage on the "flat" part of the plateau, where the background count rate is lowest.

If the operating voltage is changed from the existing setting for sample analyses, all detector/cell combinations must be recalibrated for counting efficiency.

8.1.3 EFFICIENCY CALIBRATION

The calibration constant of each detector-scintillation cell combination must be determined, using NIST-traceable ^{226}Ra solution. This calibration is performed at least annually. The constant is determined as follows:

8.1.3.1 Prepare calibration sources by adding 25mL EDTA to a 40mL VOA vial. Be sure to prepare enough sources to count one in each cell and a few extra sources in case a cell needs to be recalibrated. Calibration sources to be reused must be fitted with new septa, inverted, and allowed to ingrow.

8.1.3.2 Spike the samples with approximately 200dpm of ^{226}Ra spiking solution. The samples should be purged with helium to ensure that no radon is present prior to radon in-growth, see Section 8.2. The samples may be sealed immediately after spiking, without purging with helium, as long as they are stored for at least 26 days to achieve >99% in-growth.

8.1.3.3 The calibration constant is a composite measure of the emanation efficiency of the sample, the collection efficiency of the system, and the counting efficiency of the cell. The calibration procedure is conducted, similar to sample measurements, after the alpha emitting radon daughters have come to equilibrium with ^{222}Rn (i.e., 4 hours after transfer to the scintillation cell). The duration of the calibration count should be sufficient to allow the collection of at least 10,000 counts. Record the detector, cell ID, count start time, and count duration on the appropriate benchsheets and logbook. If a given cell is to be used with multiple detectors, it may be recounted in those detectors and calibration constants generated for each detector/cell combination.

NOTE: If a cell is to be calibrated in multiple detectors, a background measurement must be obtained for that cell in each detector prior to transferring and counting the sample.

8.1.3.4 Each detector-scintillation cell combination should be calibrated with a NIST-traceable ^{226}Ra standard at least annually.

8.1.3.5 See Section 9.5.6 for calibration constant calculations.

8.1.4 INITIAL CALIBRATION VERIFICATION (ICV) AND CONTINUING CALIBRATION VERIFICATION (CCV)

8.1.4.1 ICV and CCV sources are prepared in the same manner as efficiency calibration sources, see Section 8.1.3, using an independent second source, instead of the calibration source.

8.1.4.2 To verify that the efficiency calibration is valid, count one ICV source per cell in each detector after the calibration is complete. As with the calibration sources, ICVs may be counted for the same sample in multiple detectors, as long as a background measurement is made for the cell in a specific detector.

8.1.4.3 Calculations for ICV sources are the same as those in Section 9 for samples, assuming a 100% chemical yield.

8.1.4.4 The efficiency determined for a specific cell in a specific detector is used to determine the radiometric recovery for each ICV. The radiometric recovery must be within ±15%; if the radiometric recovery is > ±10%, approval must be obtained from the Radiochemistry Technical Manager before the cell can be used.

8.1.4.5 CCVs are analyzed once every twenty analytical runs on each detector/cell combination and are subject to the same acceptance criteria as ICVs. If a CCV falls outside the ±15% acceptance criteria, the CCV is repeated. If the failure is confirmed, the cell is removed from service until it is recalibrated.

8.1.5 DAILY CHECK SOURCE
A NIST-traceable Thorium source is counted long enough to acquire at least 2,000 counts before and after samples are counted each day, bracketing the sample counts to ensure that the detector and scalar are working properly.

8.2 AQUEOUS SAMPLE PREPARATION

8.2.1 Verify and record (on Form 631) the pH of the sample according to SOP 733.

8.2.2 Using a graduated cylinder, aliquot the sample into a labeled 1.5L or 2L beaker. A sample aliquot of 1L is typical for this method, but may need to be reduced due to matrix interference or volume limitations. All samples should be brought to a final volume of 1L with DI water. Add a stir bar to each beaker and place on a stirring hot plate.

8.2.3 Prepare QC samples according to Section 10.

8.2.4 HOW TO TAKE INITIAL ICP ALIQUOT

8.2.4.1 Prior to adding any reagents, spikes, or carriers to the sample, use a calibrated pipette to remove 1mL of sample and place into a clean test tube filled with 9mL of ICP diluting solution and labeled with the sample ID and “i”, to indicate the initial ICP aliquot. Cover with a test tube cap and invert tube several times to mix thoroughly. Set aside until final ICP aliquot has been taken.

8.2.4.2 A “reference carrier” (RC) should also be prepared by adding 1mL Ba carrier to 1L of DI water. Mix thoroughly, remove 1mL of solution and dilute to 10mL as stated above for samples. Submit with samples for ICP analysis to provide a reference concentration for the yield calculations.

8.2.5 To each water sample, add 20mL of 12N HCl, 1.0mL barium carrier, and appropriate amount of spiking solution to LCS and any MS samples. Cover with a watch glass and heat to a gentle boil.

8.2.6 Cautiously, with vigorous stirring, add 25mL 18N H_2SO_4. Continue boiling and stirring at least 10 minutes. Remove from heat. Remove

stir bar, rinsing with 0.1N H_2SO_4. Let precipitate settle overnight, or at least four hours (overnight is recommended).

8.2.7 Aspirate the supernatant into the PAR waste water treatment facility.

8.2.8 Slurry the precipitate and transfer to a labeled centrifuge tube with a minimum amount of 0.1N H_2SO_4. Centrifuge at 3500rpm for 10-15 minutes and discard supernatant into the PAR wastewater treatment facility. Wash twice with 15mL of 0.1N H_2SO_4. Centrifuge and discard washes into the PA wastewater treatment facility.

8.2.9 Add 25mL basic EDTA reagent, heat in a water bath and stir well until dissolved. After dissolution, remove from the Hot Blocks and allow the samples to cool.

NOTE: If the precipitate is difficult to dissolve, additional EDTA can be added; however, the maximum volume of EDTA that may be used is 30mL, as the VOA vials are only 40mL. Record the volume of EDTA used on the benchsheet.

8.2.10 HOW TO TAKE FINAL ICP ALIQUOT

8.2.10.1 Vortex the sample to mix thoroughly. Using a calibrated pipette, aliquot 0.1mL of sample into a clean, labeled test tube containing 9.9 or 10mL of DI water (record the volume of water used). Cover with Parafilm, and invert several times to mix completely. With a calibrated pipette, aliquot 1.0mL of the diluted sample into another clean test tube labeled with the sample ID and “f” and containing 9.0mL of ICP diluting solution. Cover with a test tube cap and mix well. Submit the initial and final test tubes to the Metals Lab with proper bench sheets for analysis.

8.2.10.2 Upon the return of ICP sample fractions to the radiochemistry lab, and after satisfactory review of the chemical yield data, the ICP fractions may be discharged into the ALS waste water treatment facility (i.e., down the laboratory sink with plenty of cold tap water). The test tubes may be soaked in a Radiacwash™ solution, rinsed with tap water and discarded into the sanitary trash. The tubes containing the intermediate, DI water diluted, sample may be disposed of in the same manner.

8.2.11 Transfer the solution remaining after Step 8.2.10 to a labeled VOA vial using approximately 2.5mL EDTA to rinse the centrifuge tube. The centrifuge tubes may be soaked in Radiacwash™, rinsed, and discarded into the sanitary trash.

8.2.12 Purge the samples in the VOA vials for approximately 20 minutes with helium to remove any radon from the solution prior to sealing the vial.

8.2.13 Seal the VOA vial and record the date and time that the purge ended as t_1, beginning of ^{222}Rn in-growth, on the benchsheet. Store the solution for at least 4 days for in-growth of ^{222}Rn (typical storage time is 7 days, full in-growth is achieved after 30 days).

8.2.14 At the end of the storage period, fill the upper half of a modified 3mL syringe with Drierite™ to about the 2.5mL mark and the lower half with ascarite to about the 3mL mark. Place a small amount of glass wool in the end of the syringe to secure the drying agents. The column is a single use column and can be discarded in the sanitary trash after transferring the sample. Store unused columns in the desiccator.

8.2.15 Purge a scintillation cell with helium and close the valves prior to obtaining the background measurement.

8.2.16 Make the connections shown in figure 1. Puncture the VOA vial septum with both needles. The long needle is inserted nearly to the bottom of the vial. The short needle is inserted into the headspace. Also, connect tubing to the scintillation cell (including the Drierite ™ tube).

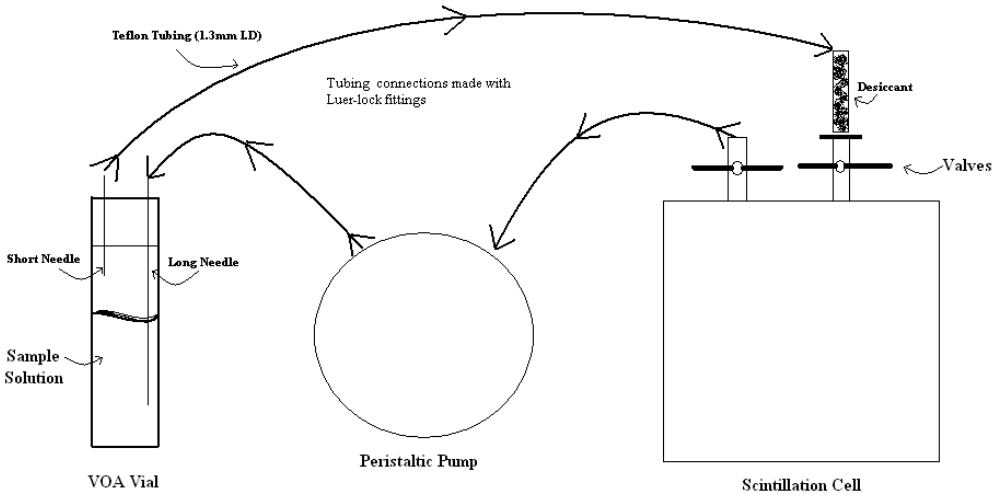


Figure 1

8.2.17 Ensure that all connections are tight and open both valves on the scintillation cell. Turn the peristaltic pump on and run at speed ~4, making sure that bubbles are issuing from the long needle in the VOA vial. Run for ~15 minutes to transfer radon from the VOA vial to the scintillation cell.

8.2.18 Turn off the pump and immediately close both valves on the scintillation cell. Disassemble the apparatus. Record the ending transfer date and time as t_2, the beginning of ^{222}Rn progeny ingrowth, on the benchsheet. .

8.2.19 Store the scintillation cell for at least 4 hours to ensure equilibrium between ^{222}Rn and its progeny, and to allow other isotopes of radon and their progeny to decay. Count the alpha scintillations from the cell in a scintillation cell counter with a light-tight enclosure that protects the photomultiplier tube. Record the beginning of the counting date and time on the benchsheet to correct for the decay of ^{222}Rn.

NOTE: After each analysis, flush the cell thoroughly with helium for at least 1 minute and store at atmospheric pressure to remove radon from the cell and prevent the build-up of radon daughter products. The cell must be stored for at least four hours prior to re-use.

8.3 PREPARATION OF SOLID SAMPLES

8.3.1 Weigh 1-4 grams dried, pulverized soil into a permanently labeled glass beaker. Typical aliquot size is 2.0g but may be adjusted due to MDA or matrix interference considerations. Record the sample weight and beaker number on the benchsheet.

8.3.2 Prepare QC samples according to Section 10.

8.3.3 Dry the beakers on a hotplate set at 2. Samples must not have any standing liquid prior to muffling. Cover the beakers with a watch glass and muffle at 600°C for at least 4 hours.

8.3.4 Transfer the sample to a 250mL polypropylene specimen cup, using at least 20mL 16N HNO_3 to rinse the beaker. Scraping with a plastic spatula may be necessary to remove all of the soil from the beaker.

8.3.5 Add 20mL HF, cover with a 100mL polypropylene specimen cup, and heat for 4 hours on Hot Blocks.

8.3.6 Remove the 100mL cup and evaporate to dryness. The 100mL cups may be rinsed thoroughly with tap water and discarded into the sanitary trash.

8.3.7 Add 10mL 8N HNO_3 to the samples while they are on the Hot Blocks to facilitate dissolution. The samples may be covered with a 100mL polypropylene cup to prevent evaporation.

8.3.8 Transfer the solution to a labeled VOA vial, rinsing the beaker with three 5mL rinses of 8N HNO_3, for a total volume of 25mL. The 250mL cups may be soaked in Radiacwash™, rinsed, and discarded into the sanitary trash.

NOTE: If the digestate residue is difficult to dissolve, additional 8N HNO_3 can be added; however, the maximum volume of 8N HNO_3 that may be used is 35mL, as the VOA vial capacity is only 40mL.

8.3.9 Proceed to Step 8.2.12.

9. CALCULATIONS

9.1 Calculate the actual volume, V_A, of sample analyzed for aqueous samples (accounting for volumes of sample removed) as follows (Note: The actual volume for solid samples is the same as the initial sample volume because no sample is removed during the process):

$$V_A = V * \frac{V_i - icp_i}{V_i} * \frac{V_f - icp_f}{V_f}$$

where:

V = sample aliquot (L, g)

V_i = sample final dilution volume (mL)

icp_i = initial aliquot taken for ICP (mL)

V_f = sample volume in EDTA (mL)

icp_f = final aliquot taken for ICP (mL)

9.2 Calculate the barium chemical recovery for aqueous samples, Y, as a percentage, as follows (barium chemical recovery is assumed to be 100% for solid samples):

$$Y_i = (V_i - V_{ICP}) * ICP_i * DF$$

$$Y_f = V_f * ICP_f * DF$$

$$Y_{RC} = V_{RC} * ICP_{RC} * DF$$

$$Y = \frac{Y_f}{Y_i + Y_{RC}} * 100\%$$

where:

Y_i = barium recovery from initial ICP aliquot (µg)

V_{ICP} = volume removed for ICP analysis

ICP_i = initial barium concentration measured by ICP (µg/mL)

DF = dilution factor

Y_f = barium recovery from final ICP aliquot (µg)

ICP_f = final barium concentration measured by ICP (µg/mL)

Y_{RC} = barium recovery from RC aliquot (µg)

V_{RC} = RC final volume (mL)

ICP_{RC} = RC barium concentration measured by ICP (µg/mL)

9.3 The sample activity concentration, counting uncertainty, instrument uncertainty, and minimum detection concentration calculations are provided in SOP 708.

9.4 TPU FACTORS
As defined in SOP 708, calculate the one-sigma (1σ) Total Propagated Uncertainty (TPU) as follows:

9.4.1 Aqueous Samples: Require a 1σ preparation uncertainty factor of 0.110. This is based on one gross aliquot, one volumetric measurement, one ICP determination, one spike/carrier addition, three quantitative transfers, one pipetting and two reagent additions:

$$0.110 = \sqrt{.05^2 + .006^2 + .083^2 + .025^2 + .025^2 + .025^2 + .025^2 + .004^2 + .006^2 + .006^2}$$

9.4.2 Solid Samples: Require a 1σ preparation uncertainty factor of 0.071. This is based on one gross aliquot, one mass measurement, one spike/carrier addition, and three quantitative transfers:

$$0.071 = \sqrt{0.05^2 + 0.003^2 + 0.025^2 + 0.025^2 + 0.025^2 + .025^2}$$

9.4.3 Instrument Uncertainty (IU):

The IU is 0.054. This is based on the in-house preparation of calibration standards, counting reproducibility, counting efficiency, and dead time estimates:

$$0.054 = \sqrt{0.05^2 + 0.01^2 + 0.015^2 + 0.01^2}$$

10. QUALITY CONTROL

Per ALS protocol, spikes are added before the sample receives any chemical treatment. Acceptance limits for quality control parameters may vary per client specifications (typically controlled via test code nicknames), consult applicable LIMS program specification.

10.1 A blank, prepared in one liter of DI water for aqueous samples, must be analyzed with each batch of 20 or fewer field samples (i.e., at a five percent frequency). No matrix is used for blanks used in soil batches - muffle an empty 100mL beaker.

10.2 One blank spike (LCS), prepared in one liter of DI water for aqueous samples, and a Whatman^{TM} filter paper for solid samples, must be analyzed with each batch of 20 or fewer field samples (i.e., at a 5 percent frequency). The spiking level for LCSs should be at least 4-10 times the requested MDA, or 100dpm, whichever is larger.

10.3 For solid samples, at least one matrix spike (MS) should be prepared for each batch of 20 samples (i.e., at a 5 percent frequency). If there is more than one type of solid matrix in the batch, an additional MS should be prepared for each type of matrix present. The spiking level should be at least 4-10 times the expected activity of the sample, or 100dpm, whichever is larger.

10.4 Duplicate sample analyses will be performed at a minimum frequency of five percent, or according to client program specifications. If there is insufficient sample volume for this frequency of sample duplicates, LCS duplicates may serve as a measure of batch reproducibility.

11. DEVIATIONS FROM METHOD

11.1 This SOP meets the requirements of EPA Method 903.1 for water samples. In addition to describing a procedure for aqueous samples, this SOP describes a procedure for determining ^{226}Ra and its progeny in soil, which the laboratory employs at a client's request. Also, this SOP provides procedures for determining the chemical yield as an addition to EPA Method 903.1. This measurement increases the accuracy of the method.

11.2 Only 1.0mL of barium carrier, instead of 2.0mL, is added to aqueous samples. The lesser amount of carrier facilitates dissolution of the precipitate in EDTA. Since Ba yield is determined by ICP, this amount is more than sufficient for $Ba(Ra)SO_4$ precipitation and Ba chemical recovery measurement.

11.3 25mL of EDTA is used to dissolve the $Ba(Ra)SO_4$ precipitate. This volume ensures a complete dissolution of the precipitate in a normal sample. For difficult matrices, up to 35mL may be used to dissolve the precipitate.

11.4 A 40mL VOA vial is used for sample storage and transfer instead of a radon bubbler. There is essentially no difference in the function of these two pieces of apparatus. VOA vials are more cost effective and easier to store, so a larger number of samples may be stored at once.

11.5 Where EPA drinking water methodologies are required by the client, the LCS and Matrix Spike recovery acceptance criteria shall be ±20%, irrespective of the lab's internally derived acceptance criteria.

12. SAFETY, HAZARDS AND WASTE DISPOSAL

12.1 SAFETY AND HAZARDS

All Safety and Hazards are managed in accordance with the current facility plans:

- Chemical Hygiene Plan (CHP)
- Radiation Protection Plan (RPP).
- Emergency and Contingency Plan (ECP)
- Respiratory Protection Plan (RESPP)

12.2 WASTE DISPOSAL
All Wastes are disposed of in accordance with the Waste Management Plan (WMP)

13. REFERENCES

13.1 Prescribed Procedures for Measurement of Radioactivity in Drinking Water, EPA-600/4-80-032, Method 903.1, Radium-226-Radon Emanation Technique.

13.2 HASL-300, Environmental Measurements Laboratory Procedure Manual, Method Ra-03, 27th Ed., Rev. Feb. 1992.

13.3 Standard Methods for the Evaluation of Water and Wastewater, Method 7500-Ra C., 18th Edition, 1992.

13.4 TLVs and BEIs, ACGIH, 1999, Cincinnati, OH.

13.5 Analysis of Ra-226 in Soils by Alpha Scintillation Without Chemical Separation (EPA 903.1m); Burns, Freda, Gallegos, Workman; RRMC, 2003, \\ALS\VOL1\ATI\OPRTNS\RAD\Meth_Dev\RaEmSol\ABSTRACT.DOC.

13.6 FMC Method Blank Contamination Trial; PA work order 0422022; Kellogg; 3/22/05, \\2ksvr2\2ksvr2_vol1\InstRawData\Rad\In-House wo\2004\Ra\0422022_FMC_MB.PDF.

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ARCADIS

ACZ SOPs

CALCULATIONS FOR ANALYTICAL METHODS

Revised by: Michael Desmarais

Approved by: _____ Date: _____
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Reviewed by: _____ Date: _____
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SVL Analytical, Inc.

I have read, understood and will comply with SOP (SVL 1028 Version 5.0)

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1.0 INTRODUCTION

The following SOP was compiled to help the analyst locate equations that are used in their day to day analysis. It is required that analysts need to understand how to perform all the calculations used in their analysis by hand, even if those calculations are done via software, macros or spreadsheets. This allows the analysts to verify that there has not been any corruption, manipulation or variables left out of the software, macros or spreadsheets.

The following test method IDs: SM 2330 B, Total Nitrogen and SM 2340 B are compiled from other accredited test methods the results of which are used in the calculations found in this document.

2.0 SCOPE

2.1 The SOP will have individual headings for each equation which can easily be located by going to the "Table of Contents". The SOP will start with calibration equations and end with calculations that are used to verify parameters before a final report goes out.

3.0 Calculations used by SVL Analytical, Inc.

3.1 Linear Regression uses the model:

y= ax + b

For this model, "a" can be calculated as

$$a = \frac{n(\sum xy) - (\sum x)(\sum y)}{n(\sum x^2) - (\sum x)^2}$$

and b can be calculated as

$$b = \frac{\sum y - a(\sum x)}{n}$$

The coefficient of determination, r^2, can be calculated as

$$r^2 = \frac{[n(\sum xy) - (\sum x)(\sum y)]^2}{[n(\sum x^2) - (\sum x)^2][n(\sum y^2) - (\sum y)^2]}$$

where:

x = concentration
y = the peak height, peak area, absorbance or other instrument output
a = the slope of the regression line
b = the intercept of the regression line
n = the number of calibration standards

The correlation coefficient is the square root of the coefficient of determination.

r = $\sqrt{r^2}$

3.2 Quadratic Regression uses the model

$y = ax^2 + bx + c$

In this model, the parameters a, b, and c can be determined by simultaneous solution of the equations

$$\sum y = cn + b\sum x + a\sum x^2$$

$$\sum x^2 y = c\sum x^2 + b\sum x^3 + a\sum x^4$$

$$\sum xy = c\sum x + b\sum x^2 + a\sum x^3$$

where:

x = can be concentration

y = is the peak height, peak area, absorbance or other instrument output

n = is the number of calibration standards

and a and b and c are parameters of the quadratic regression

3.3 **The Internal Standard Response Factor** model is a modification of linear regression. A response factor is calculated for each calibration standard according the equation:

where:

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

A_s = the peak area or height of the analyte response

A_{is} = the peak area or height of the internal standard response

C_s = the concentration of the analyte

C_{is} = the concentration of the internal standard

The standard deviation of the response factors is calculated according to the equation:

$$SD = \sqrt{\frac{\sum (RF - \overline{RF})^2}{n}}$$

The standard deviation divided by the average of the response factors is defined as the Relative Standard Deviation (RSD). If the RSD of the calibration standard response factors is less than the criterion specified in the applicable SOP, the curve is considered linear, and the average response factor is used to determine the concentration of the analyte.

3.3.1 Using an internal standard quantitation, the regression equation is rearranged as shown:

$$\frac{(A_s)(C_{is})}{A_{is}} = aC_s + B$$

where:

A_s = Area (or height) of the peak for the target analyte in the sample

A_{is} = Area (or height) of the peak for the internal standard

C_s = Concentration of the target analyte in the calibration standard

C_{is} = Concentration of the internal standard

a = Slope of the line (also called the coefficient of Cs)

b = the intercept

In calculating sample concentration by the internal standard method, the regression equation is re-arranged to solve for the concentration of the target analyte (C_s), as shown.

$$C_s = \frac{\left[\frac{A_s C_{is}}{A_{is}}\right] - b}{a}$$

3.4 Response Factor

$$RF(x) = \frac{A_x}{C_x}$$

Where:

RF = Response factor

A = Peak area or height

C = Concentration

x = Analyte of interest

3.5 Calibration Factor

$$CF = \frac{peak\ area\ (or\ height)\ of\ \ stds.}{mass\ injected}$$

3.6 Relative Standard Deviation

$$s = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{(n-1)}}$$

s = standard deviation

n = total number of values

x_i = each individual value used to calculate the mean

$\bar{x}$ = mean of n values

3.7 % Relative Standard Deviation (multiple values)

$$\% \text{ RSD} = \frac{s}{\bar{x}} \times 100\%$$

RSD = relative standard deviation

s = standard deviation

$\bar{x}$ = mean of the results

3.7.1 RSD (for 2 values)

$$\text{RSD} = \frac{\sqrt{2}[A-B]}{A+B} \times 100\%$$

RSD = the relative standard deviation calculated from duplicate determinations.

A and B = the analytical results for duplicate determinations.

[A-B] = the absolute difference between the determinations.

3.8 Precision (RPD) for Duplicate or MSD criteria

$$\text{RPD} = \frac{2[A-B]}{A+B} \times 100\%$$

RPD = the relative percent difference between duplicate determinations.

A and B = the analytical results for the duplicate determinations.

[A-B] = is the absolute difference between the determinations.

3.9 Matrix Spike (MS) Recovery

$$\text{MS \%R} = \frac{observed\ value - background\ value}{known\ value} \times 100\%$$

MS %R = the percentage recovery

observed value – the analytical result after spiking.

background value – the analytical result of the matrix before spiking.

known value – the concentration of the spike.

3.10 Laboratory Control Spike (LCS) or Blank Spike (BS) Recovery

$$\text{LCS \%R} = \frac{observed\ value}{known\ value} x100\%$$

LCS %R = the percent recovery.

observed value = the analytical result.

known value = the concentration of the spike.

3.11 Method of Standard Additions

$$\text{Sample concentrations x mg/L} = \frac{(s_2)(v_1)(c)}{(s_1 - s_2)(v_2)}$$

c = concentration of standard solution in mg/L.

s_1 = signal for fortified portion.

s_2 = signal for unfortified portion.

V_1 = volume of standard addition, L.

V_2 = volume of sample portion used for method of standard addition, L.

3.12 Cation/Anion Balance

The anion and cation sums, when expressed as milliequevalents per liter, must balance because all potable waters are electrically neutral.

$$\% \text{ difference} = 100\ \frac{\sum cations - \sum anions}{\sum cations + \sum anions}$$

Criteria for acceptance:

Anion Sum (meq/L)	Acceptance % difference
0 - 3.0	± 0.2 meq/L
3.0 - 10.0	± 2.0 meq/L
10.0 - 800	± 2-5.0 meq/L

3.13 Calculated Total Dissolved Solids (TDS)

TDS = 0.6 (alkalinity value) + Na + K + Ca + Mg + Cl + SO_4 + SiO_3 + NO_3 + F

3.14 Measured TDS = Calculated TDS

The measured TDS concentration should be higher than the calculated TDS because a contributor may not be included in the calculated TDS. If the measured value is less than the calculated one, the higher ion sum and measured value are suspect; the sample should be re-analyzed.

If the measured solids concentration is more than 20% higher than the calculated one, the low ion sum is suspect and selected constituents should be re-analyzed.

$$1.0 < \frac{measured\ TDS}{calculated\ TDS} < 1.2$$

3.15 Conductivity

If the temperature probe is not used, the conductivity must be corrected using the following equation. The correction is needed when samples are not at 25ºC.

$$\text{Conductivity in µmhos/cm} = \frac{conductivity\ reading}{1 + 0.0191(T - 25)}$$

Temperature is in degrees C.

3.16 Hardness by Standard Methods 2340 B (taken from EPA 200.7 or 6010B)

Hardness = 2.497(Ca value) + 4.118(Mg value)

3.17 Calcium Hardness (as $CaCO_3$) by EPA 200.7

Ca hardness = 2.497(Ca value)

3.18 Langelier's Index reported as SM 2330 B (taken from SM 4500 H^+ B, SM 2320 B, EPA 200.7 or 6010B and SM 2540 C and temperature)

Langelier's Index is a measure of the saturation state of water with the respect to $CaCO_3$. A value of zero indicates that the water is in thermodynamic equilibrium with $CaCO_3$. A negative value indicates that the water is corrosive with respect to precipitated $CaCO_3$. A positive Langelier's Index that the water is oversaturated with $CaCO_3$, and it will precipitate and become encrustive (a state in which it clads the inside of the pipe and may prevent lead and copper dissolution).

Langelier's Index = pH sample – pH saturation

Where pH saturation = A + B – log[Ca^{2+}] – log[alkalinity]

[Ca^{2+}] and [alkalinity] are in terms of $CaCO_3$ in mg/L.

A = constant for water temperature (ºC).

B = constant for TDS (mg/L).

Langelier's values for A **Langelier's values for B**

Temperature (ºC)	A	TDS (mg/L)	B
0	2.60	0	9.70
4	2.50	100	9.77
8	2.40	200	9.83
12	2.30	400	9.86
16	2.20	800	9.89
20	2.10	1000	9.90

3.19 Cation Exchange Capacity

$$\text{CEC} = \frac{(result)(dilution)(volume)(100)}{(weight)(meq\ \ for\ Na)}$$

where:

meq for Na is 22.9898 meq/100g

result = sodium value
dilution = amount sample was diluted by
volume = in liters
weight = in grams

3.20 Acidity, as mg $CaCO_3$

$$\text{Acidity, as mg } CACO_3 = \frac{[(A\ x\ B) - (C\ x\ D)]\ x\ 50{,}000}{mL\ sample}$$

where:

A = mL NaOH titrant used
B = normality of NaOH
C = mL H_2SO_4 used (hot peroxide addition)
D = normality of H_2SO_4

If a negative value is obtained, determine alkalinity according to SM 2320 B

3.21 Total Alkalinity, as mg $CaCO_3$/L

$$\text{Alkalinity, mg } CaCO_3/L = \frac{A\ x\ N\ x\ 50{,}000}{mL\ sample}$$

where:

A = mL standard acid used
N = normality of standard acid

3.21.1 Potentiometric titration of low alkalinity:

$$\text{Total Alkalinity (mg } CaCO_3/L) = \frac{(2B-C)\ x\ N\ x\ 50{,}000}{\text{mL of sample}}$$

Where:
B = mL titrant to first recorded pH,
C = total mL titrant to reach pH 0.3 unit lower, and
N = normality of acid

3.21.2 Calculation of Alkalinity Relationships:

Result of Titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCO_3$	Bicarbonate Concentration as $CaCO_3$
P = 0	0	0	T
P < ½ T	0	2P	T – 2P
P = ½ T	0	2P	0
P > ½ T	2P - T	2(T - P)	0
P = T	T	0	0

Where:

P = phenolphthalein alkalinity
T = total alkalinity

These classifications ascribe the entire alkalinity to bicarbonate, carbonate and hydroxide; it presupposes the incompatibility of hydroxide and bicarbonate alkalinity.

3.22 Equations used in AGP, ANP, ABA, NCV, and NAG

Acid Generating Potential (AGP)

AGP = pyritic sulfur x 31.25

Where:

Pyritic sulfur = Non Sulfate Sulfur (NSS) – Non Extractable Sulfur (NXS). These values are derived from the Leco results from the water washed and acid washed samples.

Acid Neutralization Potential (ANP)

Calculate the constant: Constant (C) = volume of the blank (mL) ÷ the volume of the NaOH titrant (mL) used in titrating the blank.

Calculate the volume of acid consumed: Volume of acid consumed (V_A) in mL = 50 – [(mL of NaOH added)(C)].

$$ANP = \frac{(50)(V_A)(N_A)}{\text{Mass of sample}}$$

Where:

V_A = Volume of acid consumed, in mL
N_A = Normality of acid

Acid Base Account (ABA)

±ABA = ANP – AGP

NCV Analysis

AGP = -1.37 x Total Sulfur – Residual Sulfur
ANP = 3.67 x Total Carbon – Residual Carbon
NCV = ANP + AGP

NAG Analysis

Calculate the NAG using the following equation:

$$NAG \text{ (in kg } H_2SO_4\text{/ton)} = \frac{49(V)(M)}{W}$$

Where:

V = Volume of base NaOH titrated, in mL
M = molarity of base NaOH (moles/L)
W = weight of sample reacted (g)

Record the NAG values for pH 4.5 and pH 7.

3.23 Sodium Exchange (Plant Available vs. Water Soluble)

Sodium Plant Available (Na-PA) = Na-PA result mg/L / meq for Na

Sodium Water Soluble (Na-H_2O) = Na-H_2O result mg/L / (2)(meq for Na)

Sodium exchange = Na PA results in meq/100g – Na H_2O results in meq/100g

where:

meq for Na is 22.9898 meq/100g

Na-PA results are based on 5g/50ml prep
Na-H_2O results are based on 10g/50ml prep

***** If the Na-PA result is greater than 0.022 (reporting limit). Then complete the sodium exchange equation to get the reportable number.

3.24 SAR Equation

$$SAR = \frac{meq\ Na}{\sqrt{\frac{(meq\ Ca + meq\ Mg)}{2}}}$$

where:

meq for Na is 22.9898
meq for Ca is 20.04
meq for Mg is 12.156

Take the result for each element and divide it by the meq for that element. Plug the results for each element into the equation.

3.25 Procedure for Cassette Filters

$$\text{Final Result (µg/L)} = \left(\frac{conc\ (mg/L)\ x\ 0.05\ L}{volume\ (L)}\right)\left(\frac{1000\ ug}{1\ mg}\right)$$

Depending on units desired, Cassette Filters may be reported out in µg/L, µg/cassette or µg/m^3. If the per cassette ratio or flow ratio is desired other units will have to be considered.

3.26 Procedure for HiVol or PM 10 Filter

Final Concentration (µg/filter) = (concentration)(0.9)(dilution factor)

0.9 is the conversion factor for 1"x 8" strips. Different sized strips will have a different conversion factor.

3.27 Specific Gravity

First calculate displacement as follows:

Displacement = Water Level (in mL) – 100 mL

Calculate displacement:

Specific Gravity = $\frac{Sample\,weight\,(in\,grams)}{Displacement\,(in\,mL)}$

3.28 Solid Silica

Raw Si concentration = $\frac{Absorbance - Intercept}{Slope}$

Raw SiO_2 = 0.100g / Sample Weight x (Raw Si concentration x 2.14)

Final SiO_2 concentration = (10 mL / Aliquot volume) x Raw SiO_2

3.29 Mass/Volume Equation

$M_1 V_1 = M_2 V_2$ $\quad V_1 = \frac{M_2 V_2}{M_1}$ $\quad V_2 = \frac{M_1 V_1}{M_2}$

$M_1 = \frac{M_2 V_2}{V_1}$ $\quad M_2 = \frac{M_1 V_1}{V_2}$

where:

M_1 = a known concentration
V_1 = the volume of the known concentration
M_2 = the concentration you need
V_2 = final volume

Example: You need a 100 ppm xenon solution; you have a 1,000 ppm parent standard of xenon.

Solution: M_1 = 1,000 ppm xenon
M_2 = 100 ppm xenon
V_2 = 100 ml (you can choose any final volume you want)
V_1 = ?

$V_1 = \frac{M_2 V_2}{M_1}$ $V_1 = \frac{(100\,ppm)(100ml)}{1000\,ppm}$ V_1 = 10.0 ml

You would need to spike 10.0 ml of the 1,000 ppm parent stock into a carrier solution and then bring it up to100 ml (final volume) to get the 100 ppm solution you need.

3.30 Total Nitrogen = Kjeldahl Nitrogen + Nitrate-Nitrite (EPA 351.2 and 353.2)

3.31 Dilution Chart

Dilution	Sample (in 10 ml)	Diluent (in 10 ml)	Sample (in 500 ml)	Diluent (in 500 ml)
2x	5 ml	5 ml	250 ml	250 ml
5x	2 ml	8 ml	100 ml	400 ml
10x	1 ml	9 ml	50 ml	450 ml
20x	0.5 ml	9.5 ml	25 ml	475 ml
40x	0.25 ml	9.75 ml	12.5 ml	487.5 ml
50x	0.20 ml	9.80 ml	10 ml	490 ml
100x	0.10 ml	9.90 ml	5 ml	495 ml
200x	0.05 ml	9.95 ml	2.5 ml	497.5 ml
500x	0.02 ml	9.98 ml	1 ml	499 ml
1000x	0.01 ml	9.99 ml	.5 ml	499.5 ml

Sometimes it is easier to make a dilution and then make a dilution of the dilution to more readily attain the higher dilutions. For example, instead of finding a micro-syringe to make a 1000x dilution in a 10 ml final volume, first make a 100x solution and then make a 10x of the 100x.

3.32 Rounding

Rounding of analytical results is dependent upon the number of significant figures used by a method. Rounding for percent recovery on QC samples is also dependent upon the number of significant figures. Element is setup and our analysts are directed to round up to the significant figure assigned to that method. SVL uses the following rounding rule: A result of 5 or greater rounds the results up to the significant figure assigned in Element.

3.32.1 All of the steps in performing calculations or equations will be completed and combined before rounding to final numbers or recoveries.

3.33 Water Density Chart

Density of Water (g/cm^3) at Temperatures from 0°C (liquid state) to 30.9°C by 0.1°C inc.

Thanks to Chuck Snelling

	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0.999841	0.999847	0.999854	0.999860	0.999866	0.999872	0.999878	0.999884	0.999889	0.999895
1	0.999900	0.999905	0.999909	0.999914	0.999918	0.999923	0.999927	0.999930	0.999934	0.999938
2	0.999941	0.999944	0.999947	0.999950	0.999953	0.999955	0.999958	0.999960	0.999962	0.999964
3	0.999965	0.999967	0.999968	0.999969	0.999970	0.999971	0.999972	0.999972	0.999973	0.999973
4	0.999973	0.999973	0.999973	0.999972	0.999972	0.999972	0.999970	0.999969	0.999968	0.999966
5	0.999965	0.999963	0.999961	0.999959	0.999957	0.999955	0.999952	0.999950	0.999947	0.999944
6	0.999941	0.999938	0.999935	0.999931	0.999927	0.999924	0.999920	0.999916	0.999911	0.999907
7	0.999902	0.999898	0.999893	0.999888	0.999883	0.999877	0.999872	0.999866	0.999861	0.999855
8	0.999849	0.999843	0.999837	0.999830	0.999824	0.999817	0.999810	0.999803	0.999796	0.999789
9	0.999781	0.999774	0.999766	0.999758	0.999751	0.999742	0.999734	0.999726	0.999717	0.999709
10	0.999700	0.999691	0.999682	0.999673	0.999664	0.999654	0.999645	0.999635	0.999625	0.999615
11	0.999605	0.999595	0.999585	0.999574	0.999564	0.999553	0.999542	0.999531	0.999520	0.999509
12	0.999498	0.999486	0.999475	0.999463	0.999451	0.999439	0.999427	0.999415	0.999402	0.999390
13	0.999377	0.999364	0.999352	0.999339	0.999326	0.999312	0.999299	0.999285	0.999272	0.999258
14	0.999244	0.999230	0.999216	0.999202	0.999188	0.999173	0.999159	0.999144	0.999129	0.999114
15	0.999099	0.999084	0.999069	0.999054	0.999038	0.999023	0.999007	0.998991	0.998975	0.998959

	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
16	0.998943	0.998926	0.998910	0.998893	0.998877	0.998860	0.998843	0.998826	0.998809	0.998792
17	0.998774	0.998757	0.998739	0.998722	0.998704	0.998686	0.998668	0.998650	0.998632	0.998613
18	0.998595	0.998576	0.998558	0.998539	0.998520	0.998501	0.998482	0.998463	0.998444	0.998424
19	0.998405	0.998385	0.998365	0.998345	0.998325	0.998305	0.998285	0.998265	0.998244	0.998224
20	0.998203	0.998183	0.998162	0.998141	0.998120	0.998099	0.998078	0.998056	0.998035	0.998013
21	0.997992	0.997970	0.997948	0.997926	0.997904	0.997882	0.997860	0.997837	0.997815	0.997792
22	0.997770	0.997747	0.997724	0.997701	0.997678	0.997655	0.997632	0.997608	0.997585	0.997561
23	0.997538	0.997514	0.997490	0.997466	0.997442	0.997418	0.997394	0.997369	0.997345	0.997320
24	0.997296	0.997271	0.997246	0.997221	0.997196	0.997171	0.997146	0.997120	0.997095	0.997069
25	0.997044	0.997018	0.996992	0.996967	0.996941	0.996914	0.996888	0.996862	0.996836	0.996809
26	0.996783	0.996756	0.996729	0.996703	0.996676	0.996649	0.996621	0.996594	0.996567	0.996540
27	0.996512	0.996485	0.996457	0.996429	0.996401	0.996373	0.996345	0.996317	0.996289	0.996261
28	0.996232	0.996204	0.996175	0.996147	0.996118	0.996089	0.996060	0.996031	0.996002	0.995973
29	0.995944	0.995914	0.995885	0.995855	0.995826	0.995796	0.995766	0.995736	0.995706	0.995676
30	0.995646	0.995616	0.995586	0.995555	0.995525	0.995494	0.995464	0.995433	0.995402	0.995371
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9

3.33.1 Whatever volume (in mL) you are working with, multiplied by the above corresponding density will give you the true weight of the water at that temperature in order to verify accurate dispensing.

4.0 References

4.1 Standard Methods for the Examination of Water and Wastewater, 18th edition. 1992.

4.2 Standard Methods for the Examination of Water and Wastewater, 20th edition. 1999.

4.3 Handbook of Environmental Analysis, Fourth Edition. 1999.

4.4 Element Data Systems, 6.01:4015. CequelLogic/Promium.

5.0 Change History

Date	Version	Change
09/08/09	2.0	Added sections: 3.20 Acidity, as mg $CaCO_3$, 3.21 Total Alkalinity, as mg $CaCO_3$/L and 3.22 Equations used in AGP, ANP and ABA.
09/09/10	3.0	Added 10.21.1 "Potentiometric titration of low alkalinity". 3.22 changed ANP calculations and added NCV and NAG equations.
12/29/10	3.1	1.0 added "The following test method IDs: SM 2330 B, Total Nitrogen and SM 2340 B are compiled from other accredited test methods the results of which are used in the calculations found in this document". 3.16 changed section header to "Hardness by Standard Methods 2340 B (taken from EPA 200.7 or 6010B)". 3.18 changed section header to "Langelier's Index reported as SM 2330 B (taken from SM 4500 H^+ B, SM 2320 B, EPA 200.7 or 6010B and SM 2540 C and temperature)". 3.28 added "Total Nitrogen = Kjeldahl Nitrogen + Nitrate-Nitrite (EPA 351.2 and 353.2)".
03/13/12	3.1	No changes
03/19/13	4.0	Added equations for 3.27 Specific Gravity and 3.28 Solid Silica. 3.32 added "Rounding of analytical results is dependent upon the number of significant figures used by a method. Rounding for percent recovery on QC samples is also dependent upon the number of significant figures. Element is setup and our analysts are directed to round up to the significant figure assigned to that method. SVL uses the following rounding rule: A result of 5 or greater rounds the results up to the significant figure assigned in Element." 3.32.1 added "All of the steps in performing calculations or equations will be completed and combined before rounding to final numbers or recoveries."
04/25/14	5.0	Added the table under 3.33. 3.33.1 added "Whatever volume (in mL) you are working with, multiplied by the above corresponding density will give you the true weight of the water at that temperature in order to verify accurate dispensing."

DETERMINATION OF MERCURY (CVAA)
By EPA 245.1, 7470A and 7471B

Revised by: Michael Desmarais

Approved by: _____ Date: _____
Inorganic Instrument Department Supervisor

Reviewed by: _____ Date: _____
Quality Assurance Manager

I have read, understood and will comply with SOP (SVL 4010 Version 17.0)

Print Name	Signature	Date
Sam Achord		
Heidi Barnes		

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1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedure used to analyze samples for mercury, including the operation of a CETAC Mercury Analyzer. The procedure measures total mercury (organic and inorganic) in water, soil, sediment, bottom deposits, and sludge. SVL uses a Laboratory Management Information System (LIMS) – Element, to manage client's samples. In Element the current aqueous MDL is 0.045 µg/L and the soil MDL is 0.0043 mg/kg. The aqueous reporting limit is 0.2 µg/L and the soil reporting limit is 0.033 mg/kg. Definitions for words used in this SOP may be found in SVL's Quality Manual. The holding time is 28 days when aqueous samples are preserved with HNO_3 to pH <2, aqueous samples are stored at ambient temperature and solid samples are stored between 0-6 °C.

2.0 SUMMARY OF METHOD

This SOP is intended to satisfy the requirements of EPA methods 245.1, 7470A, and 7471B. Samples must be digested prior to analysis. Organic mercury compounds are oxidized by a mixture of potassium permanganate and potassium persulfate. Then the mercury is reduced to the elemental state by stannous chloride and aerated from solution in a closed system. Sample analysis is performed by a CETAC mercury analyzer. The mercury vapor passes through a cell positioned in the light path of the CETAC. Concentration is measured as a function of absorbance by mercury atoms at 253.7 nm.

3.0 INTERFERENCES

3.1 Very high levels of chloride interfere. During the oxidation step chloride is converted to free chlorine. Free chlorine absorbs at the same wavelength as mercury vapor. An excess of hydroxylamine reagent will remove the chlorine.

4.0 SAFETY

4.1 Hydrochloric acid can cause severe burns if it comes into contact with skin or eyes. The fumes are also irritating to nasal and lung tissues. Work with hydrochloric acid in a hood. Wear safety glasses or goggles. Wear gloves and a lab coat or an apron. In the case of exposure, flush with water for at least fifteen minutes.

4.2 Sulfuric acid can cause severe burns if it comes into contact with skin or eyes. Wear safety glasses or goggles. Wear gloves and a lab coat or an apron. In the case of exposure, flush with water for at least fifteen minutes.

4.3 Nitric acid is a strong oxidizer and can cause severe burns if it comes into contact with skin or eyes. The fumes are also irritating to nasal and lung tissues. Work with Nitric Acid in a hood. Wear safety glasses or goggles. Wear gloves and a lab coat or an apron. In the case of exposure, flush with water for at least fifteen minutes.

4.4 Mercury is a toxic heavy metal. Do not swallow, inhale or absorb through skin.

4.5 Read the MSDSs for the chemicals used in this SOP. Be aware of the possible hazards.

4.6 Addition of acids to some samples may release toxic gases such as hydrogen cyanide or hydrogen sulfide. Add acids under a hood.

5.0 EQUIPMENT, INSTRUMENTATION AND MATERIALS

Equivalent equipment, instrumentation and materials may be used.

5.1 CETAC M6100 Mercury Analyzer

5.2 CETAC M7500 Mercury Analyzer

5.3 ASX - 510 Autosampler

5.4 ASX520 AUTOSAMPLER

5.5 Nafion Dryer, CETAC

5.6 254 nm Mercury Lamp, BHK, Inc. Model No. 80-8024-01

5.7 Argon, 99.99% pure, or better

5.8 Volumetric flasks, 50 mL, 100 mL, 200 mL, 1 L

5.9 Micropipets, Corning, Lambda, Wheaton, Socorex

5.10 “Snap cap” vials, 4 oz., with 100-mL fill line, Fisher Catalog No. 14377807

5.11 Block digestors, capable of maintaining a temperature of 90 to 95 degrees, Environmental Express

5.12 Balance, capable of weighing to the nearest 0.01 gram

5.13 pH strips, 0 – 6 pH range, EM colorpHast, Fisher M95863

5.14 Sieves and splitters, project specific, see SOP 2018

6.0 REAGENTS AND STANDARDS

Guidelines for the storage, tracking and expiration of chemicals and reagents can be found in SVL 1032. The procedure for purchasing chemicals and reagents can be found in SVL 1015. Any exceptions to the above mentioned SOPs will be found in this section: as well as, all of the preparatory steps needed to construct or prepare reagents, and standards. Equivalent reagents or standards may be used.

6.1 Concentrated sulfuric acid (H_2SO_4): Fisher TraceMetals Grade

6.2 Concentrated nitric acid (HNO_3): Fisher TraceMetals Grade

6.3 Concentrated hydrochloric acid (HCl): Fisher TraceMetals Grade

6.4 Potassium permanganate: Fisher Certified ACS/Hg Determination

6.5 Potassium persulfate: J.T. Baker Instra-Analyzed

6.6 Stannous chloride ($SnCl \cdot 2H_2O$): CCI GCS Grade

6.7 Hydroxylamine hydrochloride, Fisher Certified ACS/Hg Determination

6.8 Sodium chloride, CCI ACS Grade Crystals

6.9 Potassium dichromate, MCB Reagent, crystals

6.10 Hydroxylamine hydrochloride solution: Dissolve 300 grams of sodium chloride (6.8) and 300 grams of hydroxylamine hydrochloride (6.7) in deionized water (6.21). Dilute to 2.5 liters with deionized water. Mix well. Expiration date is six months after date prepared.

6.11 Potassium permanganate, 5% solution: Dissolve 125 grams of potassium permanganate (6.4) in 2.5 liters of deionized water (6.21). Mix well. Expiration date is six months after date prepared.

6.12 Potassium persulfate, 5% solution: Dissolve 125 grams of potassium persulfate (6.5) in 2,500 mL of deionized water (6.21). Mix well. Expiration date six months after date prepared.

6.13 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated hydrochloric acid (6.3) to one volume of concentrated nitric acid (6.2). Mix well. Prepare 5 mL for each "Snap-cap" vial that will be used.

6.14 Stannous chloride solution, 10% solution: Prepare according to the CETAC instrument manufacturer's instructions by dissolving 400 grams of $SnCl \cdot 2H_2O$ (6.6) in 280 mL concentrated hydrochloric acid (6.3). Dilute to 4 liters with deionized water (6.21). Expiration date six months after date prepared.

6.15 Rinse solution: Solution of 5.2% hydrochloric acid (6.3) and 2% nitric acid (6.2).

6.16 Stock mercury solution, 1000 µg/mL mercury: Commercially-prepared High Purity Standards.

6.17 Stock mercury solution, 100 µg/mL mercury: Commercially-prepared High Purity Standards.

6.18 Intermediate standard solution, 10 µg/mL mercury: Transfer 1.00 mL of 1000 µg/mL stock mercury solution (6.16) to a 100 mL volumetric flask. Add 2 mL concentrated nitric acid (6.2). Dilute to the mark with deionized water (6.21). Mix well. Prepare each day of use.

6.19 Working standard solution, 100 µg/L mercury: Transfer 2.00 mL of Intermediate standard solution (6.18) to a 200 mL volumetric flask. Add 2 mL concentrated nitric acid (6.2). Dilute to the mark with deionized water (6.21). Mix well. Prepare each day of use.

6.20 Mercury ICV stock solution: Transfer about 50 mL deionized water (6.21) to a 100 mL volumetric flask. Add 10 mL concentrated nitric acid (6.2). Then dissolve 0.05 grams potassium dichromate (6.9) in the solution. Add 0.50 mL of the 100 µg/mL Hg single-element stock solution (6.17). Dilute to the mark with deionized water (6.21) and mix well. The final concentration of the mercury solution is 500 µg/L. Expiration date is six months after date prepared, but no later than the expiration date of the stock solution.

6.21 Type II deionized water.

6.22 Sand, Fisher S23-3.

7.0 INSTRUMENT SETTINGS

7.1 Verify that the power is on for both the autosampler and the mercury lamp.

7.2 Fill the reagent reservoir with stannous chloride solution (6.14).

7.3 Fill the rinse reservoir with rinse solution (6.15).

8.0 CALIBRATION

8.1 Verify the volume of the “Snap-cap” vials.

8.1.1 Select three vials at random from each lot.

8.1.2 Place each vial on the balance. Tare the weight.

8.1.3 Fill the vials to the 50 mL fill line with deionized water (6.21).

8.1.4 Weigh the full vials. Record the weights in the Soil Digest logbook.

8.1.5 All three of the net weights should fall within the range 48.50 to 51.50 grams.

8.1.6 If any of the net weights fall outside the range 48.50 to 51.50 grams, return the entire box of vials to the manufacturer for replacement.

8.1.7 Repeat the test with three vials filled to the 100 mL fill line with deionized water.

8.1.8 All of the net weights should fall within the range 97.0 to 103.0 grams.

8.1.9 If any of the net weights fall outside the range 97.0 to 103.0 grams, return the entire lot of vials to the manufacturer for replacement.

8.2 For aqueous samples, prepare calibration standards by transferring the following amounts of working standard solution (6.19) into “Snap-cap” vials. Dilute to the 50 mL mark with deionized water (6.21) Mix well. Follow the steps outlined in 10.1.10 thru 10.1.15.

Standard Conc.	Volume of Working Standard	Final Volume
0.0 µg/L	0.00 mL	50 mL
0.2 µg/L	0.10 mL	50 mL
0.5 µg/L	0.25 mL	50 mL
1.00 µg/L	0.50 mL	50 mL
2.00 µg/L	1.00 mL	50 mL
5.00 µg/L	2.50 mL	50 mL
10.0 µg/L	5.00 mL	50 mL

8.3 For soil/sludge samples, prepare calibration standards by transferring the following amounts of working standard solution (6.19) into "Snap-cap" vials. Add enough deionized water (6.21) to make an initial volume of 10 mL. This initial volume will be brought up to a final volume of 100 mL (the concentrations below are based upon the 100 mL final volume. Follow the steps outlined in

Standard Conc.	Volume of Working Standard	Initial Volume
0.0 µg/mL	0.00 mL	10 mL
0.2 µg/mL	0.20 mL	10 mL
0.5 µg/mL	0.50 mL	10 mL
1.0 µg/mL	1.00 mL	10 mL
2.0 µg/mL	2.00 mL	10 mL
5.0 µg/mL	5.00 mL	10 mL
10.0 µg/mL	10.0 mL	10 mL

9.0 SAMPLE HANDLING AND PRESERVATION

9.1 Samples for total metals should have been preserved by acidification with nitric acid to a pH of 2 or lower immediately upon collection in the field or upon being accepted by Sample Receiving as per SVL 2001.

9.2 Refrigerate solid samples between 0-6 °C until analyzed.

9.3 Ask the supervisor for the client instructions on sample preparation. Prepare the sample in accordance with those instructions. Record the instructions in the Mercury Prep Logbook. Some possible instructions are:

9.3.1 Do not dry the sample. Determine percent moisture on a separate portion according to SOP 4022.

9.3.2 Dry the sample at ambient temperature. Sieve the sample through a 10-mesh screen. Divide the sample into two parts. Archive one portion for future analysis. Sieve the second portion through an 80-mesh screen. Digest the - 80 mesh fraction.

9.3.3 Dry the sample at ambient temperature. Sieve the sample through an 80-mesh screen. Digest the - 80 mesh fraction.

9.4 If the sample contains a noticeable amount of liquid, ask the supervisor for instructions. Prepare the sample in accordance with those instructions. Record the decision in the Mercury Prep Logbook and in a Work Order memo. Some possible instructions are:

9.4.1 Analyze the entire sample, homogenizing the solids and the liquid.

9.4.2 Decant the liquid from the sample. Analyze the solid fraction.

9.4.3 Decant the liquid. Analyze the liquid and the solids as two different samples.

10.0 SAMPLE PREPARATION AND ANALYSIS

10.1 Preparation of aqueous samples for method 245.1 and 7470A

10.1.1 Prepare a method blank for every 20 samples by transferring 50 mL of deionized water (6.21) into a “Snap-cap” vial.

10.1.2 Prepare an LCS for every 20 samples. Transfer 0.5 mL of the mercury ICV stock solution (6.20) to a “Snap-cap” vial. Dilute to the 50 mL mark with deionized water (6.21). The LCS concentration is 5.0 µg/L.

10.1.3 Mix the sample well to ensure that it is homogenous. Transfer 50 mL of each sample to a “Snap-cap” vial**.** If the history of the sample indicates that this volume may contain more than 1.0 µg mercury, use of a smaller volume diluted to 50 mL is permitted. A smaller volume may also be used if the client has provided insufficient sample (samples should be qualified; ref, SVL 2009).

10.1.4 Prepare a matrix spike by transferring an additional 50 mL aliquot of sample to a “Snap-cap” vial and adding 0.50 mL of working standard solution (6.19). Final volume on benchsheet should be adjusted to 50.5 mL. The expected concentration of the spike added is 1.0 µg/L.

10.1.5 Prepare a matrix spike duplicate by following the steps outlined in 10.1.4.

10.1.6 Prepare an ICV. Transfer 0.5 mL of the mercury ICV stock solution (6.20) into a "Snap-cap" vial. Dilute to the 50 mL mark with deionized water (6.21). The ICV concentration is 5.0 µg/L.

10.1.7 Prepare an ICB and a CCB by transferring 50 mL of deionized water (6.21) into a "Snap-cap" vial.

10.1.8 Prepare a CCV by transferring 1.0 mL of the working standard solution (6.19) to a "Snap-cap" vial. Dilute to the 50 mL mark with deionized water (6.21) and mix well. The final concentration of the CCV is 2.0 µg/L.

10.1.9 Prepare a RLCS by transferring 0.1 mL of the working standard solution (6.19) to a "Snap cap" vial. Dilute to the 50 mL mark with deionized water (6.21) and mix well. The final concentration of the RLCS is 0.2 µg/L.

10.1.10 Add 2.5 mL concentrated sulfuric acid (6.1) to each vial and mix.

10.1.11 Add 1.25 mL concentrated nitric acid (6.2) to each vial and mix.

10.1.12 Add 7.5 mL potassium permanganate solution (6.11) to each vial. For sewage samples, or samples with high organic content, additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if the purple color does not persist for at least 15 minutes reduce the concentration of the original sample by dilution (dilute with deionized water (6.21)) and repeat 10.1.9 thru 10.1.11 on 50 mL of the diluted sample.

10.1.13 Add 4.0 mL potassium persulfate solution (6.12) to each vial.

10.1.14 Heat the vials in a block digester for 2 hours at 95°C.

10.1.15 Cool the vials and add 5.0 mL of hydroxylamine hydrochloride (6.10) to reduce the excess permanganate.

10.2 Preparation of soil/sludge samples for method 7471A.

10.2.1 Prepare a method blank by weighing 0.60 g ± 0.005 g of sand (6.22) add 5.0 mL of deionized water (6.21) into a "Snap-cap" vial. Mix well.

10.2.2 Prepare an LCS by transferring 1.0 mL of the mercury ICV stock solution (6.20) to 0.60 g ± 0.005 g of sand (6.22) in a "Snap-cap" vial, add 4.0 mL deionized water (6.21). Mix well. The concentration of the LCS is 5.0 µg/L.

10.2.3 Weigh out a 0.60 g ± 0.005 g portion of a well homogenized sample in a "Snap-cap" vial. Add 5.0 mL deionized water (6.21).

10.2.4 Prepare a matrix spike by weighing another 0.60 g ± 0.005 g portion of a well homogenized sample in a "Snap-cap" vial and add 2.0 mL of the working standard solution (6.19). Add 3.0 mL deionized water (6.21). The initial concentration of the matrix spike is 2.0 ppb.

10.2.5 Prepare a matrix spike duplicate. Follow the process outlined in 10.2.4.

10.2.6 Prepare an ICV by transferring 1.0 mL of the mercury ICV stock solution (6.20) into a "Snap-cap" vial. Add 9.0 mL of deionized water (6.21). The final concentration of the ICV is 5.0 µg/L

10.2.7 Prepare an ICB and a CCB by transferring 10.0 mL of deionized water (6.21) into a "Snap-cap" vial.

10.2.8 Prepare a CCV by transferring 2.0 mL of the working standard solution (6.19) into a "Snap-cap" vial. Add 8.0 mL of deionized water (6.21). The final concentration of the CCV is 2.0 µg/L

10.2.9 Prepare an RLCS by transferring 0.2 mL of the working standard solution (6.19) into a "Snap-cap" vial. Add 9.8 mL of deionized water (6.21). The initial concentration of the RLCS is 0.2 µg/L.

10.2.10 Add 5.0 mL of aqua regia (6.13) into each "Snap-cap" vial.

10.2.11 Heat the vials in a block digester for two minutes at 95 ± 3°C.

10.2.12 Cool the vials and add 40 mL deionized water (6.21).

10.2.13 Add 15 mL potassium permanganate solution (6.11) into each "Snap-cap" vial. Mix thoroughly, and then wait 15 minutes. Add additional portions of permanganate solution, if needed to standards and blanks until the purple color persists for at least 15 minutes. If more potassium permanganate is added ensure that equal amounts of permanganate are also added to standards and

blanks. Place samples or standards into the block digester for 30 minutes at 95 ± 3°C.

10.2.14 Cool the vials and add 6 mL of hydroxylamine hydrochloride solution (6.9) to reduce the excess permanganate. Add 49 mL deionized water (6.21) into samples, prep blank, LCS, matrix spike and matrix spike duplicate. Add 44 mL deionized water to the calibration standards, ICB, CCBs, RLCS, ICV, and CCVs. Add proportionally less water if additional permanganate is used. The final volume of all standards and samples should be 120 mL.

10.3 Operation of the CETAC M6100 Mercury Analyzer

10.3.1 Turn the computer on and double-click the "Quicktrace" icon. The "M6100A Mercury Analyzer" window will appear.

10.3.2 Connect the pump tubing.

10.3.3 Turn the pump on.

10.3.4 Turn on the argon gas valve, and set the psi to 40.

10.3.5 Disconnect the "Hg Vapor" tubing from the Nafion Dryer. Pinch the Nafion dryer waste line and allow the waste solution to coat the post in the gas/liquid separator.

10.3.6 Stop pinching the line and allow liquid to flow through the waste line. Connect the "Hg Vapor" tubing to the gas/liquid separator. Allow the system to equilibrate for about 15 minutes.

10.3.7 Click the down arrow on the "load" button. Select the "new from" option and the "create a new worksheet from template worksheet" window will appear.

10.3.8 Click the "browse" button for the template worksheet field. Navigate to the quicktrace templates folder, and select M6100.

10.3.9 Choose the appropriate starter template for the analysis. Use the "version 2" files to attain proper sequence information.

10.3.10 In the new worksheet "name field", enter the date in the format yymmdd followed by "01" for the first run of the day, "02" for the second run, and so on. This is the file name.

10.3.11 Ensure that the "retain sequence information" box is checked, and

then click Ok.

10.3.12 A new sequence will appear, click the sequence editor button. Enter the total number of samples to be analyzed in the sample count field. Click "generate sequence" and a new sequence will appear.

10.3.13 Highlight lines 9 and 10, right click, and choose insert rows. Right click anywhere on the sequence and select "auto renumber tubes." Enter ICB for the sample name on line 9, and enter RLCS for the sample name on line 10. Left click the dropdown arrow in the "type" column next to ICB and RLCS. Change the sample types to "Initial Calibration Blank" and "Contract Required Detection limit" respectively.

10.3.14 Beginning on line 13 (tube 1:3) enter the SVL sample names to be analyzed.

10.3.15. If analyzing a sample dilution, type the "@" sign followed by the dilution factor (e.g. @10X) immediately after the SVL sample number (in the same column).

10.3.16 A CCV and CCB is required per every 10 samples, double check the sequence to ensure that there is a CCV and CCB after every 10 samples.

10.3.17 Scroll to the end of the sequence and ensure that there is a final CCV and CCB, if there is not then add them by typing in CCV and CCB for the sample names, change their tube numbers to S:9 for CCV, and S:10 for CCB. Left click in the "type" field next to the CCV, click the dropdown arrow and select "Continuing Calibration Verification." Left click in the "type" field next to the CCB, click the dropdown arrow and select "Continuing Calibration Blank."

10.3.18 Thoroughly check the "Sample Label" column for errors. Click the "Save" icon in the upper left of the quicktrace window to save your worksheet.

10.3.19 Pour the calibration standards, QC standards and samples in the appropriate vials. The autosampler racks are numbered 1-2, from left to right and tubes are numbered from back to front, left to right for each rack (1:1, 2:1, etc.). The standard rack at the back of the autosampler tray is called "S", with positions 1-10. Pour the calibration standards in S:1-S:7. Pour the ICV in S:8, the CCV in S:9, and the CCB in S:10. Pour the ICB into tube 1:1, and the

RLCS in 1:2.

10.3.20 Click the “method editor” icon.

10.3.21 Click on the “Conditions” button.

10.3.22 Click on the “Read a Sample” button. The “Now Zeroing the Mercury Analyzer” window will open.

10.3.23 When the zeroing process is finished, the “Select Tube” window will open. Click tube number S:7.

10.3.24 Click “OK.” Standard 7 will be analyzed and the absorbance-versus-time will be displayed on the screen.

10.3.25 Set the Time Profile by moving the green and red bars to the flattest portion at the top of the signal peak.

10.3.26 Click “Save” from the file menu. Close the Method Editor window.

10.3.27 Click on the “GO” icon. The “Please set the gas flow to 40 psi” dialogue box will open, ensure the psi is at 40, and then click OK.

10.3.28 The instrument will begin analyzing the samples.

10.3.29 Click on the “Analysis” icon to see the calibration curve, run progress and sample absorbance displayed.

10.3.30 Analysis will stop if a calibration standard or QC standard fails. ICV, ICB, RLCS, CCV, and CCB are allowed to be run a second time (see section 13).

10.3.31 Check the run to ensure that the prep blanks and LCSs meet method criteria. If the sample absorbance display indicates a failure, DO NOT STOP THE ANALYSIS until the analysis has registered.

10.3.31.1 All instrument reads must be allowed to go to completion, the Cetac allows for stopping an analysis prior to the final read, this is not allowed. All failures must be re-inserted at a later point in the run.

10.3.32 Under 245.1 **i**f the concentration in a sample exceeds 90% of the linear dynamic range, the sample must be re-analyzed at a lower dilution. 7471B requires that samples that exceed the calibration

range be diluted back to within the calibration range.

10.3.33 Analysis must be stopped to add additional samples or diluted samples to the end of the run. Ensure that there is a CCV and CCB every 10 samples.

10.3.34 Save the sequence.

10.3.35 Click "GO" to restart the run.

10.3.36 Re-running a sequence if Calibration, ICV, ICB, RLCS, CCV, or CCB fail.

10.3.36.1 Close the existing sequence. In File menu choose "Close"

10.3.36.2 Click the down arrow on the "Load" icon.

10.3.36.3 Click "New From." The "Create A New Worksheet From Template Worksheet" window will open.

10.3.36.4 Click the top "Browse" button. The "New Worksheet" window will open.

10.3.36.5 On the "Look in" menu, choose "quicktrace" and then choose "worksheets." Choose the file name desired.

10.3.36.6 Change the number at the end of the file name.

10.3.36.7 Delete any unneeded CCV/CCBs and non-usable data.

10.3.36.8 Set the Time Profile and start the run.

10.4 Operation of the CETAC M7500 Mercury Analyzer

10.4.1 Turn the computer on and double-click the "QuickTrace" icon. The "CECTA QuickTrace" window will appear.

10.4.2 When the "Confirm" window appears, click the "No" button. The "Sequence" page will appear.

10.4.3 Connect the pump tubing and insert the sipper tube into the Stannous Chloride bottle.

10.4.4 Open the Argon gas valve.

10.4.5 Click on the “Instrument” icon. The “Instrument” window will appear.

10.4.6 Click on the “Analyzer” button.

10.4.7 In the “Pump” section, enter 50. Click the “Set Speed” button, then click the “On” button.

10.4.8 In the “Lamp” section, click the “Status” button to determine if the lamp is on. If the lamp is off, click the “Lamp On” button.

10.4.9 In the “Gas” section, enter 150 and click the “Set Gas” button.

10.4.10 Close the “Instrument” window.

10.4.11 Click the “Gas/Liquid Separator” icon. Pinch the Nafion Dryer waste line and allow the waste solution to coat the post in the gas/liquid separator.

10.4.12 Stop pinching the line and allow liquid to flow through the waste line. Connect the “Hg Vapor” tubing to the gas/liquid separator. Open the “Instrument” window and reset the pump speed. Allow the system to equilibrate for about 15 minutes.

10.4.13 Click the down arrow on the “Load” icon. Click on “New Form”. The “Create A New Worksheet From Template Worksheet” window will open.

10.4.14 Click the top “Browse” button. The “New Worksheet” window will open.

10.4.15 Double click on”M7500”. Double click on one of the following: 245.1 START, 7470 START, 7471 STARTER, CLP STARTER.

10.4.16 In the “Enter new worksheet name” box, enter the date in the format mm.dd.yy with the letter A (letter B for the second run, letter C for the 3rd run, etc.) This is the file name for the run.

10.4.17 Click “OK” and the “Sequence” window will appear with the Calibrations and QC Standards entered.

10.4.18 Click on the “Sequence Editor” icon. Click on the “Sequence” button.

10.4.19 In the “Sample count” space, enter the number of samples to be included in the run. Do not count calibrations standards, ICV/ICB, RLCS, or CCV/CCB.

10.4.20 Check the “Begin with calibration” box. Click” Generate Sequence”.

10.4.21 The ”Sequence” window will appear. On line 10 (CRDL Standard) type in RLCS.

10.4.22 Highlight lines 14 and 15 (Duplicate and Matrix Spike). Right click and choose “Delete Selected row(s)”.

10.4.23 Highlight lines 13, 14 and 15. Right click and choose “Insert Row”.

10.4.24 Right click on any line and choose “Auto-Renumber Tubes”. Now the sequence is set for 10 samples between every “CCV/CCB”.

10.4.25 Starting on line 13, tube 1:1, in the “Sample Label” column type in the SVL sample numbers for the samples to be analyzed.

10.4.26 If analyzing a sample dilution, type the “@” symbol and then the dilution factor (e.g. @10X) immediately after the sample number.

10.4.27 Thoroughly check the “Sample Label” column for errors. To make corrections to the sample labels click on the line number. Right click and select the appropriate action.

10.4.28 After making any corrections, click on any box then right click and choose “Auto-Renumber Tubes”. Make sure there are only 10 samples between each “CCV/CCB”.

10.4.29 Ad the end of the sequence there will be 3 extra samples. Click on the line number for each of them. Right click and choose “Delete Selected Row(s)”.

10.4.30 Save the sequence by clicking the “Save” icon or clicking “File” and choosing “Save”.

10.4.31 Pour the calibration standards, QC standards and samples in the appropriate vials. The autosampler racks are numbered 1- 4, from left to right and tube are numbered from back to front, left to right for each rack (1:1, 2:1, etc.). The standard rack at the back of the autosampler tray is called “S”, with positions 1-10. The QC

Standards are in rack 4 (ICV = 4:1, ICB = 4:2, RLCS = 4:3, CCV = 4:4 and CCB = 4:5).

10.4.32 Click on the “Method Editor” icon.

10.4.33 Click on the “Conditions” button.

10.4.34 Click on the “Read a Sample” button. The “Now Zeroing the Mercury Analyzer” window will open.

10.4.35 When the zeroing process is finished, the “Select Tube” window will open. Click tube number S:7.

10.4.36 Click “OK”. Standard 7 will be analyzed and the absorbance-versus-time will be displayed on the screen.

10.4.37 Set the Time Profile by moving the green and red bars to the flattest portion at the top of the signal peak.

10.4.38 Click “Save” from the file menu.

10.4.39 Click on the “GO” icon. Click “OK” on the “Confirm” window.

10.4.40 The instrument will begin analyzing the samples.

10.4.41 Click on the “Analysis” icon to see the calibration curve, run progress and sample absorbance displayed.

10.4.42 Analysis will stop if a calibration standard or QC standard fails. ICV, ICB, RLCS, CCV AND CCB are allowed to be run a second time (see section 13).

10.4.43 Check the run to ensure that the prep blanks and LCSs meet method criteria. If the sample absorbance display indicates a failure, DO NOT STOP THE ANALYSIS until the analysis has registered.

10.4.43.1 All analyses are to finish, the Cetac allows for stopping an analysis prior to the final read, this is not allowed. All failures must be re-inserted at a later point in the run.

10.4.44 Under 245.1 **if** the concentration in a sample exceeds 90% of the linear dynamic range, the sample must be re-analyzed at a lower dilution. 7471B requires that samples that exceed the calibration range be diluted back to within the calibration range.

10.4.45 Add additional samples or diluted samples to the end of the run.

10.4.45.1 Click on “Sequence Editor” icon.

10.4.45.2 Enter the number of samples to be added in the “Sample count” box.

10.4.45.3 Uncheck “Begin with Calibration”.

10.4.45.4 Click “Generate Sequence”.

10.4.45.5 A “Warning” window will open. Click “OK”.

10.4.45.6 Delete the CCV/CCB before the added samples.

10.4.45.7 Delete the Duplicates and Matrix.

10.4.45.8 Add 2 lines. Now the sequence is set for 10 samples between each CCV/CCB.

10.4.45.9 Entered the additional sample and/or diluted sample numbers.

10.4.45.10 Save the sequence.

10.4.45.11 Click on “GO” to restart the run.

10.4.46 Re-running a sequence if Calibration, ICV, ICV, RLCS, CCB OR CCB fail.

10.4.46.1 Close existing sequence. In File menu choose “Close”.

10.4.46.2 Click the down arrow on the “Load” icon.

10.4.46.3 Click “New From”. The “Create A New Worksheet From Template Worksheet” window will open.

10.4.46.4 Click the top “Browse” button. The “New Worksheet” window will open.

10.4.46.5 On the “Look in” menu, choose “Quick Trace”.

10.4.46.6 Choose “worksheets.

10.4.46.7 Choose the file name desired.

10.4.46.8 Change the letter at the end of the file name.

10.4.46.9 Delete any unneeded CCV/CCBs and no-usable data.

10.4.46.10 Set the Time Profile and start the run.

11.0 DATA REDUCTION

11.1 The instrument software will generate a linear calibration curve of absorbance versus concentration. The correlation coefficient must be 0.995 or greater. If the correlation coefficient is less than 0.995, recalibrate the instrument prior to analyzing samples. The software will calculate mercury concentrations based on the curve. The analyst must correct for any sample dilution factors manually.

11.1.1 Use the calibration verification template (located at H:\Templates\Calibration Curve Check) to verify the curve. There is a 30% acceptance range for the low standard and a 10% acceptance range for the remaining calibration standards. As long as the minimum number of calibration standards are maintained, the low and high standards may be removed and the calibration used; otherwise re-calibrate the instrument (prepare fresh calibration standards as necessary.

11.2 For aqueous samples:

µg/L Hg = (concentration Hg in digest) (dilution factor)

11.3 To determine mg/kg from a result in µg/L for soil and sludge samples use:

mg/kg Hg = (µg/L Hg in digest)(0.1) / (wt of sample in g) (% dry solids)

11.4 Calculate the percent recoveries of the matrix spikes and the LCS.

11.5 Calculate the relative percent differences (RPDs) of the sample duplicates.

11.6 If the result is above the MDL but below the Reporting Limit, report the result to the client as “< (the Reporting Limit)”, unless the client instructs otherwise. If the client requests numerical results below the Reporting Limit, report the results with one of the following qualifiers:

11.6.1 E4 – Concentration estimated. Analyte was detected below laboratory minimum reporting limit.

11.6.2 J – The reported value was less than the CRDL (Reporting Limit) but greater than or equal to the MDL.

12.0 DATA AND RECORDS MANAGEMENT

12.1 Data from the CETAC M6100 Mercury Analyzer

12.1.1 In the File menu, click on “Export”. The “Specify Export File” window will open .

12.1.2 In the “Save as Type” menu, choose “Text File (*.txt*)”.

12.1.3 Choose “Data”.

12.1.4 In the “File Name” box, enter the file name.

12.1.5 Click “Save”. The “Export Complete” window will open.

12.1.6 Click “OK”.

12.1.7 Click on the File drop down menu and select “Printer setup”.

12.1.8 In the Name drop down menu choose “pdfFactory pro”, click “OK”.

12.1.9 Click the “Print button”. The “pdfFactory Pro” window will open. Click on “Doc Info” and enter the file name. Click on “Preview”, if no corrections or comments are needed click on “Print”. Select the correct printer and print the raw data.

12.1.10 Next, click the “Save” button. Select the correct month. Enter file name and choose PDF in the Save as Type drop down menu. Select “Save” and close out pdfFactory Pro.

12.2 Data from the CETAC M7500 Mercury Analyzer

12.2.1 In the File menu, click on “Export”. The “Specify Export File” window will open.

12.2.2 In the “Save as Type” menu, choose “Text File (*.txt)”.

12.2.3 Choose “Data”.

12.2.4 In the “File Name” box, enter the file name.

12.2.5 Click “Save”. The “Export Complete” window will open.

12.2.6 Click “OK”.

12.2.7 Click on the “Report” icon. The “Reports” window will open.

12.2.8 Click on the “Worksheet” button.

12.2.9 In the “Look in” box, select “Worksheets”.

12.2.10 Click on the file name.

12.2.11 Click on the “Settings” button.

12.2.12 Check “Mean Absorbance” and “Dilution factor”.

12.2.13 Click the “Print” button. The “pdfFactory Pro” window will open. Click on “Doc Info” and enter the file name. Click on “Preview”. If no corrections or comments are needed click on “Print”. Select the correct printer and print the raw data.

12.2.14 Close the “pdfFactory Pro” window. Open “My Documents” on the “Start Menu”. Click on “PDF Files”. Click on “Cetac M7500”. Click on the file name. Corrections and comments can be made here.

12.2.15 Click on “Comments”. Use the “Strikeout Text Tool” or the “Polyline Tool” located under “Drawing Markup Tools” to make a single line cross-out of incorrect data. The pencil on the toolbar is used to initial and date the correction and add any other necessary comments.

12.2.16 Save the changes and print the raw data.

12.2.17 Close this window, leave “Cetac M7500” window open.

12.2.18 Open “My Documents” again. Select the “H” drive. Select “Mercury”. Select “PDFs. Select “Cetac M7500”. Select the correct month. Drag the file in the “Cetac M7500 PDFs” window to the file on the “H” drive.

12.3 Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batching.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the samples began.

12.3.1 Indicate all reagents used in the batch by including them in the reagent section of the "Batch" screen.

12.3.2 Complete the bench sheet, initial and date the sheet. Enter the time of digestion and the time of the analytical run. Identify and record the temperature of the hot block(s) used for the digestion of the samples in that batch. Check the box for the analyzer used. Enter the filename.

12.3.3 Fill out and attach a sheet that includes all of the support equipment used in preparing and analyzing this batch of samples.

12.4 File the raw data in the M7500 or M6100 Run log. Include a CVAA standards sheet, with each set of raw data.

12.5 File a copy of the bench sheet in the Mercury Digestion log.

12.6 The analyst will upload the data via Data Tool. They shall perform all reviews on the "Data Entry/Review" page in Element and verify their data uploads.

12.7 If an input comes up color coded, apply the appropriate data flags or undertake any corrective actions.

12.8 The analyst shall assign any qualifiers.

12.9 The analyst will then update the status of the batch to "Analyzed".

12.10 The analyst will then lock the results so that any future imports will not overwrite acceptable results.

12.11 The data review process is outlined in SVL 2009.

13.0 QUALITY CONTROL

13.1 Prepare and analyze a RLCS (10.1.9) (10.2.9). This standard will be prepared from either a primary or secondary source at a concentration that reflects the current reporting limit. Run this standard once per run before the ICV. Acceptance limits are 70 to 130%. If the recovery falls outside these limits, re-analyze the RLCS. If the recovery still falls outside

these limits, re-calibrate the instrument. The results of the RLCS will be tracked to show the viability of the current reporting limit.

13.2 Analyze a Quality Control Sample (QCS) (10.1.6) (10.2.6) as an ICV immediately after the calibration curve. Acceptance limits are 95 to 105% of the expected value for waters and 90 to 110% for soils. If the recovery falls outside these limits, re-analyze the ICV. If the recovery still falls outside these limits, re-calibrate the instrument.

13.3 Analyze an ICB (10.1.7) (10.2.7) after every ICV. The recovery must be less than the half of the Reporting Limit. If the recovery is greater than half of the Reporting Limit re-analyze the blank, if it is still greater than half of the Reporting Limit re-calibrate the instrument.

13.4 Analyze a method blank (PBW or PBS) (10.1.1) (10.2.1) at a frequency of one per batch of 20 or fewer samples. The recovery must be less than one half of the Reporting Limit or less than 10% of the lowest concentration of the analyte in all of the samples associated with that batch. If the recovery exceeds the criteria, re-analyze the PBW or PBS. If the recovery still exceeds the criterion, re-digest and re-analyze all samples in the affected batch.

13.5 Analyze a Laboratory Control Sample:

13.5.1 For aqueous analysis (LCSW) (10.1.2). Analyze a LCSW at a frequency of 1 per batch of 20 or fewer samples. The acceptance limits for the recovery are 85 to 115%. If the recovery falls outside these criteria, re-analyze the LCSW. If the recovery still falls outside these criteria, re-digest and re-analyze the samples associated with the LCSW.

13.5.2 For soil analysis (LCSS) (10.2.2). analyze a LCSS at a frequency of 1 per batch of 20 or fewer samples. The acceptance limits for the recovery are 80 to 120%. If the recovery falls outside these criteria, re-analyze the LCSS. If the recovery still falls outside these criteria, re-digest and re-analyze the samples associated with the LCSS.

13.5.3 For aqueous extract analysis (EPA 7470A) (LCSW) (10.1.2). Analyze a LCSW at a frequency of 1 per batch of 20 or fewer samples. The acceptance limits for the recovery are 80 to 120%. If the recovery falls outside these criteria, re-analyze the LCSW. If the recovery still falls outside these criteria, re-digest and re-analyze the samples associated with the LCSW.

13.6 Analyze a matrix spike:

13.6.1 For aqueous analysis, analyze a matrix spike (10.1.4) at a frequency of 1 per batch of 10 or fewer samples. The acceptance limits for spike recoveries are 70 to 130% of the expected value if the spike added is greater than 25% of the concentration of the un-spiked sample. There are no acceptance limits if the spike added is less than 25% of the concentration in the un-spiked sample. If the recovery falls outside these limits, flag the client report.

13.6.2 For methods 7470A and 7471B, analyze a matrix spike (10.2.4) at a frequency of 1 per batch on 20 or fewer. The acceptance limits for spike recoveries are 80 to 120% of the expected value. If the recovery falls outside these limits, flag the client report.

13.7 Analyze a matrix spike duplicate (10.1.5) (10.2.5) (10.2.5) for methods 245.1, 7470A and 7471B. The recoveries are as listed in 13.6.1 and 13.6.2. The acceptance limit for RPD between matrix spike and matrix spike duplicate is 20%. If the recoveries or RPDs fall outside of the above limits, flag the client report.

13.11 Analyze a Continuing Calibration Verification (CCV) (10.1.8) (10.2.8) at a frequency of every 10 samples, and at the end of the run. The acceptance limits for method 245.1 (wastewater and drinking water) are 90% to 110% of the expected value. The acceptance limits for methods 7470A and 7471B are 80% to 120% of the expected value. If the recovery falls outside these criteria, determine the cause, perform corrective action, and re-analyze it. If the recovery still exceeds these criteria, re-calibrate the instrument and re-analyze all samples run since the last successful CCV.

13.12 Analyze a Continuing Calibration Blank (CCB) (10.1.7) (10.2.7) at a frequency of every 10 samples, and at the end of the run. The CCB must be less than half of the reporting limit. If the recovery exceeds this criterion, determine the cause, perform corrective action, and re-analyze it. If the recovery still exceeds the limit, re-calibrate the instrument and re-analyze all samples run since the last successful CCB.

13.13 Perform a method detection limit (MDL) study for aqueous and soil (using sand (6.22)) matrices annually.

13.14 Perform a linear dynamic range study annually.

13.14.1 Calibrate the instrument.

13.14.2 Analyze standards at concentrations above the calibration range until recoveries are outside of 10%.

13.14.3 The determined LDR must be documented and kept on file.

13.14.4 For method 245.1 determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and reanalyzed.

14.0 REFERENCES

14.1 Method 7470A, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Third Edition, Update III (December 1996).

14.2 Method 7471B, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Revision II, February 2007.

14.4 Method 245.1, Methods for the Chemical Analysis of Water and Wastes, EPA-600.4-79-020, revised March 1983.

14.5 Method 245.1, Revision 3.0, Methods for the Determination of Metals in Environmental Samples—Supplement I, EPA/600/R-94/111, May 1994.

14.6 Manual for the Certification of Laboratories Analyzing Drinking Water, Fifth Edition.

15.0 POLLUTION PREVENTION

15.1 All standards are prepared and reagents used in volumes consistent with good laboratory practice, to minimize the volume of disposable waste.

15.2 Efficient laboratory practices that reduce the need for re-digestions and/or re-extractions minimize contributions to pollution.

16.0 WASTE MANAGEMENT

16.1 Waste generated by this method includes plastic-ware, chemicals used in the digestion and/or analysis, and paper.

16.2 Plastic-ware is emptied, rinsed, and discarded to a sanitary landfill.

16.3 Most chemicals used during digestion and/or analysis are neutralized and/or diluted prior to disposal by permit to the public sewer. Any hazardous chemicals and/or residues are disposed of through SVL's hazardous waste disposal system (see SOP SVL 1008).

17.0 CHANGE HISTORY

DATE	VER.	CHANGE
01/04/10	13.0	Multiple changes were made to the document plus the addition of the CETAC M7500 requirements. Consult the archived version for comparisons.
01/18/11	14.0	1.0 changed to "aqueous samples are stored at ambient temperature". 6.11 changed to 125 grams and 2.5 liters. 6.14 changed to 400 grams $SnCl_2$ and 280 mL of HCL diluted to 4 liters. 12.1.12 and 12.2.19 added "Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batching.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the samples began". 12.1.12.1 and 12.2.19.1 added "Indicate all reagents used in the batch by including them in the reagent section of the "Batch" screen". 12.1.12.2 and 12.2.19.2 added "Identify and record the temperature of the hot block(s) used for the digestion of the samples in that batch". 12.1.12.3 and 12.2.19.3 added "Fill out and attach a sheet that includes all of the support equipment used in preparing and analyzing this batch of samples". 10.3.59 changed to "concentration". Added 13.5.3 "For aqueous extract analysis (EPA 7470A) (LCSW) (10.1.7). Analyze a LCSW at a frequency of 1 per batch of 20 or fewer samples. The acceptance limits for the recovery are 80 to 120%. If the recovery falls outside these criteria, re-analyze the LCSW. If the recovery still falls outside these criteria, re-digest and re-analyze the samples associated with the LCSW".

DATE	VER.	CHANGE
5/02/12	15.0	6.22 Added “Sand, Fisher S23-3”. 9.4 added “Logbook and in a Work Order memo”. 10.1.1 added “(samples should be qualified; ref, SVL 2009)”. 10.1.3 added “Final volume on benchsheet should be adjusted to 50.5 mL”. 10.2.1 added “± 0.005 g”. 10.2.2 added “Final volume on benchsheet should be adjusted to 101.0 mL”. Re-wrote section 10.3 to account for the changes in operating the M6100 instrument. 10.2.7 changed to “Prepare an LCS by transferring 1.0 mL of the mercury ICV stock solution (6.20) to 0.6 g ± 0.005 g of sand (6.22) into a “Snap-cap” vial, add 4.0 mL deionized water (6.21). Mix well. The concentration of the LCS is 5.0 µg/L”. 10.2.8 changed to “Prepare a method blank by weighing 0.6 g ± 0.005 g of sand (6.22) add 5.0 mL of deionized water (6.21) into a “Snap-cap” vial. Mix well”. 11.1.1 added “Use the calibration verification template (located at H:\Templates\Calibration Curve Check) to verify the curve. There is a 30% acceptance range for the low standard and a 10% acceptance range for the remaining calibration standards. As long as the minimum number of calibration standards are maintained, the low and high standards may be removed and the calibration used; otherwise re-calibrate the instrument (prepare fresh calibration standards as necessary”. Re-wrote Section 12.0 to include the M6100 procedures. 13.13 added “(using sand (6.22)”.

DATE	VER.	CHANGE
11/26/12	16.0	4.4 changed to "Do not swallow, inhale or absorb through skin". 8.3 added a column for 10 ml initial volume. 10.1.5 added "Prepare a matrix spike duplicate by following the steps outlined in 10.1.4". 10.2.3 changed to "Weigh out a 0.6 g ± 0.005 g portion of a well homogenized sample in a "Snap-cap" vial". 10.2.4 changed to "Prepare a matrix spike by weighing another 0.6 g ± 0.005 g portion of a well homogenized sample in a "Snap-cap" vial". 10.2.5 changed to "Prepare a matrix spike duplicate. Follow the process outlined in 10.2.4". 10.2.11 added "± 3°C". 10.2.12 changed to "40 mL deionized water". 10.2.13 changed to "15 mL potassium permanganate solution". 10.2.14 changed to "Cool the vials and add 6 mL of hydroxylamine hydrochloride solution (6.9) to reduce the excess permanganate. Add 49 mL deionized water (6.21) into samples, prep blank, LCS, matrix spike and matrix spike duplicate. Add 44 mL deionized water to the calibration standards, ICB, CCBs, RLCS, ICV, and CCVs. Add proportionally less water if additional permanganate is used. The final volume of all standards and samples should be 120 mL". 10.3.31 and 10.4.43 changed to "DO NOT STOP THE ANALYSIS until the analysis has registered". 10.4.43.1 added "All analyses are to finish, the Cetac allows for stopping an analysis prior to a final read, this is not allowed. All failures must be re-inserted at a later point in the run". 10.3.32 and 10.4.44 changed to "Under 245.1 **i**f the concentration in a sample exceeds 90% of the linear dynamic range, the sample must be re-analyzed at a lower dilution. 7471B requires that samples that exceed the calibration range be diluted back to within the calibration range". 13.6.2 changed to "are 80 to 120% of the expected value". 13.7 changed to "Analyze a matrix spike duplicate (10.1.5) (10.2.5) (10.2.5) for methods 245.1, 7470A and 7471B. The recoveries are as listed in 13.6.1 and 13.6.2. The acceptance limit for RPD between matrix spike and matrix spike duplicate is 20%. If the recovery falls outside these limits, flag the client report". 13.14 changed to "Perform a linear dynamic range study annually ". 13.14.1 changed to "Calibrate the instrument". 13.14.2 changed to "Analyze standards at concentrations above the calibration range until recoveries are outside of 10%". 13.14.3 changed to "The determined LDR must be documented and kept on file". 13.14.4 changed to "For method 245.1 determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and reanalyzed". 14.2 changed to "Method 7471B, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Revision II, February 2007".

DATE	VER.	CHANGE
12/23/13	17.0	10.2.4 changed “Prepare a matrix spike by weighing another 0.60 g ± 0.005 g portion of a well homogenized sample in a “Snap-cap” vial and add 2.0 mL of the working standard solution (6.19). Add 3.0 mL deionized water (6.21). The initial concentration of the matrix spike is 2.0 ppb.”

CONDUCTIVITY
By
SM 2510B and EPA 120.1

Revised by: Robin Stribling and Michael Desmarais

Approved by: _____ Date: _____
Classical Chemistry Department Supervisor

Reviewed by: _____ Date: _____
Quality Assurance Manager

SVL Analytical, Inc.

I have read, understood and will comply with SOP (SVL 4025 Revision 11.0)

Print Name	Signature	Date
Jennifer Sieg		
Anita Guzman Freedle		
Jerome Meier		

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1.0 SCOPE AND APPLICATION

This SOP describes the procedure used to determine specific conductance. This method is applicable to drinking, surface, and saline waters, and domestic and industrial wastes. SVL uses a Laboratory Information Management System (LIMS) – Element, to manage client's samples. In Element the reporting limit is 5.0 µmhos/cm. Definitions for words used in this SOP may be found in SVL's Quality Manual. The holding time is 28 days when samples are stored between 0-6ºC. This SOP is intended to satisfy the requirements of EPA Method 120.1, and Standard Methods 2510 B.

2.0 SUMMARY OF METHOD

The specific conductance of a sample is measured using a self-contained conductivity meter. Samples are analyzed with an Accumet AB 30 that self corrects for temperature variations. If temperatures are not being automatically corrected for, then the equation listed in 11.1 must be used to account for the difference in temperature from the 25°C constant before results are reported out.

3.0 INTERFERENCES

3.1 Temperature variations represent the largest source of potential error.

3.2 The conductivity probe must be kept clean.

4.0 SAFETY

4.1 There are no specific safety hazards.

5.0 EQUIPMENT, INSTRUMENTATION AND MATERIALS

5.1 Conductivity meter with conductivity and temperature probes, Accumet Basic, AB 30, or equivalent.

6.0 REAGENTS AND STANDARDS

Guidelines for the storage, tracking and expiration of chemicals and reagents can be found in SVL 1032. The procedure for purchasing chemicals and reagents can be found in SVL 1015. Any exceptions to the above mentioned SOPs will be found in this section: as well as, all of the preparatory steps needed to construct or prepare reagents, and standards. Equivalent reagents or standards may be

used.

6.1 LCS Standard Solution, ERA "Minerals". Used for secondary verification check and as the LCS.

6.2 Traceable Conductivity Standard, Certified Reference Material, 1000 µmhos/cm (nominal value), Fisher #H1380932831A.

6.3 Type II deionized water.

7.0 INSTRUMENT SETTINGS

7.1 Ensure that the instrument is set to read conductivity, not TDS.

8.0 STANDARDIZATION

Standardize the conductivity probe each day prior to use.

8.1 Press "std" to enter the standardize screen. The STD solution icon will appear along with the measured value in both the upper and lower displays. Verify that the appropriate unit (µmhos/cm) is being used.

8.1.1 If the operator chooses to use a different standard they must use the "setup" key to go to the screen where the value can be changed (this is done in the upper screen).

8.1.2 The "up arrow" key allows the user to change the value of the blinking cursor, "setup" key allows changes between digits and the "enter" key sets and confirms the input.

8.1.3 Press "setup" key until "clear" is displayed. Press "enter" followed by "standard."

8.1.4 Place probe into certified standard (6.2), press "setup," and the digits will begin to flash. Using the arrows, change each digit until "1000" is displayed. After changing each digit, press "setup" to switch to next number.

8.1.5 After "1000" is displayed, press "enter," and then "standard" once.

8.1.6 Instrument is now standardized to 1000. Indicate standardization in log book.

8.2 After standardization, the probe is checked against a certified secondary solution (6.1) and recorded in the standardization log book.

8.3 Analyze an instrument blank using deionized water (6.3) and record the reading in the conductivity logbook.

9.0 SAMPLE HANDLING AND PRESERVATION

9.1 The holding time is 28 days when samples are stored between 0-6°C.

10.0 SAMPLE PREPARATION AND ANALYSIS

10.1 Analyze a LCS (6.1) and record the conductivity.

10.2 Pour off an aliquot of sample and immerse the conductivity probe to a depth where sample flows out of the electrode chamber hole (assure that no air bubbles are trapped in the probe's chamber by plunging the probe 2-3 times into sample or by tapping the electrode).

10.2.1 The meter automatically performs any necessary temperature corrections for measuring conductivity

10.3 Analyze a similar aliquot of a sample as a sample duplicate (follow 10.2).

10.4 Record the reading, date and time.

10.5 Rinse the conductivity probe with deionized water (6.3) between each analysis, allowing water to flow around and through the probe.

10.5.1 If a reading seems odd, repeat 10.5 then check the probe by reading the LCS solution (6.1) again. If the reading does not meet the LCS requirement (13.2) then troubleshoot and fix the probe or replace the probe and begin the analytical run over.

11.0 DATA REDUCTION

11.1 If the temperature probe is not used, the conductivity must be corrected using the following equation if the samples are not at 25°C.

$$Conductivity\ \ in\ \ \mu mhos/cm = \frac{conductivity\ reading}{1 + 0.0191\ (T - 25)}$$

where T is in °C.

11.2 Report results as Specific Conductance in μmhos/cm.

11.3 Other calculation used in this SOP (recoveries and RPD) may be found in SVL SOP 1028.

12.0 DATA AND RECORDS MANAGEMENT

12.1 Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batches.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the samples began.

12.2 Transfer the results to the bench sheet.

12.3 The analyst will upload the data manually. They shall perform all reviews on the "Data Entry/Review" page in Element and verify their data uploads.

12.4 If input comes up color coded, apply the appropriate data flags or undertake any corrective actions.

12.5 The analyst shall assign any qualifiers, update the status of the batch to "Analyzed", and lock the results so that any future imports will not overwrite acceptable results.

12.6 Data review is governed by SVL SOP 2009.

12.7 Calibrations and daily checks must be recorded in log books.

13.0 QUALITY CONTROL

13.1 Analyze a secondary verification check (6.1). Run the check after standardization. The conductance must read between 95 and 105% of the expected value. If the check reads outside of these limits make sure the conductivity probe is clean and take another reading, if it fails again re-standardize. The secondary verification value varies based upon the lot number of the purchased standard.

13.2 Analyze a LCS (6.1) with a frequency of 1 per every batch of 20 or fewer samples. The conductance of the LCS must read between 90 and 110% of the expected value. If the LCS recovery falls outside these limits, determine the cause of the problem with either the standard or the

conductivity probe, and fix it before starting the run over. The true value of the LCS varies by lot number; verify the true value of the current standard in Element.

13.3 Analyze a sample duplicate (10.4) at a frequency of 1 per every batch of 20 or fewer samples. The acceptance criterion for the RPD is 20%. If the RPD exceeds the criterion, flag the sample result.

13.3.1 For Arizona analyze a sample duplicate at a frequency of 1 per every batch of 10. The acceptance criterion for the RPD is 20%. If the RPD exceeds the criterion, flag the sample result.

13.6 Annually a Quality Control Sample (QCS) (SVL uses ERA PT studies) must pass its study requirements; if needed, troubleshoot and repeat the study. Failure to pass a QCS annually will result in the removal of the test until a QCS is passed.

14.0 REFERENCES

14.1 Method 120.1, Methods for Chemical Analysis of Water and Wastes, revised March 1983, EPA-600/4-79-020.

14.2 Method 2510B, Standard Methods for the Examination of Water and Wastewater, 20th Edition, 1999.

14.3 Standard Methods 2020, Standard Methods for the Examination of Water and Wastewater, 22nd edition. 2012.

14.4 40 CFR 136 Table II, Item 64.

14.5 Manual for the Certification of Laboratories Analyzing Drinking Water, Fifth Edition.

15.0 POLLUTION PREVENTION

15.1 There is no specific environmental pollution associated with this method.

16.0 WASTE MANAGEMENT

16.1 There is no measurable waste associated with this method.

17.0 CHANGE HISTORY

DATE	VER.	CHANGE
09/01/09	7.0	Major portions of this SOP have been changed; for questions relating to the changes please compare the methods and archived SOPs.
09/20/10	8.0	12.1 added "Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batches.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the samples began".
10/04/11	9.0	6.1 added "Used for ICV and LCS". 8.0 added "Standardize the conductivity probe each day prior to use". 8.1.3 added "Press "setup" key until "clear" is displayed. Press "enter" followed by "standard". 8.14 added "Place probe into certified standard (6.2), press "setup," and the digits will begin to flash. Using the arrows, change each digit until "1000" is displayed. After changing each digit, press "setup" to switch to next number ". 8.1.5 added "After "1000" is displayed, press "enter," and then "standard" once". 8.1.6 added "Instrument is now standardized to 1000. Indicate standardization in log book". 8.2 changed to "After standardization, the probe is checked against a certified solution (6.1) as an ICV and recorded in log book. Type II deionized water (6.3) is checked as an ICB and recorded in log book". 13.1 changed to "The ICV value varies based on lot number of the purchased standard". 13.4 changed to "If the LCS recovery falls outside these limits, determine the cause of the problem with either the standard or the conductivity probe, and fix it before starting the run over".
08/23/12	10.0	Removed references to blanks throughout document. 10.6.1 added "If a reading seems odd, repeat 10.6 then check the probe by reading the LCS solution (6.1) again. If the reading does not meet the LCS requirement (13.2) then troubleshoot and fix the probe or replace the probe and begin the analytical run over. 13.3 changed to "Analyze a sample duplicate (10.4) at a frequency of 1 per every batch of 20 or fewer samples. The acceptance criterion for the RPD is 20%. If the RPD exceeds the criterion, flag the sample result". 13.6 added "Annually a

DATE	VER.	CHANGE
		Quality Control Sample (QCS) (SVL uses ERA PT studies) must pass its study requirements; if needed, troubleshoot and repeat the study. Failure to pass a QCS annually will result in the removal of the test until a QCS is passed". 14.3 added "Standard Methods 2020, Standard Methods for the Examination of Water and Wastewater, 22nd edition. 2012".

09/19/13	11.0	8.3 added "Analyze an instrument blank using deionized water (6.3) and record the reading in the conductivity logbook." 13.1 added "For Arizona analyze a sample duplicate at a frequency of 1 per every batch of 10. The acceptance criterion for the RPD is 20%. If the RPD exceeds the criterion, flag the sample result."

pH by SM 4500 H^+ B

Reviewed by: Michael Desmarais

Approved by: _____ Date: _____
Classical Chemistry Department Supervisor

Reviewed by: _____ Date: _____
Quality Assurance Manager

SVL Analytical, Inc.

I have read, understood and will comply with SOP (SVL 4028 Version 12.0)

Print Name	Signature	Date
Debbie Schultz		
Heather Green		
Anita Guzman-Freedle		

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1.0 SCOPE AND APPLICATION

This SOP describes the procedure for the determination of pH by electrode. The method is appropriate for aqueous matrices including drinking water, surface, and saline waters, domestic and industrial wastes, and acid rain (atmospheric deposition). Samples should be analyzed as soon as possible after receipt. SVL typically uses an autotitrator procedure for pH determination (refer to the SOP SVL 4084) but may use an electrode when necessary. Definitions for words used in this SOP may be found in SVL's Quality Manual.

2.0 SUMMARY OF METHOD

The pH of a sample aliquot is measured using a pH electrode and meter. The SOP is intended to meet the requirements found in SM 4500-H^+ B.

3.0 INTERFERENCES

3.1 During testing, oily matter, suspended solids, soaps, precipitates, or other waste matter may coat the glass electrode and cause a sluggish response and may manifest in an erratic response. Do not remove interferences from sample because they may contribute to its alkalinity. Allow the electrode to come to equilibrium, clean the electrodes occasionally.

3.2 Samples may not be diluted or filtered.

3.3 Depletion of ionic species near the probe may cause errors. Stir the sample gently while measuring pH.

4.0 SAFETY

4.1 Read the MSDSs for the chemicals used in this SOP. Be aware of the possible hazards.

5.0 EQUIPMENT, INSTRUMENTATION, AND MATERIALS

Equivalent equipment, instruments, and materials may be used.

5.1 Thermo Scientific pH Meter, Model Orion 320

5.2 Thermo Scientific pH Meter, Model Orion 2 Star

5.3 VWR Symphony Electrode, Catalog # 14002-860

6.0 REAGENTS AND STANDARDS

Equivalent buffers or standards may be used.

6.1 pH 7 Buffer Solution, BDH, cat # BDH0194-20L

6.2 pH 4 Buffer Solution, BDH, cat # BDH0198-20L

6.3 pH 9 Buffer Solution, BDH, cat # BDH5064-4L

6.4 pH QC check, ERA, catalog number 552

7.0 INSTRUMENT SETTINGS

There are no instrument settings.

8.0 CALIBRATION

8.1 For the Orion 320 and the Orion 2 Star, rinse the electrode with deionized water.

8.2 Calibrate the pH meter.

8.2.1 Press “Calibrate” until “7-4” is displayed, and then press “Yes”.

8.2.2 Place the electrode in a pH 7 buffer solution. Wait until “Ready” is displayed. Press “Yes”. Rinse electrode.

8.2.3 Place the electrode in a pH 4 buffer solution. Wait until “Ready” is displayed. Press “Yes”. Rinse electrode.

8.2.4 The slope must be within 90-102 range. If the slope is outside of this range – recalibrate.

8.2.5 Read the pH 7 and 4 buffers using the new calibration. The values must be ± 0.1 pH units from the true value.

8.2.6 Check an independent buffer (6.3) to verify linearity, the reading must be within +/- 0.1 pH units. If the reading is outside of the requirement clean the probe and perform any necessary maintenance prior to re-calibrating.

8.2.7 Record on benchsheets the following: The electrode's calibration, slope**,** pH readings (for samples and QC) and buffer readings. These will be copied and inserted into a run log.

9.0 SAMPLE HANDLING AND PRESERVATION

9.1 Samples should be analyzed as soon as possible after collection.

9.2 Samples should be stored between 0-6°C. Avoid sample agitation and prolonged exposure to air.

10.0 SAMPLE PREPARATION AND ANALYSIS

10.1 Allow the samples to come to room temperature (25±2°C). Gently swirl the sample to achieve homogeneity.

10.2 Pour out an aliquot of the sample into a plastic cup.

10.3 Place probe into the aliquot and record the pH value and temperature when the probe registers a stable reading.

10.4 Analyze a pH QC check (6.4). This will be analyzed once per day and tracked in Element as an SRM.

11.0 DATA REDUCTION

11.1 Calculations for procedures outlined in the SOP, may be found in SVL 1028.

12.0 DATA AND RECORDS MANAGEMENT

12.1 Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batching.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the sample(s) began.

12.2 Transfer the pH reading and the temperature to the bench sheet, initial and date it.

12.3 The analyst will upload the data manually into Element. They shall perform all reviews on the "Data Entry/Review" page in Element and verify their data uploads.

12.4 If input comes up color coded, apply the appropriate data flags or undertake any corrective actions.

12.5 The analyst shall assign any qualifiers, update the status of the batch to "Analyzed", and lock the results so that any future imports will not overwrite acceptable results.

12.6 The data review process is outlined in SVL 2009.

12.7 The analyst will add the H5 qualifier to all samples tested for pH.

13.0 QUALITY CONTROL

13.1 Analyze a pH QC check (6.4) once per day. The results of this check will be tracked in Element. Verify the true value of the standard in Element. The acceptance criterion is +/- 0.1 pH units of the expected value. If the recovery falls outside the acceptance criterion, identify and correct any problems before analyzing samples.

13.2 Analyze a pH 9 buffer solution (6.3) as an ICV once per day. The acceptance criterion is +/- 0.1 pH units of the expected value. If the recovery falls outside the acceptance criterion, identify and correct any problems before analyzing samples.

13.3 Prepare and analyze a sample duplicate at a frequency of 1 per every batch of 20 or fewer samples. The acceptance criterion for the RPD is ± 0.1 pH units. If the RPD is greater than the acceptance criterion, flag the client report.

13.4 Analyze buffer solutions of pH 7 and 4 at the beginning of each run, after every 10 samples, and at the end of the run. They function as calibration verification samples. The acceptance criteria are ± 0.1 pH units of the expected value. If the buffer solutions read outside the acceptance criteria, identify and correct the problem. Re-analyze samples analyzed since the last successful buffers.

13.5 Annually a Quality Control Sample (QCS) (SVL uses ERA PT studies) must pass its study requirements; if needed, troubleshoot and repeat the study. Failure to pass a QCS annually will result in the removal of the test until a QCS is passed.

13.6 MDLs are not applicable to this method.

14.0 REFERENCES

14.1 Method 4500-H^+ B, Standard Methods for the Examination of Water and Wastes, 21st Edition, 2000.

14.2 Standard Methods 2020, Standard Methods for the Examination of Water and Wastewater, 22nd edition. 2012.

14.3 Manual for the Certification of Laboratories Analyzing Drinking Water, Fifth Edition.

15.0 POLLUTION PREVENTION

15.1 No pollution issues are associated with SM 4500-H^+ B.

16.0 WASTE MANAGEMENT

16.1 No waste is generated by SM 4500-H^+ B. Samples after analysis are diluted prior to disposal by permit to the public sewer.

17.0 CHANGE HISTORY

DATE	VERSION	CHANGE
11/17/09	8.0	6.1 added "Distilled or deionized water that has been boiled for 15 minutes or equivalent". 8.1.4 and 8.2.4 changed acceptance to +/- 0.1. 13.4 pH acceptance criteria changed to +/- 0.1.
12/09/10	9.0	Changed equipment in Section 5. Section 6 updated buffer solutions. Re-wrote all of Section 8. 12.1 added "Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batching.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the sample(s) began". 12.7 added "The

DATE	VERSION	CHANGE
		analyst will add the H5 qualifier to all samples tested for pH".
09/26/11	10.0	8.2.5 changed to "0.1 pH units". 13.3 changed to "The acceptance criterion for the RPD is ± 0.1 pH units".
09/17/12	11.0	6.3 added "pH 9 Buffer Solution, BDH, cat # BDH5064-4L". 8.2.6 added "Check an independent buffer (6.3) to verify linearity, the reading must be within +/- 0.1 pH units. If the reading is outside of the requirement clean the probe and perform any necessary maintenance prior to re-calibrating". 8.2.7 changed to" Record on benchsheets the following: The electrode's calibration, slope**,** pH readings (for samples and QC) and buffer readings. These will be copied and inserted into a run log". 10.4 changed to "This will be analyzed once per day and tracked in Element as an SRM". 13.1 changed to "Analyze a pH QC check (6.4) once per day. The results of this check will be tracked in Element. Verify the true value of the standard in Element. The acceptance criterion is +/- 0.1 pH units of the expected value. If the recovery falls outside the acceptance criterion, identify and correct any problems before analyzing samples". 13.2 added "Analyze a pH 9 buffer solution (6.3) as a pH QC check/ICV once per day. The acceptance criterion is +/- 0.1 pH units of the expected value. If the recovery falls outside the acceptance criterion, identify and correct any problems before analyzing samples". 13.5 added "Annually a Quality Control Sample (QCS) (SVL uses ERA PT studies) must pass its study requirements; if needed, troubleshoot and repeat the study. Failure to pass a QCS annually will result in the removal of the test until a QCS is passed". 14.1 changed to "21st Edition, 2000". 14.2 added "Standard Methods 2020, Standard Methods for the Examination of Water and Wastewater, 22nd edition. 2012".
11/01/13	12.0	13.6 added "MDLs are not applicable to this method."

SULFIDES BY TITRATION
By SM 4500 S^{-2} F

Revised by: **Sherry Maine and Michael Desmarais**

Approved by: _____ Date: _____
Classical Chemistry Department Supervisor

Reviewed by: _____ Date: _____
Quality Assurance Manager

I have read, understood and will comply with SOP (SVL 4032 Version 13.0)

Print Name	Signature	Date
Sherry Maine		
Nicholas Saintz		
Andrew Popchock		

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1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedure for determination of acid soluble sulfide by titration. This method is applicable to the measurement of total and dissolved sulfides in drinking, surface and saline waters, as well as domestic and industrial wastes. SVL uses a Laboratory Information Management System (LIMS) – Element, to manage client's samples. In Element the current MDL is 0.17 mg/L. The Reporting Limit is 1.0 mg/L. Definitions for words used in this SOP may be found in SVL's Quality Manual. The holding time is 7 days when samples are stored between 0-6°C with the addition of zinc acetate and preserved to a pH>9 with sodium hydroxide.

2.0 SUMMARY OF METHOD

This SOP is intended to satisfy the requirements of SM 4500-S^{-2} F; the method is an iodometric titration. Sulfides are precipitated with zinc acetate and sodium hydroxide, and zinc sulfide is filtered out. The supernatant is discarded. The filter is then placed in a flask with iodine, hydrochloric acid, and starch. The presence of sulfide will reduce iodine to iodide, and the remaining iodine is titrated with sodium thiosulfate. The concentration of sulfide is calculated.

3.0 INTERFERENCES

3.1 Reducing agents like thiosulfate and sulfite cause positive interferences. To remove the interfering compounds, add zinc acetate solution to precipitate zinc sulfide. Filter the zinc sulfide and add deionized water.

3.2 Sulfide is prone to oxidation by dissolved and atmospheric oxygen; therefore exposure to air should be minimal. Samples should be received with as little headspace as possible to minimize oxidation by exposure to air.

4.0 SAFETY

4.1 Sulfides can be toxic. Do not ingest samples or standards.

4.2 Sodium hydroxide can cause severe burns. Avoid contact with skin or eyes. Wear safety glasses or goggles. Wear gloves and a lab coat or an apron. In the case of exposure, flush with water for at least fifteen minutes.

4.3 Hydrochloric acid can cause severe burns if it comes into contact with skin or eyes. The fumes are also irritating to nasal and lung tissues. Work with hydrochloric acid in a hood. Wear safety glasses or goggles. Wear gloves and a lab coat or an apron. In the case of exposure, flush with water for at least fifteen minutes.

4.4 Iodine is a severe corrosive. All possible precaution should be taken to ensure that no iodine comes in contact with skin or is inhaled or ingested. If Iodine makes contact with any flesh, flush immediately with water for at least fifteen minutes. If inhaled move immediately to fresh air. For any exposure get help ASAP.

4.5 Analysts should read the appropriate MSDSs for all compounds used in this method.

5.0 EQUIPMENT, INSTRUMENTATION, AND MATERIALS

Equivalent equipment, instruments, and materials may be used.

5.1 Erlenmeyer flasks, 500 mL

5.2 Micropipets-adjustable volume 200-1000µL, accurate to 3%, Socorex

5.3 Class A buret, 10.0 mL

5.4 Whatman 934AH filter paper, 90 mm ash less

5.5 Vacuum source, filter, and Flask

5.6 Class A graduated cylinder, 250 mL, Pyrex.

6.0 REAGENTS AND STANDARDS

Guidelines for the storage, tracking and expiration of chemicals and reagents can be found in SVL 1032. The procedure for purchasing chemicals and reagents can be found in SVL 1015. Any exceptions to the above mentioned SOPs will be found in this section: as well as, all of the preparatory steps needed to construct or prepare reagents, and standards. Equivalent reagents or standards may be used.

6.1 Potassium iodide, KI, free from iodate: J.T. Baker Analytical Reagent.

6.2 Iodine, J.T. Baker Analytical Reagent.

6.3 Sodium thiosulfate pentahydrate ($Na_2S_2O_3 \bullet 5H_2O$), J.T. Baker Analytical Reagent.

6.4 Potassium biiodate, $KH(IO_3)_2$, EM Science Analytical Reagent.

6.5 Zinc acetate dehydrate, $Zn(C_2H_3O_2)_2 \bullet 2H_2O$, Analytical Reagent grade.

6.6 Iodine solution: Dissolve 20 to 25 grams of potassium iodide ((6.1) (KI) in deionized water (6.16). Add 3.2 grams of iodine (6.2). Dissolve and dilute to 1 liter. Standardize against a 0.025 N sodium thiosulfate solution (6.10). Store the solution in a dark place. Expiration date is one year after date of preparation.

6.7 1:1 hydrochloric acid: Carefully dissolve 50 mL concentrated hydrochloric acid (6.17) in 50 mL deionized water (6.16).

6.8 6 N sodium hydroxide: Carefully dissolve 24.0 grams sodium hydroxide (6.18) in deionized water (6.16). WARNING! This reaction produces heat! Cool and dilute to 100mL with deionized water.

6.9 Starch Indicator: Dissolve 2 g laboratory-grade soluble starch with 0.2 g salicylic acid (6.15) as preservative in 100 mL hot deionized water (6.16).

6.10 0.025 N sodium thiosulfate titrant: Dissolve 6.205 g sodium thiosulfate pentahydrate (6.3) and 1.5 mL 6 N sodium hydroxide (6.8) in 1 L deionized water (6.16).

6.11 0.0021 M potassium biiodate solution: Dissolve 812.4 mg potassium biiodate (6.4) in 1 L deionized water (6.16).

6.12 2 N zinc acetate solution: Dissolve 22.0 g zinc acetate dehydrate (6.5) in 100 mL of deionized water (6.16).

6.13 Zinc acetate/sodium hydroxide preservative, Eagle Pitcher. Prepare preservative by mixing 4 drops of 2 N zinc acetate solution (6.12) and 2 drops of a 6 N sodium hydroxide solution (6.8) per 100 mL of sample.

6.14 Commercially manufactured solution for Laboratory Control Sample and Matrix Spikes (LCS/MS):1000mg/L Sulfide stock solution good for 1 month after opening 3 years unopened and refrigerated Absolute Standards, Inc . LCS: half fill a 100 mL volumetric flask with di-water added 0.25 mL 1000 mg/L stock solution preserve immediately with 0.2mL 2N Zinc Acetate and

0.1mL 6 N NaOH fill to 100 mL mark and check that pH >9 Let stand about 30 minutes before running. True Value for LCS =2.5mg/L.

6.14.1 Measure out 2-100mL allocates of sample to be spiked into secondary containers and check that the pH>9. To each container add 0.25mL of the 1000mg/L stock solution let stand 30 minutes before running. This equals a 2.5mg/L Matrix spike**.**

6.15 Salicylic acid, Mallinckrodt Analytical Reagent.

6.16 ASTM Type II water.

6.17 Concentrated hydrochloric acid, Fisher TraceMetals Grade.

6.18 Sodium hydroxide (NaOH) pellets, Fisher, S318-10, ACS Grade.

6.19 Soluble starch, EM Science, 1252-2.

6.20 RLC half fill a 100 mL volumetric flask with di-water added 0.1 mL 1000 mg/L stock solution(6.14) preserve immediately with 0.2mL 2N Zinc Acetate and 0.1mL 6 N NaOH fill to 100 mL mark and check that pH >9 Let stand about 30 minutes before running. True Value for LCS =1.0mg/L.

7.0 INSTRUMENT SETTINGS

7.1 There are no instrument settings

8.0 CALIBRATION

Open the sulfide template found at H:\Templates to enter calibration and sample data into.

8.1 Standardize the sodium thiosulfate titrant.

8.1.1 Dissolve 2.0 g potassium iodide (6.1) in a 500 mL Erlenmeyer flask in 100 -150 mL deionized water (6.16).

8.1.2 Add 2.0 mL 1:1 hydrochloric acid (6.7).

8.1.3 Add a known volume 5.0 mL of 0.0021 M potassium biiodate solution (6.11).

8.1.4 Dilute to 200 mL with deionized water (6.16).

8.1.5 Titrate with sodium thiosulfate titrant (6.10) to a pale yellow color.

8.1.6 Add few drops starch indicator solution (6.9); the solution will turn blue.

8.1.7 Continue titrating until solution turns colorless. Enter the amount of titrant used in the sulfide template.

8.2 Standardize the Iodine solution

8.2.1 Place 150 mL deionized water (6.16) in an Erlenmeyer flask.

8.2.2 Add 2.0 mL 1:1 hydrochloric acid (6.7).

8.2.3 Add 5 mL iodine solution (6.6).

8.2.4 Titrate with sodium thiosulfate titrant (6.10) to a pale yellow color.

8.2.5 Add a few drops of starch indicator (6.9); the solution will turn blue. Continue to titrate until solution turns colorless. Enter the amount of titrant used in the sulfide template.

9.0 SAMPLE HANDLING AND PRESERVATION

9.1 The holding time is 7 days when samples are stored between 0-6°C and preserved with 0.2 mL zinc acetate solution per 100 mL of sample plus sodium hydroxide until the pH>9.

9.2 Check and record pH of samples and LCS on bench sheet.

10.0 SAMPLE PREPARATION AND ANALYSIS

10.1 Titrating Zinc Acetate/NaOH Preserved Samples

10.1.1 All samples should have been preserved with zinc acetate solution and sodium hydroxide.

10.1.2 Prepare an RLCS as directed in section 6.20. Analyze as a sample.

10.1.3 Prepare a method blank by adding 0.5 mL 2N zinc acetate and 0.25 mL 6N NaOH to 250 mL deionized water. Analyze as a sample.

10.1.4 Prepare an LCS as directed in section 6.14. Analyze in the same manner as a sample.

10.1.5 Prepare a matrix spike and a matrix spike duplicate by spiking 0.25 mL of LCS/MS solution (6.14.1) into separate 100 mL like aliquots of the selected QC sample (as prepared in 10.1.6).

10.1.6 Thoroughly mix and then measure out 100 mL of sample using a clean Class A graduated cylinder and filter. Discard the filtrate.

10.1.7 Sample and QC procedures. Transfer 5.0 mL of a 0.025 N iodine solution and 2.0 mL 1:1 hydrochloric acid to a 500 mL Erlenmeyer flask filled with 150 mL of deionized water (more hydrochloric acid may be used in order to achieve an acidic pH).

10.1.8 Immediately place the filter paper in the 500 mL Erlenmeyer flask. If the iodine color disappears, add more 0.025 N iodine until the color is stable. Record the total amount of 0.025 N iodine added.

10.1.9 Titrate sample quickly using a 0.025 N sodium thiosulfate solution until it turns a very pale yellow color.

10.1.10 Add a few drops starch indicator to the mixture; the solution will turn blue.

10.1.11 Continue adding sodium thiosulfate until the solution turns colorless. Record the total number of mL required to reach that point directly on the sulfide template.

11.0 DATA REDUCTION

11.1 Use the sulfide template found at H:\Templates to calculate the normality of the sodium thiosulfate titrant, iodine, and to calculate the sulfide concentration in samples. All calculations can be done manually using the following equations:

11.1.1 Normality of sodium thiosulfate =
0.025 (mL sodium thiosulfate) / (mL of potassium biiodate)

11.1.2 Normality of iodine = (MT) (NT) / MI

Where:
MI = Volume of iodine solution (in mL)
NI = Normality of iodine
MT= Volume of sodium thiosulfate titrant used (in mL)
NT = Normality of sodium thiosulfate titrant

11.1.3 mg/L sulfide = 16,000 [(MI $\times$ NI) – (MT $\times$ NT)] / (mL of sample)

Where:

MI = volume of iodine solution (in mL)
NI = Normality of iodine
MT= Volume of sodium thiosulfate titrant used (in mL)
NT = Normality of sodium thiosulfate titrant

11.1.4 Calculations for procedures outlined in the SOP, may be found in SVL 1028.

12.0 DATA AND RECORDS MANAGEMENT

12.1 Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batching.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the samples began.

12.1.1 Indicate all reagents used in the batch by including them in the reagent section of the "Batch" screen.

12.2 Print out and attach a copy of the completed sulfide template to the benchsheet.

12.3 The sulfide template is set up to import and export data compatibly with element. Under laboratory in the data entry/review bring up the bench sheet you are working with than "create" and "export" a temp file will come up select and save. Open the template and select the import icon then the temp file (this should populate the columns with the work order numbers from the bench sheet). Once finished Save to the sulfide file on H drive. Go to data entry/review and select open then H:\sulfide in the folder select the correct set of data and double click. This should import the data into the element data entry screen then "Save".

12.4 If an input comes up color coded, apply the appropriate data flags or

undertake any corrective actions.

12.5 The analyst shall assign any qualifiers.

12.6 The analyst will update the status of the batch to “Analyzed”.

12.6.1 The analyst will then lock the results so that any future imports will not overwrite acceptable results.

12.7 The data review process is outlined in SVL 2009.

13.0 QUALITY CONTROL

13.1 Standardize the sodium thiosulfate with each batch of 20 or fewer samples. The normality must fall between 0.024 N and 0.026 N.

13.2 Analyze a method blank (10.3) at a frequency of one per batch of 20 or fewer samples. The recovery of the must be within ≤ ½ the reporting limit. If the recovery exceeds this criterion, re-analyze the method blank. If the recovery still exceeds the criterion, re-analyze all samples associated with the blank.

13.3 Analyze an LCS at a frequency of at least one per batch of 20 or fewer samples. The acceptance limits for the LCS recovery are from 80% to 120% of the true value. If an LCS recovery exceeds the criteria, re-analyze the LCS. If the recovery again falls outside these criteria, do not proceed with sample analysis.

13.4 Analyze a matrix spike (10.1.4) at a frequency of at least one per batch of 20 or fewer samples. The acceptance limits for the matrix spike recovery are 80% to 120% of the expected value. If the recovery is outside of this range, flag the client report.

13.5 Analyze a matrix spike duplicate (10.1.4) at a frequency of 1 per batch of 20 or fewer samples. Acceptance limits for the spike recovery are 80% to 120% (see 13.6). The control limit for the RPD between MS and MSD is 20%. If the MSD fails the recovery range or the RPD exceeds the control limit, flag the client report.

13.6 Annually a Quality Control Sample (QCS) (SVL uses ERA PT studies) must pass its study requirements; if needed, troubleshoot and repeat the study. Failure to pass a QCS annually will result in the removal of the test until a QCS is passed.

13.7 Analyze a Reporting Limit Check Standard (RLCS) at a frequency of at least one per batch of 20 or fewer samples. The acceptance limits for the RLCS recovery are from 70% to 130% of the true value. If an RLCS recovery exceeds the criteria, re-analyze the RLCS. If the recovery again falls outside these criteria, do not proceed with sample analysis.

14.0 REFERENCES

14.1 Method 4500-SF, Standard Methods for the Examination of Water and Wastewater, 20th edition.

14.2 Method 4500-SF, Standard Methods for the Examination of Water and Wastewater, 21st edition.

14.3 Standard Methods 4020, Standard Methods for the Examination of Water and Wastewater, 22nd edition. 2012.

15.0 POLLUTION PREVENTION

15.1 Efficient laboratory practices that reduce the need for re-digestions and/or re-extractions minimize contributions to pollution.

16.0 WASTE MANAGEMENT

16.1 Most chemicals used during digestion and/or analysis are neutralized and/or diluted prior to disposal by permit to the public sewer. Any hazardous chemicals and/or residues are disposed of through SVL's hazardous waste disposal system (see SOPs SVL 1001 & 1008).

17.0 CHANGE HISTORY

DATE	VERSION	CHANGE
05/14/09	10.0	Changed Section 1.0. 3.2 added "Sulfide is prone to oxidation by dissolved and atmospheric oxygen; therefore exposure to air should be minimal". Changed opening paragraph of Section 6.0. 8.0

		added "Open the sulfide template found at H:\Templates to enter calibration and sample data into". 8.1.3 changed to "5.0 mL". 8.1.7 changed to "Enter the amount of titrant used in the sulfide template". 8.23 added "5 mL". Made changes to Section 10.0. 11.1 added "Use the sulfide template found at H:\Templates to calculate the normality of the sodium thiosulfate titrant, iodine, and to calculate the sulfide concentration in samples. All calculations can be done manually using the following equations".
05/20/10	11.0	3.2 added "Samples should be received with as little headspace as possible to minimize oxidation by exposure to air". 4.4 added "Iodine is a severe corrosive. All possible precaution should be taken to ensure that no iodine comes in contact with skin or is inhaled or ingested. If Iodine makes contact with any flesh, flush immediately with water for at least fifteen minutes. If inhaled move immediately to fresh air. For any exposure get help ASAP". New requirements in Section 9.0. 12.2 changed to "The sulfide template is set up to import and export data compatibly with element. Under laboratory in the data entry/review bring up the bench sheet you are working with than "create" and "export" a temp file will come up select and save. Open the template and select the import icon then the temp file (this should populate the columns with the work order numbers from the bench sheet). Once finished Save to the sulfide file on H drive. Go to data entry/review and select open then H:\sulfide in the folder select the correct set of data and double click. This should import the data into the element data entry screen then "Save"".
06/06/11	12.0	Removed all references to raw analysis, all samples will be preserved with zinc acetate and NaOH. 10.1.10 added "Analyze a sample duplicate by following the steps outlined in 10.1.4 thru 10.1.9". 12.1 added "Procedures for

		constructing bench sheets can be found at R:\Promium Stuff\How to's\Batching.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the samples began". 12.1.1 added "Indicate all reagents used in the batch by including them in the reagent section of the "Batch" screen". 13.4 added "Analyze a sample duplicate at a frequency of at least one per batch of 20 or fewer samples. The control limit for the RPD between sample duplicates is 20%. If the RPD exceeds the control limit, flag the client report".
06/14/12	12.1	No changes.
08/24/12	12.2	6.14.1 added "Matrix spike solution (variable concentrations): Prepare a parent solution (LCS/MS) by adding 2.0 mL of 2N zinc acetate and 1 mL 6N NaOH to a 1 L volumetric flask. Using an ERA standard (6.14), mix parent vial then pipette 10.0 mL of the suspension to a 1 L volumetric flask. Dilute to mark with deionized water. Verify that the pH is above 9. Let precipitate settle for 30 minutes. True value varies based upon the lot number purchased; the value will be placed into Element". 10.1.4 added "Prepare a matrix spike and a matrix spike duplicate by spiking 20 mL of LCS/MS solution (6.14.1) into separate 100 mL like aliquots of the selected QC sample (as prepared in 10.1.5)". 13.2 added "≤ ½ the reporting limit". 13.6 added "Analyze a matrix spike (10.1.4) at a frequency of at least one per batch of 20 or fewer samples. The acceptance limits for the matrix spike recovery are 50 to 150% of the expected value. If the recovery is outside of this range, flag the client report". 13.7 added "Analyze a Matrix Spike Duplicate (10.1.4) at a frequency of 1 per batch of 20 or fewer samples. Acceptance limits for the spike recovery are 50 to 150% (see 13.6). The control limit for the RPD between MS and MSD is 20%. If the MSD fails the recovery range or the RPD exceeds the control limit, flag the client report". 13.12 added "Annually a Quality Control Sample (QCS) (SVL uses ERA PT studies) must

		pass its study requirements; if needed, troubleshoot and repeat the study. Failure to pass a QCS annually will result in the removal of the test until a QCS is passed". 14.2 added "Method 4500-SF, Standard Methods for the Examination of Water and Wastewater, 21st edition". 14.3 added "Standard Methods 4020, Standard Methods for the Examination of Water and Wastewater, 22nd edition. 2012".
13.0	09/17/13	6.14 changed to "1000mg/L Sulfide stock solution good for 1 month after opening 3 years unopened and refrigerated Absolute Standards, Inc . LCS: half fill a 100 mL volumetric flask with di-water added 0.25 mL 1000 mg/L stock solution preserve immediately with 0.2mL 2N Zinc Acetate and 0.1mL 6 N NaOH fill to 100 mL mark and check that pH >9 Let stand about 30 minutes before running. True Value for LCS =2.5mg/L." 6.14.1 changed to "Measure out 2-100mL allocates of sample to be spiked into secondary containers and check that the pH>9. To each container add 0.25mL of the 1000mg/L stock solution let stand 30 minutes before running. This equals a 2.5mg/L Matrix spike**."** 6.20 changed to "6.20 RLC half fill a 100 mL volumetric flask with di-water added 0.1 mL 1000 mg/L stock solution(6.14) preserve immediately with 0.2mL 2N Zinc Acetate and 0.1mL 6 N NaOH fill to 100 mL mark and check that pH >9 Let stand about 30 minutes before running. True Value for LCS =1.0mg/L." 10.1.4 changed to "0.25". Section 13.0 changed recoveries from 50-150 to 80-120%. 13.7 added "Analyze an RLCS at a frequency of at least one per batch of 20 or fewer samples. The acceptance limits for the RLCS recovery are from 70% to 130% of the true value. If an RLCS recovery exceeds the criteria, re-analyze the RLCS. If the recovery again falls outside these criteria, do not proceed with sample analysis."

TOTAL DISSOLVED SOLIDS AND TOTAL SUSPENDED SOLIDS

By SM 2540 C and SM 2540 D

Revised by: Michael Desmarais

Approved by: _____ **Date:** _____

Classical Chemistry Department Supervisor

Reviewed by: _____ **Date:** _____

Quality Assurance Manager

SVL Analytical, Inc.

I have read, understood and will comply with SOP (SVL 4034 Version 12.0)

Print Name	Signature	Date
Jerome Meier		
Anita Guzman-Freedle		
Robin Stribling		

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1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedure used for the determination of Total Dissolved Solids (TDS) and Total Suspended Solids (TSS) in drinking water, surface water, saline waters, and domestic and industrial wastes. SVL uses "Element" as our Laboratory Management Information System (LIMS), to manage client's samples. The reporting limit for TDS is 10.0 mg/L. The reporting limit for TSS is 5.0 mg/L. Definitions for words used in this SOP may be found in SVL's Quality Manual. The holding time for both analyses is 7 days when the samples are stored between 0-6ºC.

2.0 SUMMARY OF METHOD

The SOP is intended to satisfy the requirements of Standard Methods 2540C and 2540D. For TDS an aliquot of a sample is filtered through 1.2 µm filter paper into a previously weighed vessel. After evaporating and then baking the sample at 180ºC ± 2ºC, the vessel and remaining solids are weighed again. For TSS the glass fiber filter paper is dried at a temperature of 103 -105 ºC and weighed.

3.0 INTERFERENCES

3.1 Exclude large floating particles of submerged agglomerates of non-homogeneous materials from sample if it is determined that their inclusion is not representative.

3.2 Large concentrations of magnesium, calcium, and sulfate may leave residues that are hygroscopic. These residues may require prolonged drying.

3.3 Large residues may form a crust that traps water during the drying process. Sample volumes should be limited so that residues do not exceed 200 mg.

4.0 SAFETY

4.1 The drying ovens are hot. Care must be taken when handling beakers and pans to avoid burns.

5.0 EQUIPMENT, INSTRUMENTATION AND MATERIALS

Equivalent equipment, instruments, and materials may be used.

5.1 Drying oven, capable of maintaining 180ºC ± 2ºC, Thermolyne 9000.

5.2 Drying oven, capable of maintaining 103 -105ºC, Fisher Scientific

5.3 Filters: pre-weighed ProWeigh™ filters, Environmental Express, Cat # F93447MM or Whatman 47-mm GF/C, Millipore, Cat# AP4004700.

5.4 Beakers: 150 ml, 200 mL or 250 mL.

5.5 Analytical balance, capable of weighing to 0.0001 g, Mettler AE 240.

5.6 Gelman Sciences filtration apparatus.

6.0 REAGENTS AND STANDARDS

There are none

7.0 INSTRUMENT SETTINGS

7.1 Ensure that the oven temperature is within the required range before putting samples in the oven.

7.2 If the observed temperature is outside the range specified for that oven, check that the set point is correct and recheck the temperature after 20-minutes. If the temperature remains outside the specified range, adjust the set point and recheck after 20-minutes. Record in the logbook any changes to the set point. If the temperature continues to be out of range, notify the Department Supervisor.

7.3 If a temperature is observed outside the oven's limits (internal temperature should be given time to equilibrate, no readings should be taken right after opening and closing the ovens doors) any samples that are within the oven should be transferred to an oven that can maintain the required temperature.

8.0 CALIBRATION

8.1 The analytical balance must be serviced and calibrated every year.

8.2 The analyst must check the calibration of the analytical balance each day before use (see SVL 1025).

8.3 Digital temperature readouts are verified quarterly according to SVL 1004.

9.0 SAMPLE HANDLING AND PRESERVATION

9.1 Samples must be analyzed within 7 days when stored between 0-6°C.

10.0 SAMPLE PREPARATION AND ANALYSIS

For TDS by SM 2540C:

10.1 Wash beakers according to the procedure listed in SOP 4013

10.2 Dry beakers in oven for 1 hour at 180°C ± 2ºC.

10.3 Allow beakers to cool to room temperature in desiccator for at least one hour.

10.4 Weigh beakers to 4 decimal places (0.0001 g) and record the weight under “Tare Weight (g)” column (see TDS/TSS template located at H:\Templates\TDS_TSS Worksheet.xls).

10.5 Assemble the vacuum filtration apparatus.

10.6 Filter a 100 mL or smaller aliquot (choose a volume that will yield between 2.5 and 200 mg dried residue) of sample through a GF/C filter into a pre-weighed beaker.

10.6.1 After sample transfer, rinse filtration flask with 3 separate 10 mL aliquots of deionized water (allow complete drainage between rinses), adding the rinse solution to the pre-weighed beaker.

10.6.2 Continue suction for about 3 minutes or until no liquid is drawn from the filter.

10.6.3 If a sample takes more than 10 minutes to filter decrease the

sample volume and repeat 10.6 to 10.6.2.

10.7 Prepare a sample duplicate by following the process outlined in 10.6 using a similar aliquot of sample.

10.8 Evaporate to the contents of the beakers to dryness at 140°C (monitor beakers for any splattering of contents). Record oven temperature on benchsheet.

10.9 Transfer beakers to 180°C ± 2°C oven and bake for one hour.

10.10 Record the date and time the beakers are placed in the oven.

10.11 SM 2540 C requires the samples to be dried to a constant weight. Weigh and compare every sample (including duplicate) until a constant weight is verified.

10.11.1 Remove the samples from the oven and let them cool in the desiccator for about 1 hour.

10.11.2 Weigh the samples individually to 4 decimal places and record the weights (notate under “Prelim Weight (g)” column of the TDS/TSS template).

10.11.3 Return the samples to the oven for a minimum of hour at 180°C. Remove the samples from the oven and as before, allow them to cool in the desiccator for about 1 hour.

10.11.4 Again, weigh the samples individually to 4 decimal places and record the weights (notate under the “Final Weight (g)” column of the TDS/TSS template).

10.11.5 If the number generated in the “Result (mg/L)” column is greater than 0.5 mg or 4% of the preliminary weight then the template will display a “NOT DRY” in the “Constant Weight?” column of the TDS/TSS template for any of the samples, then the samples must be returned to the oven. The process must be repeated until a constant weight is obtained within 0.5 mg or there is a less than 4% difference from the previous weighing (whichever is less), this will be indicated as “DRY” under the same “Constant Weight?’ column.

10.11.6 Record the date and time the beakers were removed from the oven.

10.12 If the sample volume yields more than 200 mg of residue by weight (i.e. 2000 mg/L in a 100 mL volume, or 20,000 mg/L in a 10 mL volume) re-analyze the sample with a smaller volume.

10.12.1 If residue is in excess and a smaller volume is not applicable qualify the result with the E11 qualifier "Sample exceeds method specified limit for solids content".

10.13 TDS and TSS can be run using the same sample. For TSS follow all the steps out lined in 10.14 thru 10.20.

10.13.1 After filtering the TSS collect the filtrate and run a TDS analysis on it following the steps outlined in 10.6 thru 10.6.3 and then by 10.8 thru 10.12.

10.13.2 The TSS duplicate sample would also be assigned as a duplicate under the TDS analysis.

For TSS by SM 2540 D:

10.14 Record the weights of the ProWeigh™ filters on the benchsheet.

10.14.1 If ProWeigh™ filters are not available, condition GF/C filters by washing with deionized water through filter funnel, dry at 103-105 ºC, cool in a desiccator, weigh, and record the weights on the TDS/TSS template under the "Tare Weight (g)" column.

10.15 Filter 100 mL aliquot of sample (choose a volume that will yield between 2.5 and 200 mg dried residue). Record the sample volume on the TDS/TSS template in mL.

10.16 Prepare a sample duplicate by filtering another 100 mL or smaller aliquot of sample. Record the sample volume on the TDS/TSS template in mL.

10.17 Dry filters in oven for a minimum of one hour at 103 -105°C.

10.18 Record the date and time the filters are placed in the oven.

10.19 SM 2540 D requires the samples/filters be dried to a constant weight. Weigh and compare every sample/filter until a constant weight is verified.

10.19.1 Remove the samples from the oven and let them cool in the desiccator for about 30 minutes.

10.19.2 Weigh the samples individually to 4 decimal places and record the

weights (under "Prelim Weight (g)" column of the TDS/TSS template).

10.19.3 Return the samples to the oven for a minimum of one hour at 105°C. Remove the samples from the oven and as before, allow them to cool in the desiccator for about 1 hour.

10.19.4 Again, weigh the samples individually to 4 decimal places and record the weights (notate under the "Final Weight (g)" column of the TDS/TSS template).

10.19.5 If the number generated in the "Result (mg/L)" column is greater than 0.5 mg or 4% of the preliminary weight then the template will display a "NOT DRY" in the "Constant Weight?" column of the TDS/TSS template for any of the samples, then the samples must be returned to the oven. The process must be repeated until a constant weight is obtained within 0.5 mg or there is a less than 4% difference from the previous weighing (whichever is less), this will be indicated as "DRY" under the same "Constant Weight?' column.

10.19.6 Record the date and time the filters are removed from the oven.

10.20 Samples may contain contaminants that volatize slowly thus not allowing a stable reading from the balance; therefore, after the fourth weighing of a sample it will be reported with the appropriate qualifier.

11.0 DATA REDUCTION

11.1 Calculation for TDS:

Dissolved Solids (mg/L) = (B – A) x 1000 / (mL of sample)

Where:

A = weight of beaker (in mg)

B = weight of dried residue + beaker (in mg)

11.2 Calculation for TSS:

TSS (mg/L) = (B – A) x 1000 / (mL of sample)

Where:

A = weight of filter (in mg)

B = weight of dried residue + filter (in mg)

11.3 Calculations can be found in SVL 1028.

12.0 DATA AND RECORDS MANAGEMENT

12.1 Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batching.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the samples began.

12.2 On the benchsheet record the date and times the samples were entered/removed from oven. Record the balance or oven used on the benchsheet.

12.2.1 In Element change sample status from batched to prepared once samples are placed in the oven.

12.3 Record the work order number, the sample numbers and conductivity, on the spreadsheet/template. Record any dilution factors as well.

12.4 WinWedge will transfer balance readings directly into an Excel spreadsheet which will be saved by the batch number followed by –TSS or -TDS in the H:\TDS_TSS folder.

12.5 Attach a copy of the spreadsheet to the benchsheet.

12.6 The analyst will upload the Excel spreadsheet into Element. They shall perform all reviews on the "Data Entry/Review" page in Element and verify their data uploads.

12.7 If input comes up color coded, apply the appropriate data flags or undertake any corrective actions.

12.8 The analyst shall assign any qualifiers, update the status of the batch to "Analyzed", and lock the results so that any future imports will not

overwrite acceptable results.

12.9 The data review process is outlined in SVL 2009.

13.0 QUALITY CONTROL

13.1 Analyze a method blank (100 mL of deionized water) at a frequency of at least one per batch of 20 or fewer samples. Passing criteria must be ≤ ½ the reporting limit.

13.2 Analyze a sample duplicate at a frequency of at least one per batch of 10 or fewer samples. Duplicate determinations should agree within 5% of their average weight. If outside of this percentage flag the report.

14.0 REFERENCES

14.1 Method 2540C. Standard Methods for the Examination of Water and Wastewater. 20th Edition, 1999.

14.2 Method 2540D. Standard Methods for the Examination of Water and Wastewater. 20th Edition, 1999.

14.3 Standard Methods 2020, Standard Methods for the Examination of Water and Wastewater, 22nd edition. 2012.

14.4 Manual for the Certification of Laboratories Analyzing Drinking Water, Fifth Edition.

15.0 POLLUTION PREVENTION

15.1 There is no pollution associated with this method.

16.0 WASTE MANAGEMENT

16.1 There is no waste generated with this method.

17.0 CHANGE HISTORY

DATE	VERSION	CHANGE
01/06/09	9.1	Changed section 1.0. 6.0 changed to "There are none". Changed the following sections: 10.0, 12.0 and 13.0. Comparisons can be made against SOPs in the archive. Changed 15.1 to "There is no pollution associated with this method".
10/09/09	9.2	10.6.1 added "After transfer, rinse filtration flask with deionized water and add the rinse solution to the pre-weighed beaker".
03/04/11	10.1	10.6.3 added "If a sample takes more than 10 minutes to filter decrease the sample volume and repeat 10.6 to 10.6.2". 12.2.1 added "In Element change sample status from batched to prepared once samples are placed in the oven". Added 13.1 "Analyze a method blank (100 mL of deionized water) at a frequency of at least one per batch of 20 or fewer samples. Passing criteria must be less than the method reporting limit".
03/01/12	11.0	7.3 added "If a temperature is observed outside the oven's limits (internal temperature should be given time to equilibrate, no readings should be taken right after opening and closing the ovens doors) any samples that are within the oven should be transferred to an oven that can maintain the required temperature". 10.11.1 added "about". 10.13 added "TDS and TSS can be run using the same sample. For TSS follow all the steps out lined in 10.14 thru 10.20". 10.13.1 added "After filtering the TSS collect the filtrate and run a TDS analysis on it following the steps outlined in 10.6 thru 10.6.3 and then by 10.8 thru 10.12". 10.12.1 added "If residue is in excess and a smaller volume is not applicable qualify the result with the E11 qualifier "Sample exceeds method specified limit for solids content"". 10.13.2 added "The TSS duplicate sample would also be assigned as a duplicate under the TDS analysis".

DATE	VERSION	CHANGE
08/27/12	11.1	3.1 added "Exclude large floating particles of submerged agglomerates of non-homogeneous materials from sample if it is determined that their inclusion is not representative". 10.6 changed to "2.5 and 200 mg dried residue". 10.9 added "± 2°C". 10.15 changed to "(choose a volume that will yield between 2.5 and 200 mg dried residue)". 10.17 changed to "one". 13.1 changed to "≤ ½ the reporting limit". 14.3 added "Standard Methods 2020, Standard Methods for the Examination of Water and Wastewater, 22nd edition. 2012".
09/13/13	12.0	8.3 added "Digital temperature readouts are verified quarterly according to SVL 1004." 10.8 changed to "Evaporate to the contents of the beakers to dryness at 140°C (monitor beakers for any splattering of contents). Record oven temperature on benchsheet." Re-wrote Section 12.0.

NITRATE/NITRITE AS NITROGEN: AUTOMATED CADMIUM REDUCTION By EPA 353.2

Revised by: Michael Desmarais

Approved by: _____ Date: _____
Classical Chemistry Department Supervisor

Reviewed by: _____ Date: _____
Quality Assurance Manager

SVL Analytical, Inc.

I have read, understood and will comply with SOP (SVL 4048 Version 15.0)

Print Name	Signature	Date
Andrew Popchock		
Sherry Maine		

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1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedure used at SVL to determine nitrate/nitrite by using an Astoria 2 AutoAnalyzer. This SOP is applicable to drinking water and wastewater. SVL uses a Laboratory Information Management System (LIMS) – Element, to manage client's samples. In Element the current aqueous nitrite + nitrite as N MDL is 0.01 mg/L and the RL is 0.05 mg/L. The current soil MDL is 0.23 mg/L and RL is 0.5 mg/L. Definitions for words used in this SOP may be found in SVL's Quality Manual. The holding time is 28 days for combined nitrate/nitrite (if preserved correctly). Samples for nitrate/nitrite should be preserved with H_2SO_4 to a pH <2 and refrigerated between 0-6°C.

2.0 SUMMARY OF METHOD

The purpose of this SOP is to describe the procedure used for the determination of combined nitrate and nitrite (measured as nitrogen) by automated cadmium reduction. The SOP is intended to satisfy the requirements of EPA Method 353.2. The pH of a sample aliquot is adjusted to between 5 and 9. An aliquot of sample is passed through an open tubular cadmium reactor to reduce nitrate to nitrite. A flow injection autoanalyzer creates a reaction in the aliquot with sulfanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride producing an azo dye. Concentration is measured as a function of absorbance of the dye at 540 nm.

3.0 INTERFERENCES

3.1 Build-up of suspended matter in the reduction coil will restrict sample flow. The sample may be filtered before analysis to remove particulate matter.

3.2 High concentrations of iron, copper may cause low results. Stock ammonia chloride-EDTA solution (6.4) is added to the sample to complex the heavy metals.

3.3 Free chlorine may cause low results by limiting the reduction efficiency of the coil. If detected, sodium thiosulfate (6.34) may be added (amount to be determined by the analyst) to the sample to reduce the chlorine. Samples may also be diluted to manage interference caused by free chlorine.

3.4 Oil or any highly organic solution may coat the cadmium in the coil. The

oil may be removed from samples by extracting them with hexane before analysis. Samples may also be diluted to manage interference caused by oil or any highly organic solution.

4.0 SAFETY

4.1 Hydrochloric acid can cause severe burns if it comes into contact with skin or eyes. The fumes are also irritating to nasal and lung tissues. Work with hydrochloric acid in a hood. Wear safety glasses or goggles. Wear gloves and a lab coat or an apron. In the case of exposure, flush with water for at least fifteen minutes.

4.2 Phosphoric acid can cause severe burns if it comes into contact with skin or eyes. Work with phosphoric acid in a hood. Wear safety glasses or goggles. Wear gloves and a lab coat or an apron. In the case of exposure, flush with water for at least fifteen minutes.

4.3 Sulfuric acid can cause severe burns if it comes into contact with skin or eyes. Work with sulfuric acid in a hood. Wear safety glasses or goggles. Wear gloves and a lab coat or an apron. In the case of exposure, flush with water for at least fifteen minutes.

4.4 Cadmium and copper sulfate are environmental hazards. Take care not to spill them. Dispose of them in appropriate waste containers.

4.5 Ammonium hydroxide can cause severe burns if it comes into contact with skin or eyes. Work with ammonium hydroxide in a hood. Wear safety glasses or goggles. Wear gloves and a lab coat or an apron. In the event of exposure, flush with water for at least fifteen minutes.

5.0 EQUIPMENT/APPARATUS AND MATERIALS

Equivalent equipment, instrumentation and materials may be used.

5.1 Astoria 2 AutoAnalyzer, S/N 200104; with 311XYZ Autosampler, S/N 4632A11096

5.2 Volumetric Flasks: 100 mL, 50 mL, Class-A

Graduated Cylinders: 100 mL, 50 mL, Class-A

5.3 Micropipets, Lambda, S/N 378437 and 380236; Fisher, S/N EH87017

5.4 Open Tubular Cadmium Reactor (OTCR) Astoria-Pacific p/n 303-0500-24

5.5 Autosampler Vials

5.6 FASPacII operating program

5.7 Syringe Filter, 0.45 µm, Environmental Express

5.8 Nitrogen gas

5.9 pH meter, Beckman

5.10 Chlorine test strips, Hydron QT catalog CM240

5.11 Kimwipes®

6.0 REAGENTS AND STANDARDS

Guidelines for the storage, tracking and expiration of chemicals and reagents can be found in SVL 1032. The procedure for purchasing chemicals and reagents can be found in SVL 1015. Any exceptions to the above mentioned SOPs will be found in this section: as well as, all of the preparatory steps needed to construct or prepare reagents, and standards. Equivalent reagents or standards may be used.

6.1 Disodium EDTA: ethylenediamine tetraacetic acid, disodium salt, dihydrate, $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$, Fisher Reagent grade. Cat. # O2793-500.

6.2 Ammonium hydroxide, concentrated, NH_4OH, Fisher Reagent grade. Cat. # A669S-212.

6.3 Ammonium chloride, NH_4Cl, VWR Cat #: BDH0208-2KG.

6.4 Stock ammonium chloride–EDTA buffer, pH 8.5: Dissolve 255 g of ammonium chloride (6.3) and 0.3 g of disodium EDTA (6.1) in about 3 liters of deionized water (6.27) in an appropriate container. Adjust the pH to 8.5 with concentrated ammonium hydroxide (6.2). Filter through a 0.45 µm filter before using if particles are present. The expiration date is two months after date of preparation.

6.5 BRIJ-35, Polyoxyethylene 23 lauryl ether, 20-30% solution. Astoria Pacific Product # 90-0710-32.

6.6 Working ammonium chloride–EDTA buffer solution: Add about 2 mL of a 20% or 1mL of 30% BRIJ-35 solution (6.5) to 500 mL of stock ammonium chloride – EDTA buffer (6.4). Mix gently, trying not to introduce air in order to minimize formation of foam.

6.7 Phosphoric acid, concentrated, H_3PO_4, Fisher, Cat. # A242- 212.

6.8 Sulfanilamide, $C_6H_8N_2O_2S$, GFS Chemicals, CAS # 7631-99-4.

6.9 N-(1-naphthyl) ethylenediamine dihydrochloride 96%, Alfa Aesar CAS #: 1465-25-4.

6.10 Color Reagent: Carefully dissolve 50 mL of concentrated phosphoric acid (6.7) in about 200 mL of deionized water (6.27). Dissolve 20.0 g of sulfanilamide (6.8), and 1.0 g of N-(1-napthyl) ethylenediamine dihydrochloride (6.9) in the solution. Warm this solution if necessary to dissolve the chemicals. Dilute to 500 mL with deionized water and mix well. Filter through a 0.45 µm filter before using if particles are present. Store solution in a brown bottle and keep in a refrigerator. Take out and warm the solution to room temperature before using. The expiration date is one month after date of preparation.

6.11 Sodium nitrite, $NaNO_2$, EM GR grade, or equivalent, dried in a 100 to 105° C oven. Cat. # SX0665-1.

6.12 Sodium nitrate, $NaNO_3$, EMD, CAS #: 7631-99-4, dried in a 100 to 105°C oven.

6.13 Stock nitrite solution (1000 mg/L): Weigh out 0.4926 g of sodium nitrite (6.11). Dissolve in about 40 mL of deionized water (6.27). Dilute to 100 mL with deionized water. Add 0.2 mL chloroform (6.28) to stabilize the solution. Store the solution in a refrigerator. The expiration date of this solution is six months after date of preparation.

6.14 Stock nitrate solution (1000 mg/L): Weigh out 0.6068 g of sodium nitrate (6.12). Dissolve in about 40 mL of deionized water (6.27). Dilute to 100 mL with deionized water. Add 0.2 mL chloroform (6.28) to stabilize the solution. Store the solution in a refrigerator. The expiration date of this solution is six months after date of preparation.

6.15 Intermediate nitrate solution (100 mg/L): Dilute 10.0 mL of stock nitrate solution (6.14) with deionized water (6.27) to 100 mL in a volumetric flask. Mix well. Store the solution in a refrigerator. The expiration date of this solution is two weeks after date of preparation.

6.16 Secondary source sodium nitrate, NaNO3, Baker, Cat. #: 3770, or equivalent, dried in a 100 to 105°C oven.

6.17 Secondary stock nitrate solution (1000 mg/L) for preparation of ICV/LCS: Weigh out 1.5170 g of sodium nitrate (6.16). Dissolve in about 100 mL of deionized water (6.27). Dilute to 250 mL with deionized water. Add 0.5 mL chloroform (6.28) to stabilize the solution. Store the solution in a refrigerator. The expiration date of this solution is six months after date of preparation.

6.17.1 Intermediate secondary nitrate solution (100 mg/L): Dilute 10.0 mL of secondary stock nitrate solution (6.17) with deionized water (6.27) to 100 mL in a volumetric flask. Mix well. Store the solution in a refrigerator. The expiration date of this solution is two weeks after date of preparation.

6.18 Sulfuric acid, concentrated, J.T. Baker, Cat. # 9673-33.

6.19 Copper sulfate, pentahydrate: $CuSO_4 \cdot 5H_20$, Fisher Reagent grade, Cat. # C495-500.

6.20 Copper sulfate solution (2%): Dissolve 20.0 g copper sulfate pentahydrate (6.19) in approximately 900 mL of deionized water (6.27). Dilute to 1 L with deionized water in a volumetric flask. Mix well. Expiration date is six months from the time the solution is prepared.

6.21 1N hydrochloric acid (recharging coil): Carefully add 83 mL of concentrated hydrochloric (6.29) acid to about 100 mL of deionized water (6.27). Dilute to 1000 mL with deionized water. Mix well.

6.22 1:1 sulfuric acid: Slowly add 500 mL of concentrated sulfuric acid (6.18) to 500 mL of deionized water (6.27), with stirring. WARNING! This process produces heat! Use an ice bath! Mix well.

6.23 1:3 sulfuric acid: Carefully add 25 mL of concentrated sulfuric acid (6.18) to 50 mL of deionized water (6.27) with stirring. WARNING! The process produces heat! Mix well.

6.24 Hexane, Fisher, Cat. # H306.

6.25 Startup/shutdown solution: Dissolve 4.0 mL of a 20% or 2 mL of a 30% BRIJ-35 solution (6.5) in 1 L deionized water (6.27). Prepare fresh each day of analysis.

6.26 pH adjusted deionized water: Fill a 2 L container with deionized water (6.27). Adjust the pH of the water to approximately 8.3 using ammonium hydroxide (6.2). Use this water for blanks, sample dilution, and calibration standards. Prepare fresh each day of analysis.

6.27 Type I deionized water.

6.28 Chloroform: Fisher, Cat. # C298SK-4.

6.29 Concentrated hydrochloric acid, Fisher Reagent Grade, Cat. # A142-212.

6.30 PFTE Boiling Stones, Chemware Cat. # D1069103.

6.31 Bleach solution, Chlorox.

6.32 Chemwash solution, add 50 mL of bleach (6.31) to 950 mL of deionized water (6.27). Mix well.

6.33 $Na_2S_2O_3 \cdot 5\ H_2O$, Fisher Reagent Grad, Cat. #S445-500.

6.34 Dechlorinating reagent: dissolve 0.175 g $Na_2S_2O_3 \cdot 5\ H_2O$ (6.33) in water and dilute to 100 mL. Prepare fresh weekly; use 0.1 mL reagent to remove 1 mg/L residual chlorine in a 25 mL sample.

7.0 INSTRUMENT SETTINGS

7.1 Turn on the instrument and sampler by means of the toggle switches on the backs of the respective equipment.

7.2 Start FASPac II software. Click the “connect” icon (next to green light). Click menu arrow for “current configuration.” Window. Select the “Nitrate” configuration, the software will prompt user for run name. Enter today’s date and an A, B, C etc. to indicate run name. Click “OK”, software will bring up template table, channel window and run table.

Verify that the sample line from the autosampler is connected to the

sample line on the nitrate/nitrite cartridge.

7.3 Place all the pump tubes (including sampler wash line) in fresh deionized water (6.27). Open valve on N_2 pillow, start pumps before clamping down the platens (red button on top and back of instrument). Allow deionized water to pump for 10 minutes.

7.4 Place all tubes, including the sampler wash line, in chemwash (6.32) container and allow solution to run for 10 minutes.

7.5 Prepare fresh startup/shutdown solution and fresh sampler wash solution (6.25). Cover solutions with Parafilm. After ten minutes of flushing with chemwash, place all applicable reagent lines (wipe lines down with Kimwipes®) in the startup/shutdown solution. Place the autosampler wash line into sampler wash solution. Pump for another 10 minutes.

7.6 Visually inspect for good flow. The bubble pattern should be evenly spaced and the shape of the bubbles should be like a capsule with well rounded ends. The capsules should move through the tubing without tearing.

7.7 Check the baseline by right clicking on the channel window and selecting display signal. Next, right click and select “zero signal all”. Monitor for several minutes – baseline should be flat and smooth.

7.8 Prepare reagents: refill 500 mL bottle with color reagent (6.10). Warm to room temperature. Add 2 mL of 20% BRIJ or 1 mL of 30% BRIJ (6.5) to 500 mL of buffer (6.4). Cover both with Parafilm. Allow baseline to stabilize while in the startup/shutdown solution. Transfer tubes to the appropriate reagent bottles (be sure to wipe down tubes with Kimwipes before insertion). Pump solutions for 10 minutes to allow system to equilibrate.

7.9 Check reagent baseline for any fluctuations or drift. If baseline is stable with a solid bubble pattern then connect the OTCR. Unhook “out” tubing first, then connect the “in” tubing followed by reconnecting the “out” tubing (keep air from entering the OTCR). Allow the instrument to stabilize for at least five minutes. If the OTCR is new or the reducing efficiency is <90%, activate or re-activate the OTCR in the following steps (7.9.1 to 7.9.6)

7.9.1 Activate the Open Tubular Cadmium Reactor (OTCR).

7.9.2 Detach metal nipple from the EVA tubing at one end of the OTCR.

7.9.3 Flush with deionized water (6.27) (no BRIJ) using a 10 mL syringe fitted with a union.

7.9.4 Quickly flush with 10 mL 1 N hydrochloric acid (6.21). Then rinse with 30 mL deionized water (6.27). It is important to complete this step quickly because leaving the HCl in the coil for more than 2-3 seconds can cause pitting of the coil.

7.9.5 Slowly flush the OTCR with 10 mL of the 2% copper sulfate solution (6.20), using a 10 mL syringe fitted with a union. Repeat.

7.9.6 Forcefully flush the OTCR with deionized water (6.27) until no more loose copper particles are washed out.

7.9.7 Quickly flush coil with buffer and connect to instrument.

7.9.8 Allow the instrument to stabilize for at least five minutes.

7.9.9 When not in use, store the OTCR with NH_4CL Buffer (6.6) in it. Storing air in the OTCR can lead to pitting.

7.10 Enter sample IDs into table along with any additional information (dilutions, repeats etc.). It is not necessary to enter the CCVs, CCBs or auto wash as these are automatically inserted by the software.

Note:
Select “File” and save after entering all the samples.

8.0 CALIBRATION

8.1 Prepare the following calibration standards while the instrument warms up. Dilute the below volumes of the intermediate nitrate solution (6.15) in 100 mL volumetric flasks. Bring solution up to volume with pH adjusted deionized water (6.26).

Standard	Amount of Intermediate	Final Volume
0.05 mg/L	50 µL	100 mL
0.10 mg/L	100 µL	100 mL
0.50 mg/L	500 µL	100 mL
1.00 mg/L	1.00 mL	100 mL

3.00 mg/L	3.00 mL	100 mL
5.00 mg/L	5.00 mL	100 mL

8.2 Prepare a Reporting Limit Check Standard (RLCS). This standard can be made from either primary or secondary sources but it must be made fresh and not a re-pour or re-dilution of the calibration standard. The concentration of the standard will be at the reporting limit.

8.2.1 Prepare the RLCS by diluting 0.05 mL of intermediate nitrate solution (6.15) to final volume of 100 mL with pH adjusted water (6.26).

8.3 Prepare a standard for use as both the ICV and LCS by diluting 0.20 mL of the secondary stock nitrate solution (6.17) to 100 mL with pH adjusted deionized water (6.26). This will result in a 2.0 mg/L nitrate concentration.

8.4 Prepare a nitrite check solution, dilute 0.2 mL of the primary stock nitrite solution (6.13) to 100 ml with deionized water (6.27). This will result in a 2.0 mg/L nitrite concentration.

8.5 Prepare a column check solution. Use 0.20 mL of the secondary stock nitrate solution (6.17) to 100 mL with pH adjusted deionized water (6.29). This will result in a 2.0 mg/L nitrate concentration.

8.6 Prepare a CCV by diluting 2.0 mL of the intermediate nitrate solution (6.15) to 100 ml with deionized water (6.27).

8.7 Reminder: Use the nitrate standards for the nitrate + nitrite analysis.

8.8 For the analysis use pH adjusted deionized water (6.26) as the ICB and CCBs.

8.10 Place appropriate standards in the autosampler in order of decreasing concentration.

9.0 SAMPLE HANDLING AND PRESERVATION

9.1 Aqueous samples for combined nitrate + nitrite should have been preserved in the field with sulfuric acid to a pH<2. They should be refrigerated between 0-6 ºC. Nitrate + nitrite has a holding time of 28 days.

9.2 Prior to analysis, adjust the pH to between 5 and 9 with either 1:3 sulfuric acid or concentrated ammonium hydroxide. If the sample becomes turbid after neutralization, filter it with a 0.45 µm syringe filter (or centrifuge, if necessary).

10.0 SAMPLE PREPARATION and ANALYSIS

10.1 For aqueous samples, pour aliquots into autosampler vials (3/4 full). If a CCV fail is observed, test the preceding 10 samples with chlorine test strips. If positive, dilute sample or use de-chlorinating reagent (6.33) to manage interference.

10.1.1 Prepare a method blank by pouring pH-adjusted deionized water (6.26) into an autosampler vial.

10.1.2 Prepare a LCS by pouring an aliquot of the prepared 2.0 ppm secondary (8.3) nitrate into an autosampler vial (3/4 full).

10.1.3 Prepare a matrix spike by measuring a 5 mL aliquot of sample into a dilution tube. Add 200 µL of the intermediate nitrate solution (6.15) and bring up to 10.0 mL with more sample. This constitutes a 2.0 mg/L spike add.

10.1.4 Prepare a matrix spike duplicate. Prepare in the same manner as 10.1.3.

10. 2 For soil samples extract the samples prior to analysis. Weigh 5.0 g of sample into a centrifuge tube. Fill with 50 mL of deionized water (6.27) and cap the tube. Shake tubes by hand to loosen sample from the bottom of the tubes. Place tubes in shaker for thirty minutes, then centrifuge for ten minutes at 3000 RPM. Decant then filter the supernatant with a 0.45 µL filter prior to placing the samples into auto sampler tray.

10.2.1 Prepare a method blank by adding 5.0 g of boiling stones (6.30) and add 50 mL deionized water (6.27) into a centrifuge tube.

10.2.2 Prepare a LCS by weighing 0.5 g of ERA “Anions in Soil” and add 50 mL of deionized water. The soil LCS true value will vary dependent upon the ERA lot used.

10.2.3 Prepare a matrix spike by repeating 10.2 with a similar aliquot of soil. Add 49.5 mL of deionized water (6.27). Add 0.5 mL of 100

PPM intermediate nitrate solution (6.15). This constitutes a 1.0 mg/L spike add.

10.2.4 Prepare a matrix spike duplicate. Prepare in the same manner as 10.2.3.

10.3 Load the calibration standards, RLCS, ICV, ICB, method blank, LCS, samples, matrix spikes, matrix spike duplicates, CCVs, and CCBs onto the autosampler.

10.4 Prior to analyzing, load the nitrate (2.0 mg/L concentration) standard followed by the "Column Check" nitrite (2.0 mg/L concentration) standard, after the SYNC Peak standard is loaded. The condition of the coil is monitored with the NOX% function in the table.

10.4.1 Ensure the column check function is 90% or greater.

10.5 When all the standards, QC and samples are loaded click the green "Go" button. The software will prompt for LCS and ICV check samples – click "Yes" for both.

10.6 To add samples during the course of a run, observe that sampler is not currently sampling from the PAUSE cup or any other software inserted cups. Enter new sample labels at the end of the sequence in the sample table and not in the run table (ensure appropriate cup positions). Data collection and sampler can be paused separately as long as the analyst first pauses the sampler, waits for the data collection to reach the sample cup the sampler is paused at, and then pauses data collection. The sample at which both the sampler and data collection were paused will automatically be RR.

10.7 To pause during a run.

10.7.1 Ensure sampler is not engaged in drawing sample from the QC or any other PAUSE cup. It is in the analyst best interest if the yellow bar in the run table is at least three positions away from any of the above.

10.7.2 Click on the desired cell in the position column. Hold the control key and "N". The software will prompt for a rack position. Enter location and click "Ok".

10.7.3 Click on "Identifier" cell and type "PAUSE". Hit enter. Ensure that

"pause" appears in the "type" column. Allow auto-update timer to catch up. Fill tube with deionized water and place in correct rack position.

10.7.4 The Run Table will insert SYNC, CCV, CCB and two auto washes after sampling from the PAUSE cup. The probe will move to its "Rest" position in the corner. Data collection will catch up and pause after about seven minutes.

10.7.5 When ready to continue analysis, click the green "Go" button. The software will prompt to be started click "Yes".

10.7.6 At the end of the run, remove the OTCR by disconnecting the outlet first, then the inlet. Flush the OTCR with buffer (6.4) which contains no brij. Do not allow any air bubbles to be stored in the OTCR.

11.0 DATA REDUCTION

11.1 SVL has chosen to use the instrument generated quadratic calibration curve. The curve measures absorbance (peak height) versus concentration. The correlation coefficient must be at least 0.995. If the correlation coefficient is less than 0.995, re-calibrate the instrument prior to analyzing samples. The software will calculate results based upon the curve.

11.1.1 Use the calibration verification template (located at H:\Templates\Calibration Curve Check) to verify the curve – select the quadratic function. There is a 30% acceptance range for the low standard and a 10% acceptance range for the remaining calibration standards. As long as the minimum number of calibration standards are maintained, the low and high standards may be removed and the calibration used; otherwise re-calibrate the instrument.

11.2 Calculations for procedures outlined in the SOP, may be found in SVL 1028.

11.3 If the result exceeds the highest calibration standard, dilute the sample and re-analyze it.

12.0 DATA AND RECORDS MANAGEMENT

12.1 Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batches.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the samples began.

12.2 After analysis is completed, go to the show report icon – click on it. In the report screen go to "file" and then "properties". Double check that the cup position, comment, dates, time, total dilution, corrected peak height and correct status "flags" are selected. Click "OK" then go to "file" and "print". Use the pdfFactory pro software to create an electronic "printout" of the report. Use the "highlight" tool to highlight the samples run in each batch. Use the "stylus" tool to make any necessary comments. Save the pdf file in the appropriate data folder. Indicate on the bench sheet the file name and highlight color used.

12.3 Data Tool is used to upload the data into Element.

12.4 In the main screen go to "File" then "Export" then "Results", choose one of the five export files. Overwrite and save file.

12.5 Locate the Export folder on the desktop and open the file. Change the column heading from "Channel 1" to "mg/l." Save and close the file.

12.6 In Element, the analyst shall perform all reviews on the "Data Entry/Review" page and verify their data uploads.

12.7 If an input comes up color coded, apply the appropriate data flags or undertake any corrective actions.

12.8 The analyst shall assign any qualifiers.

12.9 The analyst will then update the status of the batch to "Analyzed".

12.10 The analyst will then lock the results so that any future imports will not overwrite acceptable results.

12.11 The data review process is outlined in SVL 2009.

13.0 QUALITY CONTROL

13.1 Prepare and analyze an RLCS (8.2). This standard will be prepared from either a primary or secondary source at a concentration that reflects the current reporting limit. Run this standard once per run before the ICV. Acceptance limits are 70 to 130%. If the recovery falls outside these limits, re-analyze the RLCS. If the recovery still falls outside these limits, re-calibrate the instrument. The results of the RLCS will be tracked to show the viability of the current reporting limit.

13.2 Analyze a "mid-range" standard as an ICV (8.3) (this standard covers the QCS requirements) immediately after the calibration standards. The recovery must lie between 90 and 110% of the expected value. If the recovery lies outside the limits, re-analyze the ICV. If the recovery still lies outside the limits, re-calibrate the instrument.

13.3 Analyze a "mid-range" standard as a CCV (8.6) after every ten samples or fewer and at the end of the run. The recovery must lie between 90 and 110% of the expected value. If the recovery lies outside the limits, re-analyze the CCV. If the recovery still lies outside the limits, re-calibrate the instrument and re-analyze the samples run since the last successful CCV**.**

13.4 Analyze an ICB after the ICV and a CCB after every CCV (8.8). If a blank exceeds the RL, re-analyze the blank. If the blank still exceeds the RL, re-calibrate the instrument and re-analyze any associated samples ran before and after the failure.

13.5 Analyze a method blank (10.1.1) and (10.2.1) at a frequency of 1 per batch of 20 or fewer samples. The concentration in the blank must be less than the RL. If the blank exceeds the RL, re-analyze the blank. If the blank still exceeds the RL, re-calibrate the instrument and re-analyze any associated samples.

13.6 Analyze a LCS (10.1.2) and (10.2.2) at a frequency of at least one per batch of 20 or fewer samples. The LCS serves as a Laboratory Fortified Blank (LFB) and a Quality Control Sample (QCS). The recovery of the LCS must lie between 90 and 110% for waters and between 80 and 120% for soils of the expected value. If the LCS falls outside these criteria, re-analyze the LCS. If the recovery still falls outside these limits, re-calibrate the instrument and re-analyze any affected samples.

13.7 Analyze a matrix spike (10.1.3) and (10.2.3) at a frequency of 1 per batch

of 10 or fewer samples. SVL logs in a matrix spike with most jobs so that a sufficient number of spikes appear on bench sheets. Spike recovery must lie between 90 to 110% for waters, and between 75 and 125% for soils of the expected value. If the recovery lies outside these limits but the LCS is in control, report the spike recovery and flag the report.

13.8 Analyze a matrix spike duplicate (10.1.4) and (10.2.4) at a frequency of 1 per batch of 20 samples. Spike recovery must lie between 90 to 110%. The acceptance limit for the RPD between sample duplicates is 20%. If the recovery or RPD exceeds acceptance limits, flag the client report.

13.9 The NOX% in the report window should be 90% or greater, if not reactivate the OTCR and recalibrate the instrument.

13.10 Perform an aqueous MDL study every six months (see SOP SVL 1011).

13.10.1 Perform a soil MDL using boiling stones (6.30) annually.

13.11 LCR studies are conducted initially, or whenever a significant change is noted in the instrument response and when a new analyst is trained.

13.11.1 Since SVL does not report above its calibration range, twice a year the analyst will use the linear calibration verification template mentioned in 11.1.1 to verify that the quadratic curve is linear over a portion of the curve. Any three points from the quadratic curve may be fitted into the linear template in order to prove linearity. Copies of these runs will be placed in an electronic folder titled "H:/Linearities."

14.0 REFERENCES

14.1 Astoria Analyzer Nitrate + Nitrite A173, Astoria-Pacific International, Revision F, Sept. 2004.

14.2 Manual for the Certification of Laboratories Analyzing Drinking Water, Fifth Edition.

14.3 Method 353.2, "Determination of Nitrate-Nitrite Nitrogen by Automated Colorimetry", Revision 2.0, Methods for the Determination of Inorganic Substances in Environmental Samples, EPA/600/R-93/100, August 1993.

14.4 FASPac™II Flow Analyzer Software Package Version 2.12, Astoria Pacific International, Revision 08/2005.

14.5 Methods of Soil Analysis Part 2, 2nd edition.

15.0 POLLUTION PREVENTION

15.1 Efficient laboratory practices that reduce the need for re-digestions and/or Re-extractions minimize contributions to pollution.

15.2 All standards are prepared and reagents used in volumes consistent with good laboratory practice to minimize the volume of disposable waste.

16.0 WASTE MANAGEMENT

16.1 Most chemicals used during digestion and/or analysis are neutralized and/or diluted prior to disposal by permit to the public sewer. Any hazardous chemicals and/or residues are disposed of through SVL's hazardous waste disposal system (see SOP's SVL 1001 & 1008).

16.2 It is the policy of SVL to dispose of all hazardous waste in accordance with local, state and federal regulations. Determination and disposal of hazardous waste will be conducted in accordance with Federal regulations at 40 CFR 260-262. Shipment and disposal of hazardous waste off-site will be contracted with firms that have current EPA approvals.

17.0 CHANGE HISTORY

Date	Ver.	Change
09/04/09	11.0	Changed Section 1.0. 3.2 added "This will be done when a client indicates that the samples are high in the interfering elements". 3.3 added "If detected sodium thiosulfate may be added (amount to be determined by analyst) to the sample to reduce the chlorine". Added 5.10. Changed the opening paragraph to Section 6.0. Added 6.30, 6.31, 6.32 and 6.33. 7.2 added "Verify that the sample line from the autosampler is connected to the sample line on the nitrate/nitrite cartridge". 7.3 changed time to 10 minutes. 7.4 changed to "Place all tubes in chemwash container and allow solution to run for 10 minutes". 7.7 changed to "right clicking on the channel window and selecting display signal". Changed Section 8.0 to include requirements for nitrites. 10.8.5 added "At the end of the run,

Date	Ver.	Change
		remove the OTCR by disconnecting the outlet first, then the inlet. Flush the OTCR with buffer which contains no brij". Changed Section 11.0. Added 12.11. Changed 13.11. Added 14.2 and 14.5.
10/27/10	12.0	3.2 changed to "High concentrations of iron, copper may cause low results. Stock ammonia chloride-EDTA solution (6.4) is added to the sample to complex the heavy metals". Updated Section 5.0 with the current equipment used. 6.17 added criteria for "Secondary source sodium nitrite". 6.18 added criteria for "Second source sodium nitrate". 6.19 added criteria for "Secondary stock nitrite solution". 6.20 added criteria for "Secondary stock nitrate solution". Updated catalog numbers throughout Section 6.0. 7.1 changed to "means of the toggle switches on the backs of the respective equipment". 7.4 added "including the sampler wash line". 7.7 added "Next, right click and select "zero signal all." Monitor for several minutes – baseline should be flat and smooth". Made changes throughout Section 8.0. Changed spiking procedures in Section 10.0. Added 10.1.4.1 "For samples originating in California, a matrix spike duplicate must also be prepared. Prepare in the same manner as 10.1.4.". 11.4 added "Calibration points will be verified against the curve (see SVL 1020). The low calibration standard should be within ± 30% and the remaining calibration standards within ± 10 % of the indicated concentration". 12.1 Added "Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batches.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the samples began". 12.2 consolidated to "After analysis is completed, go to the show report icon – click on it. In the report screen go to "file" and then "properties". Double check that the cup position, comment, dates, time, total dilution, corrected peak height and correct status "flags" are selected. Click "OK" then go to "file" and "print". Use the pdfFactory pro software to create an electronic "printout" of the report. Use the "highlight" tool to highlight the samples run in each batch. Use the "stylus" tool to make any necessary comments. Save the pdf file in the appropriate data folder. Indicate on the bench sheet the file name and highlight color used". 12.4 added "In the main screen go to "File" then "Export" then "Results", choose one of the five export files. Overwrite and save file". 12.5 added "Locate the Export folder on the desktop and open the file.

Date	Ver.	Change
		Change the column heading from "Channel 1" to "mg/l." Save and close the file". 13.6 added "for waters and between 80 and 120% for soils". 13.7 added "for waters and between 75 and 125% for soils".
12/08/11	13.0	Removed all references and processes to nitrate as N and nitrite as N. Document is solely for nitrate + nitrite by EPA 353.2 as per request by the Classical Department. Added sand and chlorox to reagents list. Added sand to be used for soil prep blanks and MDLs. 13.10.1 added "Perform a soil MDL using sand (6.30) annually".
12/28/12	14.0	3.3 added "Samples may also be diluted to manage interference caused by free chlorine ". 3.4 added "Samples may also be diluted to manage interference caused by oil or any highly organic solution ". 6.30 added "PFTE Boiling Stones, Chemware Cat. # D1069103". 6.33 added "$Na_2S_2O_3 \cdot 5\ H_2O$, Fisher Reagent Grad, Cat. #S445-500". 6.34 added "Dechlorinating reagent: dissolve 0.175 g $Na_2S_2O_3 \cdot 5\ H_2O$ (6.33) in water and dilute to 100 mL. Prepare fresh weekly; use 0.1 mL reagent to remove 1 mg/L residual chlorine in a 25 mL sample". 7.9 added "If the OTCR is new or the reducing efficiency is <90%, activate or re-activate the OTCR in the following steps (7.9.1 to 7.9.6)". 7.9.4 changed to "It is important to complete this step quickly because leaving the HCl in the coil for more than 2-3 seconds can cause pitting of the coil". 7.9.9 added "Storing air in the OTCR can lead to pitting". 10.1 changed to "For aqueous samples, pour aliquots into autosampler vials (3/4 full). If a CCV fail is observed, test the preceding 10 samples with chlorine test strips. If positive, dilute sample or use de-chlorinating reagent (6.33) to manage interference". 10.1.4 and 10.2.4 added "Prepare a matrix spike duplicate. Prepare in the same manner as 10.1.3". 10.3 changed to "matrix spike duplicates". 13.8 changed to "Analyze a matrix spike duplicate (10.1.4) and (10.2.4) at a frequency of 1 per batch of 20 samples. Spike recovery must lie between 90 to 110%. The acceptance limit for the RPD between sample duplicates is 20%. If the recovery or RPD exceeds acceptance limits, flag the client report". 10.21 changed to "boiling stones". 10.6 changed to "(Data collection and sampler can be paused separately as long as the analyst first pauses the sampler, waits for the data collection to reach the sample cup the sampler is paused at, and then pauses data collection. The sample at which both the sampler and data collection were

Date	Ver.	Change
		paused will automatically be RR". 10.8.6 added "Do not allow any air bubbles to be stored in the OTCR". 13.11 changed to "LCR studies are conducted initially, or whenever a significant change is noted in the instrument response and when a new analyst is trained", as per Arizona Update #114. 13.11.1 changed to "After running the quadratic curve take the low, a midlevel and the high standard and reprocess them using a linear equation. If the linear equation meets the correlation coefficient of less than 0.995, then it will have shown that the quadratic curve would meet the linear curve requirements. If the curve does not fit using both equations then adjust the upper or lower end of the curve standards until the curve meets the requirement. Include worksheets for both curves"
10/11/13	15.0	8.6 changed to "Prepare a CCV by diluting 2.0 mL of the intermediate nitrate solution (6.15) to 100 ml with deionized water (6.27)." 10.1.3 changed to "Prepare a matrix spike by measuring a 5 mL aliquot of sample into a dilution tube. Add 200 µL of the intermediate nitrate solution (6.15) and bring up to 10.0 mL with more sample. This constitutes a 2.0 mg/L spike add." 11.1.1 added "Use the calibration verification template (located at H:\Templates\Calibration Curve Check) to verify the curve – select the quadratic function. There is a 30% acceptance range for the low standard and a 10% acceptance range for the remaining calibration standards. As long as the minimum number of calibration standards are maintained, the low and high standards may be removed and the calibration used; otherwise re-calibrate the instrument." 13.11.1 changed to "Since SVL does not report above its calibration range, twice a year the analyst will use the linear calibration verification template mentioned in 11.1.1 to verify that the quadratic curve is linear over a portion of the curve. Any three points from the quadratic curve may be fitted into the linear template in order to prove linearity. Copies of these runs will be placed in an electronic folder titled "H:/Linearities"."

SYNTHETHIC PRECIPITATION LEACHING PROCEDURE

By SW-846 1312 and Nevada Extraction Procedure 1312

Revised by: Michael Desmarais

Approved by: _____ Date: _____

Classical Chemistry Department Supervisor

Reviewed by: _____ Date: _____

Quality Assurance Manager

SVL Analytical, Inc.

I have read, understood and will comply with SOP (SVL 4068 Version 9.1)

Print Name	Signature	Date
Eric Bouck		
Judy Ashcraft		
Danny Sevy		
Heidi Barnes		

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1.0 SCOPE AND APPLICATION

This SOP describes Synthetic Precipitation Leaching Procedure (SPLP) taken from SW-846 method 1312 and used by the Nevada Extraction Procedure 1312. The method is intended to determine the mobility of both organic and inorganic analytes present in liquids, soils, and wastes. SVL uses a Laboratory Information Management System (LIMS) – Element, to manage client's samples. Definitions for words used in this SOP may be found in SVL's Quality Manual. The holding time is 28 days for mercury analysis and 180 days for metals analysis.

2.0 SUMMARY OF METHOD

The procedure is based on SW-846 Method 1312. When liquid samples are filtered the filtrate is considered to be the SPLP extract. For solids, the sample is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. Extracts may then be analyzed by various methods. SPLP extracts for metals analyses are digested by Method 3010 (see SOP SVL 4079). Extracts for cyanide analysis will use Fluid #3.

3.0 INTERFERENCES

3.1 The extraction procedure has no known interferences.

4.0 SAFETY

4.1 Nitric acid is a strong oxidizer and can cause severe burns if it comes into contact with skin or eyes. The fumes are also irritating to nasal and lung tissues. Work with nitric acid in a hood. Wear safety glasses or goggles. Wear gloves and a lab coat or an apron. In the case of exposure, flush with water for at least fifteen minutes.

4.2 Sulfuric acid can cause severe burns if it comes into contact with skin or eyes. The fumes are also irritating to nasal and lung tissues. Work with sulfuric acid in a hood. Wear safety glasses or goggles. Wear gloves and a lab coat or an apron. In the case of exposure, flush with water for at least fifteen minutes.

4.3 Read the MSDSs for the chemicals used in this SOP. Be aware of the possible hazards.

5.0 EQUIPMENT INSTRUMENTATION AND MATERIALS

Equivalent equipment, instruments, and materials may be used.

5.1 Glass microfiber filters, TCLP, Acid treated Low Metal, 47 mm, Whatman, Cat # 1810 047.

5.2 pH indicator strips, pH 0-14, EMD.

5.3 Balance, Explorer Model EOF110; accurate within $\pm$ 0.1 grams.

5.4 1000 mL HDPE bottles with Teflon-lined caps used for storage of final metals TCLP filtrate.

5.5 Rotator, capable of holding 2 Liter bottles rotating in an end-over-end fashion at 30 $\pm$ 2 rpm, Millipore Corporation Model YT30ORAHW.

5.6 High Pressure Hazardous Waste Filtration System, Millipore Corp.; model YT30142HW, 142mm.

5.7 Accumet AB 15 pH meter.

5.8 Spatulas.

5.9 Weigh Boats.

5.10 Beaker, 500 mL.

5.11 Digestion cups, 50 mL, disposable, Environmental Express Catalog No. SC475.

5.12 “Snap cap” vials, 4 oz., with 100 mL fill line, Eagle Pitcher Catalog No. 156-4-BFT.

6.0 REAGENTS AND STANDARDS

Guidelines for the storage, tracking and expiration of chemicals and reagents can be found in SVL 1032. The procedure for purchasing chemicals and reagents can be found in SVL 1015. Any exceptions to the above mentioned SOPs will be found in this section, as well as all of the preparatory steps needed to construct or prepare reagents and standards. Equivalent reagents may be used.

6.1 Concentrated sulfuric acid (H_2SO_4): Fisher Trace Metals Grade.

6.2 Concentrated nitric acid (HNO_3): Fisher Trace Metals Grade.

6.3 Extraction fluid # 1 (eastern fluid): This fluid is made by adding a 60/40 weight percent mixture of sulfuric and nitric acids to DI water until the pH is 4.20 ± 0.05 (a dilution of the acid mixture is necessary before adding to the fluid).

6.4 Extraction fluid # 2 (western fluid): This fluid is made by adding a 60/40 weight percent mixture of sulfuric and nitric acids to DI water until the pH is 5.00 ± 0.05 (a dilution of the acid mixture is necessary before adding to the fluid).

6.5 ASTM Type II deionized water (used as extraction fluid # 3).

6.6 pH 7 Buffer Solution, Ricca, cat # 1551-5.

6.7 pH 4 Buffer Solution, Ricca, cat # 1500-5.

7.0 INSTRUMENT SETTINGS

7.1 Annually, check that the rotator is set to 30±2 rpm (see Rotational Log # 298).

7.1.1 Filled bottles should be used when checking rotation.

8.0 CALIBRATION

8.1 Analytical balance should be calibrated according to SVL SOP 1025.

8.2 The pH meter should be calibrated according to SVL SOP 4028.

9.0 SAMPLE HANDLING AND PRESERVATION

9.1 Samples may be stored for up to 28 days for mercury and 180 days for metals prior to SPLP extraction.

9.2 There is no hold time for the time between the extraction and when samples are prepped. Guidance is that it be done as soon as possible.

9.3 After extractions are prepped, they may be stored for up to 28-days for mercury and 180 days for metals prior to analysis if preserved with nitric acid.

9.4 Samples requested by methods that are not listed in the SPLP method will follow the hold time requirements published in the current Method Update Rule (promulgated by the EPA) upon completion of the extraction.

10.0 SAMPLE PREPARATION AND ANALYSIS

10.1 Solids

10.1.1 Begin by determining the % moisture/solids. Take an aliquot of sample, weigh and dry it according to SVL SOP 4022. Using the below equations determine the % solids. The resulting % solids value will go into the equation located at 10.1.3, in order to determine the amount of extraction fluid that is to be combined with the sample prior to rotation.

10.1.1.1 Use 8-10.0 g of initial sample to do the % moisture/solids on.

10.1.1.2 Use the following equations to determine % moisture/solids:

$$\% \text{ Moisture} = \frac{(\textit{weight of initial sample} - \textit{weight of dry sample})(100)}{\textit{weight of initial sample}}$$

% Solids = 100% - (% Moisture)

10.1.1.3 Volume of extraction fluid

$$\text{Extraction fluid needed} = \frac{20\ x\ \%\ \textit{Solids}\ x\ \textit{Sample Weight}}{100}$$

Where: “Sample Weight” is usually a minimum of 100 g of the original sample. In certain cases, when not enough of the original sample is provided, a lesser sample weight may be used.

10.2 Solids received with standing liquid

10.2.1 If a sample is received with standing liquid, Client Services will contact the client and clarify what portion of the sample is to be extracted. If the client instructs SVL to perform the test on the sample “as received”, then collect and filter any liquid from the sample and set aside. The filtered liquid will be recombined (if miscible) with the extract from the solid portion after rotation. For example, if the % solid/moisture test results in a sample that is 70% solid, by using the equation in 10.1.1.3 a volume of

1400 mL of extraction fluid would be rotated (using a 100 g starting weight). To account for the 30% liquid fraction, 30 mL of the filtered liquid (its own extract by definition) will be added to the rotated extract prior to the sample being preserved and prepped for digestion.

10.2.1.1 If the liquid fraction is not miscible with the extraction fluid then separate analyses shall be conducted (see 10.4.3) and the results mathematically combined (11.1) and then reported (check for extract compatibility before combining the separate factions).

10.3 Aqueous samples

10.3.1 If the liquid sample has < 0.5% solids then the sample will be filtered and sent to the digestive lab to be digested for analysis.

10.3.1.1 The filtered sample will be reported as extract in mg/L.

10.3.2 Batch QC will be setup following the guidelines in the SVL 4107 (total metals) and SVL 4010 (mercury). No extraction fluid will be supplied for the blank or LCS.

10.4 Oily and multi-phasic samples

A sample received for SPLP analysis that is multi-phasic shall have Client Services contact the client for clarification on which portion(s) of the sample are to be analyzed.

10.4.1 Some samples such as oily waste and some paint waste will obviously contain some material that appears to be liquid. But even after applying methods to separate the waste or in the opinion of the technician the waste will not separate, then the waste will be classified as a solid

10.4.2 Samples that are clearly oil will be prepared as a solid.

10.4.3 If the initial sample contains multi-phase liquid or liquid/solid components (where the liquid phase is not water) then these components shall be analyzed separately. After analysis the results shall be combined mathematically and reported out as one result per sample (See 11.1 for the proper equation).

10.4.4 Batch QC will be setup following the guidelines in SVL4094 (total metals), SVL 4010 (mercury) and SVL 4012 (cyanide).

10.4 Determine whether the sample requires particle-size reduction:

10.4.1 Using the solid portion of the sample, evaluate the solid for particle-size. If the solid is smaller than 1 cm in its widest dimension (capable of passing through a 9.5-mm standard sieve), particle-size reduction is not required. If the particle-size is larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the sample to a particle-size as described above.

10.5 Determination of the appropriate extraction fluid:

10.5.1 For soils, if the sample is from a site that is east of the Mississippi River, extraction fluid #1 should be used. If the sample is from a site that is west of the Mississippi River, extraction fluid #2 should be used.

10.5.2 For wastes and wastewater, extraction fluid #1 should be used.

10.5.3 For cyanide – containing waste and / or soils, extraction fluid #3 (type II deionized water) must be used because leaching of cyanide – containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

10.6 SPLP extraction procedure for metals analysis:

10.6.1 Fill an extraction vessel(s) with the extraction fluid(s) used in the batch and process the fluid(s) following all of the steps that the client samples go through. The solution(s) will be used as blanks and LCSs (13.1).

10.6.2 Although a minimum sample size of 100 grams (solid and liquid phases) is required, a smaller sample size is sometimes needed to meet clients requests. In such cases a 20:1 ratio of extractable sample to the amount of extraction fluid required will be the acknowledged procedure (see 10.1). Sometimes a larger sample size may be required depending on percent solids and whether the initial liquid phase of the sample will be miscible with the aqueous extract of the solid. Enough solids should be generated so that the volume of SPLP extract will be sufficient to support all of the analyses required.

10.6.3 If the amount of the extract generated by the performance of a single SPLP extraction will not be sufficient to perform all of the analyses to be conducted, it is recommended that more than one extraction be performed and that the extracts from each extraction be combined and then an aliquot be made available for each analysis.

10.7 If a sample contains less than 0.5% dry solids, filter the liquid and send it to the water digestion lab to be prepped for analysis. The small amount of dry solids left on the filter may be discarded (see 10.3).

10.8 When adding extraction fluid to a sample that is already in the extraction vessel, make sure to pour it in slowly so as not to "shock" the sample into releasing it's contaminates in a manner that is un-related to how a sample would be subjected to the leaching potential of a landfill. Close the extractor bottle and secure it in the rotary extractor device. Rotate it for 18±2 hours. Maintain the ambient temperature at 23±2 °C during extraction period.

10.9.1 As agitation continues, pressure may build up within the extractor bottle for some types of samples (limed or calcium carbonate containing sample may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened and vented into a hood.

10.9.2 If the ambient temperature falls outside the range 23 ± 2 °C, note the excursion on the benchsheet and on the client report.

10.10 Following the 18 ± 2 hour extraction, the material in the extractor vessel is separated into its component liquid and solid phases by filtering through a new glass fiber filter. For final filtration of the SPLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration.

10.11 Prepare the SPLP extract as follows:

10.11.1 For each extraction batch or job, a matrix spike is required. The spike will be added by the technicians in the digestion labs before any preservation or digestion of the SPLP extract. Set aside a 125 mL aliquot of raw extract for this purpose

10.11.2 Take a small portion of the un-spiked extract and adjust the pH to <2 with nitric acid.

10.11.2.1 If no precipitate forms, pour extract into a bottle and preserve it to pH <2 with nitric acid.

10.11.2.2 If a precipitate forms, do not acidify the extract. Analyze it as soon as possible.

10.11.2.3 Store any remaining extract between 0-6 ºC.

10.11.3 In Element under "Laboratory" select "Extracts". Select "Edit" then the "Add" button and add "Leachate" (the extract).

10.11.3.1 Select samples and right click to make the following adjustments: change samples from batched to analyzed, change container types, change shelf location and home location (this will necessitate a visual check to make sure there is an open spot for the new location), and finally print new labels using the Zebra printer.

10.11.3.2 Deliver the samples either directly to the digestion lab for digestion by SOP SVL 4079 or to their shelf locations .

10.11.3.3 Measure the pH of the extract with a pH meter and record the pH.

11.0 DATA REDUCTION

11.1 If the individual phases are to be analyzed separately, determine the volume of the individual phases to ± 0.5%, conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\textbf{Final Conc.} = \frac{(V_1C_1) + (V_2C_2)}{V_1 + V_2}$$

where

V_1 = the volume of the first phase (L)
C_1 = the concentration of the contaminant of concern in the first phase (mg/L)
V_2 = the volume of the second phase (L)
C_2 = the concentration of the contaminant of concern in the second phase (mg/L)

12.0 DATA AND RECORDS MANAGEMENT

12.1 Make sure all log books are completed.

12.2 Sign and date the bench sheet.

12.2.1 The following should be noted: time extraction fluid was added, temperature at which samples were rotated, and length of time the samples were rotated.

12.3 Upload the final pH results after extraction into Element.

12.4 Change status of analyses to “Analyzed”. “Analyzed” triggers all of the dependent analyses to go to “Extracted”.

12.5 Upon the completion of the extraction the “Prepared” date in Element will be set to the completion date in order for hold time flags to be accurate. The benchsheet will indicate the date the extraction began.

12.6 The Supervisor will then change the batch from “Extracted” to “Final Reviewed”; the extraction batch is now available to be batched in preparation for analysis.

13.0 QUALITY CONTROL

13.1 A minimum of one blank or combination blanks (extraction fluid #1, #2 or #3) for every extraction batch shall be sent to the digestion lab in order to have the method blank and LCS for the analytical batch constructed. The blank solution must go through the entire extraction process that the client samples undergo (e.g. tumbling, filtration).

13.2 Each analytical batch will have the appropriate duplicates, matrix spikes and matrix spike duplicates and their frequency dictated by the analytical method under which they are to be digested / prepared and analyzed by.

13.3 For each extraction batch or job, a matrix spike is required. The spike will be added by the technicians in the digestion labs before any preservation or digestion of the SPLP extract. The extraction technician will set aside a 125 mL aliquot of raw extract for this purpose.

14.0 REFERENCES

14.1 Method 1312, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Third Edition, September 1986, Update I, II, or III September 1994, Rev 0

15.0 POLLUTION PREVENTION

15.1 Efficient laboratory practices that reduce the need for re-digestions and/or re-extractions minimize contributions to pollution.

16.0 WASTE MANAGEMENT

16.1 Most chemicals used during digestion and/or analysis are neutralized and/or diluted prior to disposal by permit to the public sewer. Any hazardous chemicals and/or residues are disposed of through SVL's hazardous waste disposal system (see SOPs SVL 1001 & 1008).

17.0 CHANGE HISTORY

DATE	VERSION	CHANGE
11/18/09	6.0	No changes
07/02/10	6.1	7.1.1 added "Filled bottles should be used when checking rotation". Changed portions of Section 10. Added 12.2.1 "The following should be noted: time extraction fluid was added, temperature at which samples were rotated, and length of time the samples were rotate. Added 13.3 "For each extraction batch or job, a matrix spike is required. The spike will be added by the technicians in the digestion labs before any preservation or digestion of the SPLP extract. The extraction technician will set aside a 125 mL aliquot of raw extract for this

DATE	VERSION	CHANGE
		purpose".
8/03/11	7.0	9.3 added "Samples requested by methods that are not listed in the method will follow the hold time requirements published in the most current Method Update Rule (promulgated by the EPA) upon completion of the extraction".
08/24/12	8.0	10.6.1 added "Fill an extraction vessel(s) with the extraction fluid(s) used in the batch and process the fluid(s) following all of the steps that the client samples go through. The solution(s) will be used as blanks and LCSs (13.1)". 13.1 added "The blank solution must go through the entire extraction process that the client samples undergo (e.g. tumbling, filtration)".
09/10/13	9.0	1.0 changed to "This SOP describes Synthetic Precipitation Leaching Procedure (SPLP) taken from SW-846 method 1312 and used by the Nevada Extraction Procedure 1312." 13.1 changed to "A minimum of one blank or combination blanks (extraction fluid #1, #2 or #3) for every extraction batch shall be sent to the digestion lab in order to have the method blank and LCS for the analytical batch constructed."
12/05/13	9.1	Re-wrote Section 9.0. 12.5 added "Upon the completion of the extraction the "Prepared" date in Element will be set to the completion date in order for hold time flags to be accurate. The benchsheet will indicate the date the extraction began."

DETERMINATION OF ALKALINITY AND pH USING THE AUTOTITRATOR By SM 2320 B and SM 4500 H^+ B

Revised by: Michael Desmarais

Approved by: _____ Date: _____
ABA Department Supervisor

Reviewed by: _____ Date: _____
Quality Assurance Manager

SVL Analytical, Inc.

I have read, understood and will comply with SOP (SVL 4084 Version 12.0)

Print Name	Signature	Date
Debbie Schultz		

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1.0 SCOPE AND APPLICATION

This SOP describes the procedure for the determination of alkalinity and pH of water samples using a Metrohm autotitrator. Because pH must be determined "immediately", it should be analyzed in the field. Determination of pH by the laboratory will be out of holding time. SVL uses a Laboratory Information Management System (LIMS) – Element, to manage client's samples. In Element the alkalinity reporting limit is 1.0 mg/L. Definitions for words used in this SOP may be found in SVL's Quality Manual. The holding time for alkalinity is 14 days.

2.0 SUMMARY OF METHOD

An aliquot of sample is loaded on the autotitrator and the pH measured. If the pH is greater than or equal to 4.5, the sample is titrated to an endpoint of 4.5. The alkalinity is then calculated. If the total alkalinity is less than 20 mg/L, the sample is re-analyzed as a low alkalinity to an endpoint of 4.2. This SOP is intended to satisfy the requirements of Standard Methods 2320 B and 4500 H^+ B.

3.0 INTERFERENCES

3.1 During auto titration, oily matter, suspended solids, soaps, precipitates, or other waste matter may coat the glass electrode and cause a sluggish response. Difficulty from this source is likely to be revealed in an erratic titration curve. Do not remove interferences from sample because they may contribute to its alkalinity. Briefly pause between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally.

3.2 Alkalinity and pH samples may not be diluted or filtered.

4.0 SAFETY

4.1 Sulfuric acid can cause severe burns if it comes into contact with skin or eyes. Wear safety glasses or goggles. Wear gloves and a lab coat or an apron. In the case of exposure, flush with water for at least fifteen minutes.

4.2 Read the MSDSs for the chemicals used in this SOP. Be aware of the possible hazards.

5.0 EQUIPMENT INSTRUMENTATION AND MATERIALS

Equivalent equipment, instruments, and materials may be used.

5.1 Autotitrator, Metrohm Titrino 809 (with sample changer).

5.2 Graduated cylinders, Kimax, 25 mL, 50 mL, 100 mL, Fisher 08-548B, 08-548C, 08-548-D.

5.3 pH indicator strips, pH 0-14, EMD.

5.4 Plastic beakers.

6.0 REAGENTS AND STANDARDS

Guidelines for the storage, tracking and expiration of chemicals and reagents can be found in SVL 1032. The procedure for purchasing chemicals and reagents can be found in SVL 1015. Any exceptions to the above mentioned SOPs will be found in this section, as well as all of the preparatory steps needed to construct or prepare reagents and standards. Equivalent reagents and standards may be used.

6.1 pH 4 Buffer Solution, BDH0198-20L.

6.2 pH 7 Buffer Solution, BDH0194-20L.

6.3 pH 9 Buffer Solution, BDH5064-4L

6.4 Distilled water.

6.5 Concentrated sulfuric acid (H_2SO_4): Fisher TraceMetals Grade.

6.6 0.02N sulfuric acid solution: Carefully add 1.68 mL concentrated sulfuric acid (6.5) to about 3.0 L of distilled water (6.4). Mix well.

6.7 0.10N sulfuric acid solution: Carefully add 8.40 mL concentrated sulfuric acid (6.5) to about 3.0 L of distilled water (6.4). Mix well.

6.8 Sodium carbonate, Na_2CO_3 (crystals), Fisher HPLC Grade anhydrous, dried for four hours in an oven set at 250 ºC.

6.9 Normalizing Titrant: Dissolve 2.5 g dried sodium carbonate (6.8) in distilled water (6.4). Dilute to 1.0 L in a volumetric flask with deionized water. There is a one week expiration date.

6.10 Sodium Bicarbonate, $NaHCO_3$, (powder), J.T. Baker Catalog Number 3508-05.

6.11 Solution for Alkalinity LCS. Dissolve 1.00 grams sodium bicarbonate, $NaHCO_3$, (6.10) in 1 L of distilled water (6.4). Dilute to 6 L. True value is 99.28 mg/l.

6.12 Solution for pH QC, ERA catalog number 552.

7.0 INSTRUMENT SETTINGS

The following instructions characterize the operation of the Titrino 809 autotitrator with sample changer.

7.1 Initialize the Titrator

7.1.1 After the introductory displays are complete, the screen exhibits the "Main Menu Manager".

7.1.2 Click on "Titr-1".

7.1.3 In the "Titrator" drop-down menu, highlight "Initialize". Select "yes" to confirm the selection.

7.1.4 The monitor will display "Initializing", then "1…2…3…4…5…Init-OK".

7.2 Initialize the Changer

7.2.1 Press "Changer" in the "Main Menu Manager".

7.2.2 Pull down the "Commands" menu.

7.2.3 Select "Initialize"

7.2.4 Select "Yes" to confirm the selection.

7.2.5 The Changer will beep once; the arm will rise and rotate one time. The Changer will stop in the #1 position.

7.3 When using the 0.1N sulfuric acid titrant.

7.3.1 Click on “Configuration”.

7.3.2 Under “Titrants/Solutions” select 0.1N (number 2 solution).

7.3.2.1 Use 0.1N titrant to analyze samples that provide “invalid” results on 0.02N titrant, are historically known to have high levels of alkalinity, or if pH strip indicates high pH.

7.3.2.2 When running samples on 0.1 N titrant, blanks and samples with low alkalinity need to be analyzed with 0.02 N titrant.

8.0 CALIBRATION

8.1 Calibrate the instrument daily.

8.1.1 Load the following sequence of vials on the Changer

Vial#1: Buffer 4
Vial#2: Buffer 7

8.1.2 The calibration is performed by selecting the following program: “Calibrate with 2 buffers”.

8.1.3 The Titrino will calculate a slope and display the pH of Buffer 7. Ensure that the slope is between 92 and 102. Measure the pH of the buffers 4 and 7, and verify that the results are within +/- 0.1 pH units of the true values.

8.1.4 Check an independent buffer (6.3) and verify linearity that the reading is within +/- 0.1 pH units.

8.1.5 Transfer enough of the pH QC check (6.12) to cover the electrode into a vial, and load it on the changer. This will be tracked in Element as an SRM.

8.1.5.1 The pH QC check is run once per day (bracketed by passing calibration checks).

8.2 Calibration for 0.1N solution.

8.2.1 Click on “Workplace”.

8.2.2 Double click on the blank line in the run sequence.

8.2.3 Click on the drop down arrow for method.

8.2.4 At the top of the list, select 0.1 Norm.

8.3 Include the slope, the initial buffer readings, the independent check, pH LCS, and the normality in the data packages.

9.0 SAMPLE HANDLING AND PRESERVATION

9.1 Samples are stored between 0-6 °C.

9.2 Allow samples to come to room temperature prior to analysis.

10.0 SAMPLE PREPARATION AND ANALYSIS

10.1 Select “Work List Manager” from the “Main Menu Manager”.

10.2 Click “File”. A drop-down menu will appear.

10.3 Select “Daily Template”. The following table will appear on the screen:

ID1	ID2	SIZE	TITR#	TITR SEQ
Na_2CO_3	SVL ID #	37.5	X	NORM
PH	SVL ID #	50	X	PH
9 BUFFER	SVL ID #	50	X	PH
4 BUFFER	SVL ID #	50	X	PH
7 BUFFER	SVL ID #	50	X	PH

10.4 Load the template to the Silo Table by pushing the “Load” button. Or save the daily template, open it, and hit “Enter”.

10.5 Transfer enough of the pH 7 (6.2) buffer to cover the electrode into a vial. Load the vial onto the changer.

10.6 Transfer enough of the pH 4 (6.1) buffer to cover the electrode into a vial. Load the vial onto the changer.

10.7 Transfer 15.0 mL of the sodium carbonate normalizing titrant into a vial. Load the vial onto the changer. When titrated, the instrument software will calculate the normality and apply it to subsequent titrations. Note that the size is listed as 37.5 mL in the Silo Table (due to the A X B portion of the standardization equation in section 11.2).

10.8 Measure 50 mL of distilled water (6.4) into a vial and load it on the changer. This is the method blank.

10.9 Transfer 50 mL of the alkalinity LCS solution (6.11) to a vial and load it on the charger. This is the batch LCS.

10.10 Using a pH test strip (apply drop to test paper) check the pH of each sample. This will help predict what volume and titration endpoint to use.

10.10.1 If the indicator strip shows an approximate pH > 9, then it may be necessary to run the sample using 0.1N H_2SO_4 titrant. Use the P&TALK titration method to an endpoint of 4.5.

10.10.2 If the indicator strip shows an approximate pH < 5, use a 50 mL sample volume and the LOALK titration method to an endpoint of 4.2.

10.10.3 If the indicator strip shows an approximate pH >5 but <9, use a 50 mL sample volume and the P&TALK titration method to an endpoint of 4.5.

10.10.4 If the indicator strip shows an approximate pH < 2, use a 50 mL sample volume and evaluate pH only.

10.11 Transfer the correct volume of each sample (usually 50 mL) to a vial and load it on the changer.

10.12 Complete the Silo Table by adding the samples.

10.12.1 The autotitrator runs off information entered in a Silo Table; therefore, each sample analyzed on the instrument must first be set-up in a Silo Table. This includes the instrument QC and batch QC as well as all samples in a batch.

10.12.2 Enter the sample size in mL in the “Size” field.

10.12.3 Enter the sample number in the “ID 1” field.

10.12.4 For batches that contain multiple jobs, enter the SVL batch number for the blank, LCS, and duplicate in the “ID 2” field.

10.12.5 Enter one of the following methods in the 'Titr. Seq" field for each sample:

"NORM" - used to calculate the normality of the 0.02 N titrant,
"0.1 NORM" – used to calculate the normality of the 0.1 N titrant,
"LOALK" - used for samples which have low alkalinities as well as the analysis of blank samples,
"pH" - used for the pH buffer solutions,
"P&TALK" - used for the routine analysis of alkalinity samples,
"0.1 P&TALK" – used for the analysis of alkalinity samples on 0.1 N titrant.

10.12.6 To create a new line, click on "Add Silo line". The cursor will automatically move to the "Size" field of the next line.

10.12.7 When the Silo Table is complete, click "File", and "Store Silo" (usually identified by date).

10.12.8 If the green arrow does not appear on the menu line, select "Macro", then select "Main" from the pull-down menu.

10.13 Verify the Silo Table, to ensure that the correct volumes and sample IDs have been entered.

10.14 Push "Start" on the screen. The instrument will begin to analyze the sequence.

10.15 Review the alkalinity results. Any sample with total alkalinity less than 20 mg/L will be re-run using the LOALK method.

11.0 DATA REDUCTION

11.1 The instrument software will measure the pH and calculate the alkalinity from the titrations performed.

11.2 Standardization of H_2SO_4

Normality, N = (A x B) / (53.00 x C)

where:

A = g Na_2CO_3 weighed into 1-L flask
B = mL Na_2CO_3 solution taken for titration, and

C = mL acid used.

11.3 Manual calculations for alkalinity and total alkalinity:

Potentiometric titration to end-point pH:

Alkalinity, mg $CaCO_3$/L = $\frac{A \times N \times 50{,}000}{mL\ of\ sample}$

where:

A = mL standard acid used and
N = normality of standard used

Potentiometric titration of low alkalinity:

Total Alkalinity, mg $CaCO_3$/L = $\frac{(2B - C) \times N \times 50{,}000}{mL\ of\ sample}$

Where:

B = mL titrant to first recorded pH,
C = total mL titrant to reach pH 0.3 unit lower, and
N = normality of acid

11.4 Alkalinity relationships:

11.4.1 Carbonate (CO_3^{2-}) alkalinity is present when phenolphthalein alkalinity is not zero but is less than total alkalinity (see SVL 4031 on acidity).

11.4.2 Hydroxide (OH^-) alkalinity is present if phenolphthalein alkalinity is more than half the total alkalinity.

11.4.3 Bicarbonate (HCO_3^-) alkalinity is present if phenolphthalein is less than half the total alkalinity.

These relationships may be calculated by the following scheme, where P is phenolphthalein alkalinity and T is total alkalinity: Select the smaller value of P or (T-P). Then carbonate alkalinity equals twice the smaller value. When the smaller value is P, the balance (T-2P) is bicarbonate. When the smaller value is (T-P), the balance (2P-T) is hydroxide.

All of the results are expressed as $CaCO_3$.

11.5 Calculations for procedures outlined in the SOP, may be found in SVL 1028.

12.0 DATA AND RECORDS MANAGEMENT

12.1 Once analysis has been completed, data is printed to PDF ProFactory, where data is reviewed and corrections are made if necessary. The data file is saved using the date and the number of the machine (e.g. 0730104). It is common for each PDF file to contain more than one batch.

12.2 Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batches.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the samples began.

12.2.1 Indicate all reagents used in the batch by including them in the reagent section of the "Batch" screen.

12.3 The alkalinity template is set up to accept manually entered data from the Tiamo data results sheets. A "how to" on templates can be found at R:\Promium Stuff\How to's\SVL-Excel Template Data Transfer.doc. Included in the "how to" are instructions on tracking equipment used.

12.3.1 Once finished, save to the alkalinity file on the H drive. Go to data entry/review and manually enter results from the template.

12.3.2 The instrument software will not calculate a carbonate value and instead will calculate a negative bicarbonate. When this happens, use the alkalinity template found at H:\Templates\Alkalinity. Click on the "Others" tab at the bottom of the spreadsheet. Enter the SVL Sample ID, Total Alkalinity and P-Alkalinity. The spreadsheet will calculate the appropriate carbonate, bicarbonate and hydroxide values.

12.3.3 If a sample is ran as a low alkalinity but should have been run as a total alkalinity, use the alkalinity template found at H:\Templates\Alkalinty to calculate the total alkalinity. Click on the "Talk" tab at the bottom of the spreadsheet. Enter the SVL Sample ID, mL used in the titration (shown as Res04 on the run table) and the normality of the titrant. The spreadsheet will then calculate the alkalinity.

12.3.4 In the Tiamo software, under the "Determination" tab, select "Export" and then verify that "all selected data records" is chosen. Click "OK". Results are now exported to a temporary file where Data Tool can locate them.

12.3.5 If a sample is analyzed as a total alkalinity but should have been analyzed as a low alkalinity, another aliquot of the original sample will need to be analyzed via the low alkalinity method.

12.4 In Element, go to "Laboratory" then to "Data Entry and Review" and select the appropriate batch then select "Create". Double click on "Data Tool" and it will bring up "Select Data System Files", double click on "Tiamo4.csv", click on "Autoselect" and it will automatically select the necessary samples for the batch that is being created. Click "Done". A Data Tool main window will appear, select "Merge Files". A "Data Transfer" window will appear. Select "Save" and overwrite the Mergetemp.xls file. Verify that the merge upload file and the empty upload file on the Data Transfer window are the same. Close Data Tool and go back into Data Entry and Review. Select "Save" and then query the results.

12.5 In Element, if any data entered comes up color coded apply the appropriate data flags or undertake any corrective actions.

12.6 In Element, the analyst shall assign any qualifiers, update the status of the batch to "Analyzed", and lock the results so that any future imports will not overwrite acceptable results.

12.7 Attach a copy of the spreadsheet to the benchsheet.

12.8 The data review process is outlined in SVL 2009.

12.9 Work order memos will be created when samples show unusual characteristics.

12.10 The analyst will add the H5 qualifier to all samples tested for pH.

12.11 Corrective action is governed by SOP SVL 1019.

13.0 QUALITY CONTROL

13.1 Analyze an alkalinity method blank once per batch of 20 or fewer samples (10.8). The recovery of the blank must be ≤ the reporting limit. If the recovery

exceeds the criterion, re-pour and re-analyze another aliquot. If the recovery is still outside the criteria, identify and correct the problem. Re-analyze any associated samples.

13.2 Analyze the alkalinity LCS (10.9) at a frequency of once per batch of 20 or fewer samples. The acceptance criteria for the LCS's are between 85-115% of the true value. If a LCS recovery falls outside the acceptance criteria, re-pour and reanalyze another aliquot. If the recovery is still outside the criteria, identify and correct the problem. Re-analyze any associated samples.

13.3 Analyze a pH QC check (10.10) once per day. Track the results of this check in Element. The check true value may change, verify in Element to make sure the current LCS value is correct (6.12). If the recovery exceeds these limits, re-analyze the check. If the recovery still exceeds the limits, identify and correct the problem before analyzing samples.

13.4 Analyze a pH 9 buffer solution (6.4) as an ICV once per day. The acceptance criterion is +/- 0.1 pH units of the expected value. If the recovery falls outside the acceptance criterion, identify and correct the problem.

13.5 Analyze buffer solutions of pH 7 and 4 (6.2 and 6.1) at the beginning of each run, after every 10 samples and at the end of a run. The buffers function as calibration verification samples. The acceptance criteria are ± 0.1 pH units of the expected value. If the buffer solutions read outside the acceptance criteria, identify and correct the problem. Re-analyze samples analyzed since the last successful buffers.

13.6 For alkalinity, prepare and analyze a sample duplicate at a frequency of 1 per every batch of 20 or fewer samples. The acceptance criterion for the RPD is less than 20%; If the RPD is greater than the acceptance criterion, flag the client report.

13.6.1 For pH, prepare and analyze a sample duplicate at a frequency of 1 per every batch of 20 or fewer samples. The acceptance criterion for the RPD is ± 0.1 pH units. If the RPD is greater than the acceptance criterion, flag the client report.

13.6.2 For Arizona clients

13.6.2.1 For alkalinity, prepare and analyze a sample duplicate at a frequency of 1 per every batch of 10 or fewer samples. The acceptance criterion for the RPD is 20%. If the RPD is greater than the acceptance criterion, flag the client report.

13.6.2.2 For pH, prepare and analyze a sample duplicate at a frequency of 1 per every batch of 10 or fewer samples. The acceptance criterion for the RPD is ± 0.1 pH units. If the RPD is greater than the acceptance criterion, flag the client report.

13.7 Annually a Quality Control Sample (QCS) (SVL uses ERA PT studies) must pass its study requirements; if needed, troubleshoot and repeat the study. Failure to pass a QCS annually will result in the removal of the test until a QCS is passed.

13.8 Trend analysis can be found in SOP SVL 1033.

13.9 Demonstrations of capability requirements can be found in SOP SVL 1010.

14.0 REFERENCES

14.1 Method 2320B, Standard Methods for the Examination of Water and Wastes, 20th Edition.

14.2 Standard Methods 2020, Standard Methods for the Examination of Water and Wastewater, 22nd edition. 2012.

14.3 Manual for the Certification of Laboratories Analyzing Drinking Water, Fifth Edition.

15.0 POLLUTION PREVENTION

15.1 No pollution issues are associated with method SM 2320 B.

16.0 WASTE MANAGEMENT

16.1 No waste is generated by method SM 2320 B. Samples after titration are diluted prior to disposal by permit to the public sewer.

17.0 CHANGE HISTORY

DATE	VERSION	CHANGE
11/24/09	8.0	8.1.3 changed buffer requirements to ± 0.1 pH units. Added 11.2 and 11.3 to fulfill Arizona's requirement to have equations included in the SOP. 13.3 and 13.4 changed the buffer acceptance criteria to ± 0.1 pH units. Added 14.2 "Manual for the Certification of Laboratories Analyzing Drinking Water, Fifth Edition".
08/26/10	8.1	3.2 added "Alkalinity and". 7.3 added "When using the 0.1N sulfuric acid titrant". 7.3.1 added "Click on "Configuration"". 7.3.2 added "Under "Titrants/Solutions" select 0.1N (number 2 solution)". Added all of section 8.2. 10.7 added "(due to the A X B portion of the standardization equation in section 11.2)". 10.11.1 changed to ", then it may be necessary to run the sample using 0.1N H_2SO_4 titrant". Added 11.2. Re-wrote majority of section 12.0
12/09/10	8.2	2.0 added "and 4500 H^+ B". 12.10 added "The analyst will add the H5 qualifier to all samples tested for pH".
09/26/11	9.0	13.5 added "The acceptance criterion for pH's run on the autotitrator is ± 0.1 pH units".
09/18/12	10.0	6.3 added "pH 9 Buffer Solution, BDH5064-4L". 6.10 added "Sodium Bicarbonate, $NaHCO_3$, (powder), J.T. Baker Catalog Number 3508-05". 6.11 added " Solution for Alkalinity LCS. Dissolve 0.96 grams sodium bicarbonate, $NaHCO_3$, (6.10) in 1 L of distilled water (6.4). Dilute to 6 L. True value is 97.16 mg/l". 8.1.2 changed to "2 buffers". 8.1.3 changed to "92 and 102. Measure the pH of the buffers 4 and 7, and verify that the results are within +/- 0.1 pH units of the true values". 8.1.4 changed to "Check an independent buffer (6.3) and verify linearity that the reading is within +/- 0.1 pH units". 8.2.5 changed to "Include the slope, the initial buffer readings, the independent check, pH LCS, and the normality in the data packages". 10.8 added "Measure 50 mL of distilled water (6.4) into a vial and load it on the changer. This is the batch QC". 10.9 added "Transfer 50 mL of the alkalinity LCS solution (6.11) to a vial and load it on the charger. This is the batch LCS". 10.10 added "This will be tracked in Element as an SRM". 10.10.1 added "The pH QC check is run once a day (bracketed by passing calibration

DATE	VERSION	CHANGE
		checks)". 12.9 added "Work order memos will be created when samples show unusual characteristics". Re-wrote section 13.0 to include new QC requirements. 14.2 added "Standard Methods 2020, Standard Methods for the Examination of Water and Wastewater, 22nd edition. 2012".
10/17/13	11.0	7.3.2.1 added "Use 0.1N titrant to analyze samples that provide "invalid" results on 0.02N titrant, are historically known to have high levels of alkalinity, or if pH strip indicates high pH." 7.3.2.2 added "When running samples on 0.1 N titrant, blanks and samples with low alkalinity need to be analyzed with 0.02 N titrant." 8.1.5 added "Transfer enough of the pH QC check (6.12) to cover the electrode into a vial, and load it on the changer. This will be tracked in Element as an SRM." 8.1.5.1 added "The pH QC check is run once per day (bracketed by passing calibration checks)." 10.2.4 changed to" For batches that contain multiple jobs, enter the SVL batch number for the blank, LCS, and duplicate in the "ID 2" field." Re-wrote 10.2.5. 13.6.2.1 added "For alkalinity, prepare and analyze a sample duplicate at a frequency of 1 per every batch of 10 or fewer samples. The acceptance criterion for the RPD is 20%. If the RPD is greater than the acceptance criterion, flag the client report." 13.6.2. added in for work performed in Arizona. '13.6.2.2 added "For pH, prepare and analyze a sample duplicate at a frequency of 1 per every batch of 10 or fewer samples. The acceptance criterion for the RPD is ± 0.1 pH units. If the RPD is greater than the acceptance criterion, flag the client report."
04/24/14	12.0	12.3.5 added "If a sample is analyzed as a total alkalinity but should have been analyzed as a low alkalinity, another aliquot of the original sample will need to be analyzed via the low alkalinity method." 12.11 added "Corrective action is governed by SOP SVL 1019." 13.8 added "Trend analysis can be found in SOP SVL 1033." 13.9 added "Demonstration of capability requirements can be found in SOP SVL 1010."

ANALYSIS OF METALS BY METHODS 6010C and 200.7 USING THE PERKIN-ELMER OPTIMA ICP

Revised by: Danny Sevy and Michael Desmarais

Approved by: _____ **Date:** _____

Inorganic Instrumental Department Supervisor

Reviewed by: _____ **Date:** _____

Quality Assurance Manager

SVL Analytical, Inc.

I have read, understood and will comply with SOP (SVL 4102 Version 13.0)

Print Name	Signature	Date
Dave Tryon		
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1.0 SCOPE AND APPLICATION

This SOP describes the procedure used for the operation and analysis of samples on the Perkin-Elmer Optima instruments. It is applicable to drinking water, wastewater, soil, and hazardous waste samples. SVL uses a Laboratory Information Management System (LIMS) – Element, to manage client's samples. In Element the current aqueous and soil MDLs and RLs are shown below. Definitions for words used in this SOP may be found in SVL's Quality Manual. The holding time for aqueous samples is six months from date of sampling.

Metal	Wavelength (nm)	Aqueous Reporting Limit (mg/L)	Soil Reporting Limit (mg/Kg)	Aqueous MDLs (mg/L)	Soil MDLs (mg/Kg)
Silver	328.06	0.0016	0.5	0.00052	0.081
Aluminum	308.21	0.031	8.0	0.016	2.9
Arsenic	193.7	0.011	2.5	0.007	0.75
Barium	233.52	0.0005	0.2	0.00045	0.038
Beryllium	313.10	0.00043	0.2	0.00042	0.028
Boron	249.68	0.01	4.0	0.01	0.63
Bismuth	222.82	0.013	6.0	0.016	0.7

Metal	Wavelength (nm)	Aqueous Reporting Limit (mg/L)	Soil Reporting Limit (mg/Kg)	Aqueous MDLs (mg/L)	Soil MDLs (mg/Kg)
Calcium	315.89	0.015	4.0	0.012	2.3
Cadmium	226.50	0.00068	0.2	0.00047	0.042
Cerium	418.66				
Cobalt	228.62	0.00069	0.6	0.00094	0.079
Chromium	267.72	0.0015	0.6	0.0006	0.068
Copper	324.75	0.0062	1.0	0.0034	0.35
Iron	273.95	0.023	6.0	0.017	2.7
Gallium	417.20	0.0053	2.0	0.0036	0.77
Potassium	766.47	0.13	50	0.068	8.3

Metal	Wavelength (nm)	Aqueous Reporting Limit (mg/L)	Soil Reporting Limit (mg/Kg)	Aqueous MDLs (mg/L)	Soil MDLs (mg/Kg)
Lanthanum	379.47	0.0032	0.5	0.00074	0.16
Lithium	670.76	0.0056	2.0	0.0068	0.43
Lutetium	261.53				
Magnesium	279.08	0.039	6.0	0.021	3.4
Manganese	260.57	0.0013	0.4	0.0011	0.1
Molybdenum	202.03	0.0027	0.8	0.0011	0.18
Sodium	589.57	0.083	50.0	0.043	3.3
Nickel	232.00	0.0032	1.0	0.0031	0.31
Phosphorus	213.62	0.02	5.0	0.0087	2.6

Metal	Wavelength (nm)	Aqueous Reporting Limit (mg/L)	Soil Reporting Limit (mg/Kg)	Aqueous MDLs (mg/L)	Soil MDLs (mg/Kg)
Lead	220.35	0.0027	0.75	0.0034	0.25
Antimony	206.83	0.0089	2.0	0.0047	0.78
Scandium	361.38	0.0005	0.2	0.00043	0.055
Selenium	196.03	0.013	4.0	0.0094	0.9
Silicon	251.61	0.024		0.028	
Tin	189.93	0.0068	5.0	0.0041	0.35
Strontium	421.54	0.00081	0.5	0.00036	0.042
Titanium	336.12	0.00067	0.5	0.00033	0.034
Thallium	190.80	0.0056	1.5	0.0051	0.7

Metal	Wavelength (nm)	Aqueous Reporting Limit (mg/L)	Soil Reporting Limit (mg/Kg)	Aqueous MDLs (mg/L)	Soil MDLs (mg/Kg)
Vanadium	202.40	0.001	0.5	0.00046	0.065
Zinc	206.20	0.0023	1.0	0.0021	0.18
Mercury	194.168	N/A	1.0	N/A	0.12
Gold	208.209	N/A	N/A	N/A	N/A

2.0 SUMMARY OF METHOD

This SOP is intended to comply with the requirements of EPA methods 200.7 and 6010C. 6010B may also be run under this SOP. Argon is used to establish plasma within a quartz torch. A small amount of digested sample is transported by a peristaltic pump and tubing through an atomizer into the plasma. The metal atoms are excited by the plasma and emit light at characteristic wavelengths. A grating disperses the spectra. A photoelectric detector measures the emission of light by the metal atoms. Background is measured adjacent to the analyte wavelengths. Software creates a linear calibration curve of emission versus concentration and calculates the concentration in the sample.

3.0 INTERFERENCES

3.1 Interferences can result from background emission from continuous recombination phenomena. Use the background correction features in the software.

3.2 Interferences can result from emission by high concentrations of other elements. Use background correction features in the software.

3.3 Interferences can result from overlap of a spectral line of another element. Use an alternative wavelength or the inter-element correction factors in the software.

3.4 Interferences can result from differences in viscosity between calibration standards and samples due to high dissolved solids or acid concentrations. Use a peristaltic pump to deliver solutions.

3.5 Interferences can result from molecular compound formation and ionization effects. Modify the incident power or observing position.

3.6 Interferences may result from memory of previous samples. Use a rinse blank between samples.

4.0 SAFETY

4.1 Extremely high power is required to generate the plasma in the ICP. The RF generator must be shielded to prevent physical injury to operators. The plasma may approach a temperature of 10,000 degrees C.

5.0 EQUIPMENT, INTSTRUMENTATION AND MATERIALS

Equivalent equipment, instrumentation and materials may be used.

5.1 Perkin-Elmer Optima 4300, 5300 and 7300 DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES).

5.2 GemCone Nebulizer, Low Flow, Part No. N069-0671.

5.3 Concentric Glass Nebulizer (Meinhard), Part No. 0047-2020.

5.4 GemTip Cross-Flow Nebulizer, Part No. N077-0546.

5.5 Burgener Peek Mira Mist Nebulizer, Part No. N0775-330.

5.6 Quartz Torch, Part No. N077-0338.

5.7 Alumina Injector, 2.0-mm i.d. Part No. N077-5177, Sapphire Injector, 1.8 mm i.d. Part no. 4060-010978.

5.8 Ryton Double-Pass Scott-Type Spray Chamber, Part No. N077-5296.

5.9 Perkin-Elmer AS-93plus Autosampler, Perkin-Elmer S10 Autosampler, ESI SCFAST Autosampler.

5.10 Volumetric flasks, pyrex, 100-mL, 200-mL, 1-L.

5.11 Micropipets, Corning, Lambda, Wheaton, Socorex, variable volume, or equivalent.

5.12 WinLab32 Instrument Control Software.

5.13 Neslab CFT-75 Chiller.

5.14 Peristaltic Pump.

5.15 Standard Pump Sample Tubing: 0.76 mm (0.030 in) ID, Part No. 0990-8587.

5.16 Silicone Pump Tubing for MIBK solvent: 0.76 mm (0.30 in) inner diameter, Part No. 0047-3552.

5.17 Standard Pump Drain Tubing: 1.14 mm (0.045 in) inner diameter, Part No. 0990-8585.

5.18 Silicone Pump Drain Tubing for MIBK solvent: 1.14 mm (0.045 in) inner diameter, Part No. N069-1595.

5.19 Teflon Tubing, 1/8” outer diameter, Part No. 0250-6483.

5.20 Polyethylene Nebulizer Tubing, 0.58 mm inner diameter, Part No. 0990-8265.

5.21 PVC Spray Chamber Drain Tubing, 1.5 mm inner diameter, Part No. 0998-5735.

5.22 RF Generator Air Filter, Part No. N077-5220.

5.23 Spectrometer Air Filter, Part No. 0250-9115.

5.24 pH strips, 0 – 6 pH range, EM colorpHast, Fisher M95863 (used to adjust sample pH, if necessary).

6.0 REAGENTS AND STANDARDS

Guidelines for the storage, tracking and expiration of chemicals and reagents can be found in SVL 1032. The procedure for purchasing chemicals and reagents

can be found in SVL 1015. Any exceptions to the above mentioned SOPs will be found in this section: as well as, all of the preparatory steps needed to construct or prepare reagents, and standards. Equivalent reagents or standards may be used.

6.1 Argon, 99.99%, with regulator set between 550 and 825 kPa (80 and 120 psig).

6.2 Compressed air shear gas with regulator set between 550 and 825 kPa (80 and 120 psig).

6.3 Concentrated hydrochloric acid, Fisher TraceMetals Grade, or EMD Omni Trace.

6.4 Concentrated nitric acid, Fisher TraceMetals Grade, or EMD Omni Trace.

6.5 Commercially-manufactured single-element stock solutions:

Element	Concentration (µg/mL)	Mfg	Part No	Matrix
Aluminum	10000	HPS	10001-1-250	2% HNO_3
Antimony	1000	HPS	10002-3-250	5% HNO_3 + 0.1% HF
Arsenic	1000	HPS	10003-1-250	2% HNO_3
Barium	10000	HPS	10M4-1-250	4% HNO_3
Beryllium	1000	HPS	10005-1-250	2% HNO_3
Bismuth	10000	HPS	10M6-1-250	4% HNO_3
Boron	5000	HPS	5M7-4-250	Water
Cadmium	1000	HPS	10008-1-250	2% HNO_3
Calcium	10000	HPS	10M9-1-250	4% HNO_3
Cerium	1000	HPS	100010-1-250	2% HNO_3
Chromium	1000	HPS	100012-1-250	2% HNO_3
Cobalt	1000	HPS	100013-1-250	2% HNO_3
Copper	1000	HPS	100014-1-250	2% HNO_3
Gallium	10000	HPS	10M19-1-250	4% HNO_3
Gold	1000	HPS	1000021-2	2% HCl
Iron	10000	HPS	10M26-1-250	10% HNO_3
Lanthanum	10000	HPS	10M27-1-250	4% HNO_3
Lead	1000	HPS	100028-1-250	2% HNO_3

Element	Concentration (µg/mL)	Mfg	Part No	Matrix
Lithium	10000	HPS	100029-1-250	1% HNO_3
Lutetium	10000	HPS	10M33-1-250	4% HNO_3
Magnesium	10000	HPS	10M31-1-250	4% HNO_3
Manganese	1000	HPS	100032-1-250	2% HNO_3
Mercury	100	HPS	100 33-1	5% HNO3
Mercury	1000	HPS	100033-1	5% HN03
Molybdenum	1000	HPS	100034-3-250	2% HNO_3+0.1% HF
Nickel	1000	HPS	100036-1-250	2% HNO_3
Phosphorus	10000	HPS	10M39-1-250	0.05% HNO_3
Potassium	10000	HPS	10M41-1-250	1% HNO_3
Selenium	1000	HPS	100049-1-250	2% HNO_3
Scandium	10000	HPS	10M48-1-250	4% HNO_3
Silicon	10000	HPS	10M50-4-250	Water
Silver	1000	HPS	100051-1-250	2% HNO_3
Sodium	10000	HPS	10M52-1-250	1% HNO_3
Strontium	10000	HPS	10M53-1-250	4% HNO_3
Thallium	1000	HPS	100058-1-250	2% HNO_3
Tin	10000	HPS	10M61-3-250	4% HNO_3+2% HF
Titanium	1000	HPS	100062-3-250	2% HNO_3+0.1% HF
Vanadium	1000	HPS	100065-1-250	2% HNO_3
Yttrium	1000	HPS	100067-1-250	2% HNO_3
Zinc	1000	HPS	100068-1-250	2% HNO_3

6.6 Spiking solutions: N5, SVL11, TCLP7, QC-Sc and QC-Sn (see SVL 4119 for preparation).

6.7 QC19 stock solution: Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Tl, Ti, V, Zn at 100 µg/mL in 5% HNO_3 and trace HF, CPI S4400-004.

6.8 QC26 stock solution: Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Ag, Na, Tl, Ti, V, and Zn at 100 µg/mL, K at 1000 µg/mL, and Si at 50 µg/mL, in 4% HNO_3, High-Purity Standards QCS-26.

6.9 Standard 1 Mix: Bi, Ga, Li, Sn and Sr at 500 µg/mL as well as P at 1000 µg/mL, in 10% HCl and Tr HNO_3. High-Purity Standards SM-150-060. Expiration date as stated by the manufacturer.

6.10 Calibration blank (Seq-Cal1@S0): Solution of 2% nitric acid (6.4) and 5% hydrochloric acid (6.3) in deionized water (6.25). This solution is used as the ICB and CCB also.

6.11 Calibration standard number 1 (Seq-Cal 2@S): Add deionized water (6.25) to a 1000 mL volumetric flask. Carefully add 20 mL concentrated nitric acid (6.4), 50 mL concentrated hydrochloric acid (6.3). Add 30 mL QC 26 stock solution (6.8) and 10 mL Standard 1 Mix (6.9). Dilute to the mark with deionized water and mix well. Store in a brown bottle, or away from light. The final concentrations of the elements in this solution are:

Volume (mL)	Stock Solution (mg/L)	Final Concentration in Standard 1 (mg/L)
30.0	100 Ag	3
30.0	100 As	3
30.0	100 B	3
30.0	100 Ba	3
30.0	100 Be	3
10.0	500 Bi	5
30.0	100 Cd	3
30.0	100 Co	3
30.0	100 Cr	3
30.0	100 Cu	3
10.0	500 Ga	5
30.0	1000 K	30
10.0	800 Li	8
30.0	100 Mn	3
30.0	100 Mo	3
30.0	100 Ni	3
10.0	1000 P	10
30.0	100 Pb	3
30.0	100 Sb	3
30.0	100 Se	3
10.0	500 Sn	5
10.0	500 Sr	5
30.0	100 Ti	3

30.0	100 Tl	3
30.0	100 V	3
30.0	100 Zn	3

6.12 Calibration standard number 2 (Seq-Cal 3@S): Add deionized water (6.25) to a 1000 mL volumetric flask. Carefully add 20 mL concentrated nitric acid (6.4), 50 mL concentrated hydrochloric acid (6.3). Add the following amounts of single-element stock solutions (6.5). Then dilute to the mark with deionized water and mix well. The final concentrations of the elements in this solution are:

Volume (mL)	Stock Solution (mg/L)	Final Concentration in Standard 2 (mg/L)
5.0	10000 Al	50
5.0	10000 Ca	50
5.0	10000 Fe	50
5.0	10000 Mg	50
5.0	10000 Na	50
2.5	10000 Si	25.0
2.5	10000 SiO2	53.5

6.13 Calibration standard number 3 (Seq-Cal 4@S): Add deionized water (6.25) to a 1000 mL volumetric flask. Carefully add 20 mL concentrated nitric acid (6.4), 50 mL concentrated hydrochloric acid (6.3). Add 10 mL of Standard 3 Mix (6.26**)** and 2.5 mL Si stock solution. Then dilute to the mark with deionized water and mix well. The final concentrations of the elements in this solution are:

Volume (mL)	Stock Solution (mg/L)	Final Concentration in Standard 3 (mg/L)
1.0	10000 La	10.0
0.2	10000 Sc	2.0
2.5	10000 Si	25.0
2.5	10000 SiO_2	53.5

6.14 Calibration standard number 4 (Seq-Cal 5@S): Add deionized water (6.25) to a 1000 mL volumetric flask. Carefully add 20 mL concentrated nitric acid (6.4), 50 mL concentrated hydrochloric acid (6.3). Add the following amount of single-element stock solution (6.5). Then dilute to the mark with deionized water and mix well. The final concentrations of the elements in this solution are:

Volume (mL)	Stock Solution (mg/L)	Final Concentration in Standard 4 (mg/L)
1.0	1000 Ce	1.0

6.15 ICS-AB stock solution: Add deionized water (6.25) to a 200 mL volumetric flask. Carefully add 2 mL concentrated nitric acid (6.4), 10 mL concentrated hydrochloric acid (6.3). Add the following amounts of single-element stock solutions (6.5). Then dilute to the mark with deionized water and mix well. The final concentrations of the elements in this solution are:

Volume (mL)	Stock Solution (mg/L)	Final Concentration in ICS-AB (mg/L)
10.0	1000 Be	50
10.0	1000 Co	50
10.0	1000 Mn	50
10.0	1000 Cr	50
10.0	1000 Cu	50
10.0	1000 V	50
10.0	1000 Cd	50
10.0	1000 Pb	50
10.0	1000 Ni	50
10.0	1000 Zn	50
1.00	10000 Ba	50
10.0	1000 As	50
10.0	1000 Se	50
10.0	1000 Tl	50
10.0	1000 Sb	50

6.16 ICSA (containing Fe, Mg, Ca, Al), HPS Catalog No. 4400-INTA1-500.

6.17 Working ICS-A solution: Add deionized water (6.25) to a 200 mL volumetric flask. Add 4 mL concentrated nitric acid (6.4) and 10 mL of concentrated hydrochloric acid (6.3). Add the following amounts of stock solutions. Then dilute to the mark with deionized water and mix well. The final concentrations will be Al at 500 mg/L, Ca at 500 mg/L, Mg at 500 mg/L, Fe at 200 mg/L, and Cr, Cu, Mn, Ni, Ti, and V each at 10 mg/L. Use the following volumes of the stock standards:

Stock Solution (mg/L)	Volume Stock (mL)
Interference A Standard	20.0
1000 Cr	2.0
1000 Cu	2.0
1000 Mn	2.0
1000 Ni	2.0
1000 Ti	2.0
1000 V	2.0

6.17.1 The concentrations for the working ICSA solution are listed below:

Element	Final Conc. (mg/L)	Element	Final Conc. (mg/L)
Al	500	Ca	500
Cr	10	Cu	10
Fe	200	Mg	500
Mn	10	Ni	10
Ti	10	V	10

6.18 Working ICS-AB solution: Add deionized water (6.25) to a 200 mL volumetric flask. Carefully add 4 mL concentrated nitric acid (6.4) and 10 mL concentrated hydrochloric acid (6.3). Add the following amounts of stock solutions. Then dilute to the mark with deionized water and mix well. Store in a brown bottle, or away from light. . Use the following volumes of the stock standards:

Stock Solution	Volume (mL)
Interference A Standard	20.0
ICS-AB Stock Solution	2.00
1000 mg/L Ag	0.10

6.18.1 The concentrations for the working ICS-AB solution are listed below:

Element	Final Conc. (mg/L)	Element	Final Conc. (mg/L)
Al	500	Sb	0.5
As	0.5	Ba	0.5
Be	0.5	Cd	0.5
Ca	500	Cr	0.5
Co	0.5	Cu	0.5
Fe	200	Pb	0.5
Mg	500	Mn	0.5
Ni	0.5	Se	0.5
Ag	0.5	Tl	0.5
U	0.5	V	0.5
Zn	0.5		

6.19 Reporting Limit Check Solution (RLCS) stock: Add deionized water (6.25) to a 1000 mL volumetric flask. Add 20 mL of concentrated nitric acid (6.4) and 50 mL of concentrated hydrochloric acid (6.3). Add the following amounts of single-element stock solutions. Preparation of intermediate solutions of the single-element stock solutions is permissible. Then dilute to the mark with deionized water and mix well. The final concentrations of the elements in this solution are:

Stock Solution	Volume of Stock Solution (mL)	Final Concentration (mg/L)
1000 Ag	0.50	0.50
10000 Al	0.80	8.00
1000 As	2.5	2.50
5000 B	0.80	4.00
10000 Ba	0.02	0.20

Stock Solution	Volume of Stock Solution (mL)	Final Concentration (mg/L)
1000 Be	0.20	0.20
10000 Bi	0.60	6.00
10000 Ca	0.40	4.00
1000 Cd	0.20	0.20
1000 Cr	0.60	0.60
1000 Co	0.60	0.60
1000 Cu	1.0	1.00
10000 Fe	0.60	6.00
10000 Ga	0.20	2.00
10000 K	5.0	50.0
10000 La	0.050	0.50
10000 Li	0.20	2.00
10000 Mg	2.0	20.0
1000 Mn	0.40	0.40
1000 Mo	0.80	0.80
10000 Na	5.0	50.0
1000 Ni	1.0	1.00
10000 P	0.50	5.00
1000 Pb	0.75	0.75
1000 Sb	2.0	2.00
10000 Sc	0.020	0.20
1000 Se	4.0	4.00
10000 Si	0.80	8.00
10000 Sn	0.50	5.00
10000 Sr	0.050	0.50
1000 Ti	0.50	0.50
1000 Tl	1.5	1.50
1000 V	0.50	0.50
1000 Zn	1.0	1.00

6.20 ICV and CCV solution. Add deionized water (6.25) to a 1000 mL volumetric flask. Carefully add 20 mL concentrated nitric acid (6.4) and 50 mL concentrated hydrochloric acid (6.3). Add the following amounts of stock solutions. Dilute to the mark with deionized water and mix well. Make sure to use a secondary source or different lot number than was used for the calibration standards.

Stock Solution (mg/L)	Volume (mL)
QC26 Stock Solution	20.0
10000 Si	0.90
10000 P	1.0
10000 Sc	0.10
10000 Sr	0.20
10000 Na	1.8
10000 Bi	0.40
10000 Ga	0.40
10000 La	0.40
10000 Li	0.40
10000 Sn	0.40

6.20.1 Low Level Initial Check Verification (LLICV) solution: Add deionized water (6.25) to a 1000 mL volumetric flask. Carefully add 20 mL concentrated nitric acid (6.4) and 50 mL concentrated hydrochloric acid (6.3). Add 0.4 mL of 1000 ppm silver stock solution (6.5). Dilute to the mark with deionized water and mix well. Make sure to use a secondary source or a different lot number than was used for the calibration standards.

Stock Solution (mg/L)	Volume (mL)
1000 Ag	0.40

6.20.2 The concentrations for the ICV/CCV solution are listed below. Note: The lower silver concentration (0.4 mg/L) is for the LLICV.

Element	Final Conc. (mg/L)	Element	Final Conc. (mg/L)
Ag	2 , 0.4	Mg	2
Al	2	Mn	2
As	2	Mo	2
B	2	Na	20
Ba	2	Ni	2
Be	2	P	10
Bi	4	Pb	2
Ca	2	Sb	2
Cd	2	Sc	1
Cr	2	Se	2
Co	2	Si	10
Cu	2	Sn	4
Fe	2	Sr	2
Ga	4	Ti	2
K	20	Tl	2
La	4	V	2
Li	4	Zn	2

6.21 RLCS working: Add deionized water (6.25) to a 500 mL volumetric flask. Carefully add 10 mL concentrated nitric acid (6.3) and 25 mL concentrated hydrochloric acid (6.4). Add 5.0 mL of the RLCS stock (6.19). Store in a brown bottle, or away from light. The final concentrations of the elements in this solution are:

Element	Final Concentration (µg/L)	Element	Final Concentration (µg/L)
Ag	5	Mg	200
Al	80	Mn	4
As	25	Mo	8
B	40	Na	500
Ba	2	Ni	10
Be	2	P	50
Bi	60	Pb	7.5
Ca	40	Sb	20

Element	Final Concentration (µg/L)	Element	Final Concentration (µg/L)
Cd	2	Sc	2
Cr	6	Se	40
Co	6	Si	80
Cu	10	Sn	50
Fe	60	Sr	5
Ga	20	Ti	5
K	500	Tl	15
La	5	V	5
Li	20	Zn	10

6.22 Internal standard: Add deionized water (6.25) to a 3000 mL bottle. Add 60 mL concentrated nitric acid (6.4) and about 6 mL of a 10000 ppm lutetium stock solution (6.5). Dilute to the mark with deionized water and mix well.

6.23 Manganese solution 10 ppm: Take 1 mL of 1000 ppm manganese (6.5) and dilute to 100 mL in a volumetric flask with deionized water (6.25). Used for alignment of torch viewing position.

6.24 Manganese solution 1 ppm: Take 1 mL of 10 ppm manganese (6.23) and dilute to 10 mL in a volumetric flask with deionized water (6.25). Used for alignment of torch viewing position.

6.25 Type II deionized water.

6.26 Standard 3 Mix: La at 1000 ug/mL and Sc ug/mL at 200 in 2% HNO_3, High-Purity Standards SM-150-061. Expiration date as stated by the manufacturer.

FOR 6010 Hg

6.27 Aqua Regia Solution of 1 part nitric acid (6.4) and 3 parts hydrochloric acid (6.3) in deionized water (6.25).

6.28 Calibration blank (Seq-Cal1@S0): Solution of 25% aqua regia (6.27) in deionized water (6.25). This solution is used as the ICB, CCB, and diluent solution also.

6.29 Calibration standard number 1 (Seq-Cal 2@S): Add deionized water (6.25) to a 1000 mL volumetric flask. Carefully add 250 mL of aqua regia (6.27). Add 3 mL Molybdenum stock solution (6.5), 5 mL Gold stock solution (6.5), and 3 mL vanadium stock solution (6.5). Dilute to the mark

with deionized water and mix well. The final concentrations of the elements in this solution are:

Volume (mL)	Stock Solution (mg/L)	Final Concentration in Standard 1 (mg/L)
3	1000 Mo	3
5	1000 Au	5
3	1000 V	3

6.30 Calibration standard number 2 (Seq-Cal 3@S): Add deionized water (6.25) to a 1000 mL volumetric flask. Carefully add 250 mL of aqua regia (6.27). Add 2 mL Hg stock solution (6.5). Then dilute to the mark with deionized water and mix well. The final concentrations of the elements in this solution are:

Volume (mL)	Stock Solution (mg/L)	Final Concentration in Standard 2 (mg/L)
2	1000 Hg	2

6.31 Working ICS-A solution: Add deionized water (6.25) to a 500 mL volumetric flask. Add 125 mL of aqua regia (6.27). Add the following amounts of stock solutions (6.5). Then dilute to the mark with deionized water and mix well. The final concentrations will be Al at 500 mg/L, Ca at 500 mg/L, Mg at 500 mg/L, Fe at 200 mg/L, and Cr, Cu, Mn, Ni, Ti, and V each at 10 mg/L. Use the following volumes of the stock standards:

Stock Solution (mg/L)	Volume Stock (mL)
Interference A Standard	50.0
1000 Cr	5.0
1000 Cu	5.0
1000 Mn	5.0
1000 Ni	5.0
1000 Ti	5.0
1000 V	5.0

6.31.1 The concentrations for the working ICSA solution are listed below:

Element	Final Conc. (mg/L)	Element	Final Conc. (mg/L)
Al	500	Ca	500
Cr	10	Cu	10
Fe	200	Mg	500
Mn	10	Ni	10
Ti	10	V	10

6.32 Working ICS-AB solution: Add deionized water (6.25) to a 500 mL volumetric flask. Carefully add 125 mL of aqua regia (6.27). Add the following amounts of stock solutions. Then dilute to the mark with deionized water and mix well. Store in a brown bottle, or away from light. Use the following volumes of the stock standards:

Stock Solution	Volume (mL)
Interference A Standard (6.16)	50.0
ICS-AB Stock Solution (6.15)	5.00
1000 mg/L Ag (6.5)	0.25
1000 mg/L Hg (6.5)	0.25

6.32.1 The concentrations for the working ICS-AB solution are listed below:

Element	Final Conc. (mg/L)	Element	Final Conc. (mg/L)
Al	500	Sb	0.5
As	0.5	Ba	0.5
Be	0.5	Cd	0.5
Ca	500	Cr	0.5
Co	0.5	Cu	0.5
Fe	200	Pb	0.5
Mg	500	Mn	0.5
Ni	0.5	Se	0.5
Ag	0.5	Tl	0.5
U	0.5	V	0.5
Zn	0.5	Hg	0.5

6.33 ICV and CCV solution. Add deionized water (6.25) to a 1000 mL volumetric flask. Carefully add 250 mL of aqua regia (6.27). Add the following amounts of stock solutions. Dilute to the mark with deionized water and mix well. Make sure to use a secondary source or different lot number than was used for the calibration standards.

Stock Solution (mg/L)	Volume (mL)
QC26 Stock Solution	20.0
1000 Hg	10.0
1000 Au	2.0

6.33.1 The concentrations for the ICV/CCV solution are listed below.

Element	Final Conc. (mg/L)	Element	Final Conc. (mg/L)
Ag	2	K	20
Al	2	Mg	2
As	2	Mn	2
Au	2	Mo	2
B	2	Na	2
Ba	2	Ni	2
Be	2	Pb	2
Ca	2	Sb	2
Cd	2	Se	2
Cr	2	Si	1
Co	2	Ti	2
Cu	2	Tl	2
Fe	2	V	2
Hg	1	Zn	2

6.34 Reporting Limit Check Solution (RLCS): Add deionized water (6.25) to a 1000 mL volumetric flask. Add 250 mL of aqua regia (6.27). Add 0.2 mL of 100 mg/L Hg stock solution. Then dilute to the mark with deionized water and mix well. The final concentrations of the elements in this solution are:

Stock Solution	Volume of Stock Solution (mL)	Final Concentration (mg/L)
100 Hg	0.2	0.02

7.0 INSTRUMENT SETTINGS

7.1 Ensure that the exhaust vent is ON.

7.2 Ensure that the argon tank has enough argon, and that the tank valve is open.

7.3 Ensure that the water chiller is ON, and that it has enough water.

7.4 Ensure that the peristaltic pump tubing is in good condition.

7.5 Ensure that the drain tubing on the spray chamber is in good condition.

7.6 Ensure that the drain bottle has enough empty volume to collect waste.

7.7 Ensure that the autosampler rinse bottle has enough water, and that the lutetium internal standard bottle is full.

7.8 Ensure that the sampling probe is installed at the correct height, and that the probe capillary is attaching to the pump tubing.

7.9 Ensure that the printer has an adequate supply of paper.

7.10 Ensure that the “Main Instrument” switch is ON. Leave the “Main Instrument” switch on, even when the instrument is not in use.

7.11 Ensure that the autosampler is ON.

7.12 Ensure that the computer, monitor, and printer are ON.

8.0 CALIBRATION

8.1 Use a calibration blank (6.10) and one calibration standard for each metal. Because of chemical interactions, the metals are divided into four combination standards.

8.1.1 Load S0 (6.10)

8.1.2 Load S1 (6.11)

8.1.3 Load S2 (6.12)

8.1.4 Load S3 (6.13)

8.1.5 Load S4 (6.14)

8.2 Analyze an ICV (6.20) after the calibration standard.

8.3 Analyze an ICB (6.10) after the ICV.

8.4 Analyze a RLCS (6.19) after ICB.

8.5 Analyze an ICSA (6.17) followed by an ICSAB (6.18) after the RLCS.

8.6 Analyze a CCV (6.20) followed by a CCB (6.10) after the ICSAB to complete the calibration.

9.0 SAMPLE HANDLING AND PRESERVATION

9.1 Samples for total recoverable metals should have been preserved by acidification with nitric acid to a pH < 2 or lower immediately upon collection in the field or upon being accepted by Sample Receiving as per SVL 2001.

9.1.1 Samples that have been put on hold due to the 24-hour desorb period after preservation, may not be removed for analysis prior to Sample Receiving releasing the container(s) as per SVL 2001 section 8.15.

9.1.2 Samples for dissolved analysis are to be filtered through a 0.45 µm filter upon collection or as soon thereafter as practically possible. After filtration preserve sample by acidification with nitric acid to a pH < 2.

9.2 Soil samples are preserved by refrigeration (held between 0-6 ºC) when the client instructs. There is no published holding time for soils.

10.0 SAMPLE PREPARATION AND ANALYSIS

10.1 If a preserved aqueous sample has a turbidity of less than 1 NTU, it may be analyzed directly, without digestion. Direct analysis requires some bench prep:

10.1.1 Each batch must be accompanied by a preparation blank, LCS, matrix spike and matrix spike duplicate.

10.1.2 Add 0.1 mL of concentrated nitric acid and 10 mL of sample to each vial.

10.1.3 The matrix spike and LCS are prepared as above with the addition of 100 µL of each of the five spike solutions (6.6) as needed for the batch.

10.2 Samples for dissolved metals must be filtered and preserved prior to analysis (acidify with nitric acid to a 1% (v/v)). These samples do not require digestion.

10.2.1 Each batch must be accompanied by a preparation blank, LCS, matrix spike and matrix spike duplicate. The preparation blank and LCS must also be filtered.

10.3 All other aqueous samples must be digested prior to analysis. SOPs covering digestive procedures are as follows: If the analytical method is 6010C, SOP SVL 4079 (EPA method 3010A) should be used for total metals, SOP SVL 4080 (EPA method 3005A) should be used for total recoverable metals, if the analytical method is 200.7, SOP SVL 4106 should be used for total recoverable metals.

10.3.1 For aqueous samples containing silver at concentrations ≥ 0.1 mg/L the sample will need to be re-digested to a level below 0.1 mg/L and re-analyzed. The diluted silver sample results shall be reported.

10.4 Soil samples by EPA 6010C must be digested by SOP SVL 4094 prior to analysis.

10.4.1 Soil samples containing > 50 mg/kg of silver will also need to be diluted and re-digested below 50 mg/kg and re-ran on the ICP. The diluted silver sample results shall be reported.

10.4.2 If difficulties are noticed with the recovery of antimony, barium, lead or silver an alternative preparation method following section 7.5 of EPA 3050B may be used.

10.5 Soil samples by EPA 200.7

10.5.1 Transfer a portion of the sample to a weigh dish and perform a percent solid test on it by SVL SOP 4022.

10.5.2 To achieve homogeneity, take a dried portion of the sample and ground it up using a mortar and pestle.

10.5.3 To a 100 ml snap-top digestion container add 4 mL of (1+1) HNO_3 and 10 mL of (1+4) HCL. Cover the lip of the container with a watch glass. Place the snap-top in the digestion block. Reflux at 85 ºC.

10.5.3.1 Heat the sample and gently reflux for 30 minutes. Avoid vigorous boiling of the sample. Allow the sample to cool and bulk it up to 100 mL with de-ionized water.

10.5.4 Allow samples to stand overnight or filter using a 45 µm filter before running on the ICP.

10.6 Double-click on the “WinLab” icon to start the program.

10.7 Ignite the plasma.

10.7.1 Click “Tools” at the top of the screen and click “Plasma Control”, or click the “Plasma” icon on the Toolbar. The “Plasma Control” window will appear.

10.7.2 Click the “Plasma” switch in the “Plasma Control” window to ON.

10.7.3 Immediately examine the plasma through the viewing window to ensure that it is stable.

10.7.3.1 If the plasma is not stable, click the “Plasma” switch to OFF, or press F9. Address any potential problems and restart the plasma, observing its stabilization again.

10.7.4 Allow the plasma to stabilize for about thirty minutes before analyzing samples.

10.8 Perform a mercury realignment.

10.8.1 Click “Tools” at the top of the WinLab window. A drop-down menu will appear.

10.8.2 Click “Spectrometer Control”. The “Spectrometer Control” window will appear.

10.8.3 Select “Axial”.

10.8.4 Click the “Hg Realign” button at the bottom of the “Spectrometer Control” window. The “Hg Re-alignment” dialog box will appear.

10.8.5 Click “OK”. The alignment is finished when “Shutter Closed” appears in the spectrometer box.

10.9 Align the torch viewing position.

10.9.1 Click “Tools” at the top of the “WinLab” window; then click “Spectrometer Control”. The “Spectrometer Control” window will appear.

10.9.2 Select “Radial”.

10.9.3 Click “Align View” in the “Spectrometer Control” window. A dialog box will appear.

10.9.4 Select “Manganese”.

10.9.5 Set the “Read Delay” time to 45 seconds.

10.9.6 Aspirate a 10-ppm solution of manganese (6.23).

10.9.7 The instrument will automatically position the torch viewing position.

10.9.8 The alignment is finished when “Shutter Closed” appears in the spectrometer box.

10.9.9 Select “Axial” on the “Spectrometer Control” window.

10.9.10 Click “Align View”. The dialog box will appear.

10.9.11 Select ”Manganese”.

10.9.12 Set the “Read Delay” time to 45 seconds.

10.9.13 Aspirate a 1-ppm solution of manganese (6.24).

10.9.14 The instrument will automatically position the torch viewing position. The alignment is finished when “Shutter Closed” appears in the spectrometer box.

10.9.15 Click “File”. Select “Print”, then click on “New Page”. This will print the rest of the alignment and start the run data on a new page.

10.10 Open the method to be used for analysis.

10.10.1 Click “File” at the top of the window. A drop-down menu will appear.

10.10.2 Click “Open Method...”. A dialog box will appear.

10.10.3 Click the name of the method to be used as appropriate for the analysis.

10.10.4 Click “OK”.

10.11 Prepare a Sample Information File for the job.

10.11.1 Click “File” at the top of the window. A drop-down menu will appear.

10.11.2 Click “Open Sample Info File...”. The “Open Sample Information” dialog box will appear.

10.11.3 Select the pattern Sample Info File.

10.11.4 Click “Open”.

10.11.5 Click the “SamInfo” icon, or click “Tools” at the top of the window, then “Sample Information Editor”. The “Sample Information File” will appear.

10.11.6 Type the initials of the operator next to “Analyst Name” in the “Parameters Common to All Samples” section.

10.11.7 Type the SVL job number next to “Batch ID” in the “Parameters Common to All Samples” section and next to “JOB#”.

10.11.8 Type the EPA method number next to “EPA METHOD#” in the “Parameters Common to All Samples” section.

10.11.9 Type the sample number of each sample to be analyzed in the “Sample ID” column. Do not enter calibration standards, blanks, RLCS, ICSA, ICSAB, ICV, ICB, CCV, or CCB. These have already been listed in the “Calibration” and “QC” pages of the method.

10.11.9.1 If a sample requires a dilution it should be entered as the sample ID followed by "@xxX". For example, a 10X dilution of sample 1234567 would be 1234567@10X.

10.11.10 Type the autosampler location for each sample in the "A/S Location" column.

10.11.11 Enter matrix spike recovery checks as necessary.

10.11.12 Add PB and LCS using the QC page of the method. Open "Schedule QC's" and select the appropriate PB or LCS. Open "QC Sample Definition", scrolling to the right until the PB/LCS locations are found, and enter the PB and LCS ID labels into the appropriate positions.

10.12 Prepare the "Automated Analysis Control" window for the run.

10.12.1 Click the "Auto" icon. The "Automated Analysis Control Set Up" page will appear.

10.12.2 The selected method will already appear in the "Method" column.

10.12.3 The number of minutes the system should wait before it starts the method will already appear in the "Delay (min)" column. This may be 0.0.

10.12.4 The name of the sample information file to be used will already appear. If not, click the "Open" tab next to "Sample Information File".

10.12.5 "All Defined" will already appear in the "Sample Info File" column. If not, check "Use Sample Info" under the name of the sample information file. A drop-down menu will appear. To analyze all samples according to the specified sample information file, select "All Defined" from the drop-down menu. To analyze only certain samples, select "Sample Nos.", then list the sample numbers in the "Sample Nos." column.

10.12.6 Click "Use Method in Memory" to use the method you specified.

10.12.7 Click the "Open" button next to "Results Data Set Name". The "Select Results Data Set" dialog box will appear.

10.12.8 Type a file name for the results to be generated. This will be the last two digits of the year and the day number of that year,

followed by a letter designation coinciding with the run for the day (A for the first calibration/run, B for the second, C for the third, etc. For example the first calibration/run for January 3, 2009 would be 09003A. Then click "OK".

10.12.9 If desired to automatically shut down after the run is complete, click the "Set" tab next to "Auto Shutdown".

10.12.10 To print a report of data during analysis, check the box next to "Print Log During Analyses".

10.12.11 Click the "Analyze" tab at the bottom of the "Automated Analysis Control" window. The "Analyze" page will appear.

10.12.12 Click "Rebuild List" to transfer the contents of the Sample Info File to the "Analyze" page.

10.13 Load samples and QC standards in the autosampler tray.

10.14 Place the loaded tray on the autosampler.

10.15 Click "Analyze All" on the "Automated Analysis Control: Analyze" page to analyze the full sequence of calibration standards, QC, and samples. The instrument will automatically analyze in the following order: zero-standard, calibration standards, ICV, ICB, CRI, ICS-A, ICS-AB, CCV, CCB, samples.

10.16 To stop an analysis in the course of a run, click "Analyze All" button again. The "Stopping an Analytical Sequence" dialog box will appear. Select when the analysis will stop, either "Stop immediately" or "Complete current replicate", or "complete all replicates for current sample". Then click "OK".

10.17 To re-start the analysis where it was stopped, click "Analyze All" again. The "Continuing an Analytical Sequence" dialog box will appear. Select "Continue with next sequence#", "Re-analyze previous sequence # and continue", or "Continue with sequence # n". Then click "OK".

10.18 To add another sample to the analytical sequence, click the "Priority" button at the bottom of the "Automated Analysis Control Analyze" page. A dialog box will appear. Enter the sample information. Select an option from the "When to Analyze" menu, then click "Add Sample".

10.19 To re-analyze a calibration standard manually during the run:

10.19.1 Click the "Reset Sequence" button at the top of the "Automated Analysis Control: Analyze" page. Then close the "Automated Analysis Control" window.

10.19.2 Click “Tools” at the top of the window and then click “Manual Analysis Control”. Or click the “Manual” icon. The “Manual Analysis Control” window will appear.

10.19.3 Select the standard to be re-analyzed.

10.19.4 Click the “Analyze Standard” tab.

10.20 To re-analyze a QC sample (like a CCV or a CCB) during the course of an analysis, click the “Analyze Samples” button. The “Stopping an Analytical Sequence” dialog box will appear. Select “Reanalyze previous number”. Then click “OK”

10.21 Instrument maintenance.

10.21.1 Each day, flush the sample introduction system with 2% Nitric Acid for five minutes with the plasma on.

10.21.2 Each day check the chiller to make sure it has been filled with distilled (not deionized!) water. On the advice of Perkin-Elmer technicians, SVL does not add 1.8 grams chloramine-T to prevent algae growth as stated in the operation manual.

10.21.3 Each day check the torch to make sure there are no deposits or signs of melting.

10.21.4 Change the peristaltic pump tubing after about 24 hours of operation, but not in the middle of a calibration sequence.

10.21.5 Clean the torch at least once a week, or as necessary. Remove the copper foil igniter and soak the torch in 5% (no more than 20%) nitric acid or aqua regia. Rinse thoroughly. Then dry it with clean air or nitrogen.

10.21.6 Inspect the torch O-rings when cleaning the torch. If necessary, clean them with soap and water. Replace them if they are cracked or worn.

10.21.7 Check the nebulizer spray pattern with deionized water at least once a week. If necessary, clean the nebulizer with soap and water, then rinse thoroughly.

10.21.8 Clean the spray chamber when necessary. Soak the chamber in 5% (no more than 20%) nitric acid or aqua regia. Rinse thoroughly.

10.21.9 Clean the spectrometer and generator air filters every month. Replace them if necessary.

10.21.10 Flush the chiller every six months. Replace the water filter every three months, or as needed.

10.21.11 Log maintenance in the appropriate maintenance log.

10.22 SAMPLE PREPARATION AND ANALYSIS for Hg

10.22.1 Weigh a sample to 1.00 g ± 0.005 g (any deviations from the 1.00 g will also follow the ± 0.005 g error factor and be verified in the digestion log and on the bench sheet) and transfer to a snap-cap vial.

10.22.2 Prepare a method blank by adding 1.00 g ± 0.005 g of boiling stone and transfer to a snap-cap vial.

10.22.3 Prepare Hg LCS by adding 1.00 g ± 0.005 g of boiling stone and transfer to a snap-cap vial.

10.22.4 Prepare a matrix spike and a matrix spike duplicate by weighing additional aliquots of sample into snap-cap vials. If possible, select a sample with a low native concentration of metals.

10.22.5 Matrix spikes and LCS, add 0.400 mL of 100 mg/L Hg stock solution (6.5). When brought up to volume, this will result in a matrix spike of the 40.0 mg/kg.

10.22.6 Add 10 mL of aqua regia (6.27). Mix and partially close the lid.

10.22.7 Heat the sample mixture to 95°C and reflux for 30 minutes without boiling.

10.22.8 Cool the samples and dilute them to 40 mL with deionized water (6.25).

10.22.9 To remove insoluble materials, filter the samples or allow them to settle overnight.

11.0 DATA REDUCTION

11.1 The software creates a linear calibration curve and calculates results from that curve. Results must be corrected manually for sample dilution.

11.2 Check the instrument calculated percent recoveries of the matrix spikes and the LCS, ensuring they are within control parameters. If needed re-run or post spike a QC sample.

11.3 Check and flag as necessary the relative percent differences (RPDs) of the sample duplicates when processing the data in Element.

12.0 DATA AND RECORDS MANAGEMENT

12.1 The raw data will print to a PDF file as the run proceeds. IT IS IMPORTANT TO NOT CLOSE THIS APPLICATION WINDOW WHILE THE RUN IS STILL ACTIVE. The software overwrites the file with the new complete file (including the newest page) with each new page. IF YOU CLOSE THE "PDF PRO SOFTWARE" WHILE IT IS SAVING, THE FILE WILL BE LOST.

12.1.1 The PDF Pro software will open automatically when the instrument software sends the first page to the printer during the startup alignments. After the alignments are complete go to "File", "Print" and "New Page". This will start the run data on a new page. The PDF Pro software will open automatically after the first standard (blank) runs for second and subsequent analytical runs.

12.1.2 Change the file name in the "Doc Info" tab of the PDF Pro window. The "Title" will be the same as the instrument file name (IE 09001A). *It is very important this name be correct. If the file is misnamed the same as an existing file it (the previous file) will be overwritten with the new data and the previous file will be lost.*

12.1.3 The previous day's file should be moved into the appropriate folder (i.e. folder Jan 2009 for file 09001A) either at the end of the run or before the beginning of the next run (or start of the day). This will prevent an accidental overwrite as mentioned above.

12.2 Print the run log to the same PDF file after the run is complete by clicking on "Close" after running the macro for run logs. An additional paper copy will need to be printed for the run log book. After clicking "Close" the preview window will close and the paper copy can be obtained by going to the "File", then "Print". The "Printer" selection will need to be changed to the appropriate printer (i.e. HP Laserjet Series 4050 PCL for the Optima 1). Click "Print" after changing the printer selection.

12.2.1 If a paper printout is required for any application it must be printed from the "File", "Print" window and the "Printer" "Name" must be changed to the appropriate printer.

12.3 File the run log in the run log book.

12.4 Print the Standards Log page associated with that run to the appropriate PDF file. Also print the ICP Control Sheet associated with that run to the same PDF file.

12.5 When analysis is complete, create a transfer file and upload ICP data to Element.

12.5.1 Click "File" at the top of the WinLab window. A drop-down menu will appear.

12.5.2 Click "Utilities Data Manager". The "Data Manager" window will appear with a list of data files in the "D:\pe\Default User\Results..." section. If not, click the "Library Category" button to ensure that "Results" appears in the box to its right. Then click the "Library Name" button to ensure that "D:\pe\Default User\Results..." appears in the box to its right.

12.5.3 Click on the appropriate "Results Data" set name.

12.5.4 Click the "Export" icon on the tool bar. The "Data Export Wizard" will appear.

12.5.5 Click the button next to "Use Existing Design".

12.5.6 Click the "Browse..." button.

12.5.7 For level 1 and 2 jobs use the "LIMS_Export.xpt" template. See section 12.8 for Level 3 data upload instructions.

12.5.8 Click the "Open" button. The "Data Export Wizard" window will re-appear.

12.5.9 Click the "Next" button. The "Select Samples to Export" window will appear.

12.5.10 Select "Enable/Disable Samples". The "Enable/Disable Samples" window will appear.

12.5.11 Double-click the column header "Enabled". The "Enabled Column Fill" menu will appear.

12.5.12 Click "OK".

12.5.13 Click the box to the left of each sample necessary for the job.

12.5.14 Click the “Next” button. The “Select Analytes to Export” window will appear.

12.5.15 All analytes should be selected, if not select “All Analytes”.

12.5.17 Click the “Next” button. The “Select Export Options” window will appear.

12.5.18 Check the second of the “Name:” choices (**not** “Same as Data Set”) and fill the field with the appropriate batch number.

12.5.19 Click the “Next” button. The “Select Sample Parameters” window will appear.

12.5.20 Click the “Next” button. The “Select Mean-Related Parameters” window will appear.

12.5.21 Click the “Next” button. The “Select Replica-Related Parameters” window will appear.

12.5.22 Click the “Next” button. The “Export Data Set” window will appear.

12.5.23 Click the “Export Data” button. A pop-up window briefly appears, showing a file folder.

12.5.24 Click the “Finish” button.

12.5.25 Click the “Export” button.

12.5.26 Close the Data Manager.

12.6 Uploading Level 3 Data

12.6.1 Click “File” at the top of the WinLab window. A drop-down menu will appear.

12.6.2 Click “Utilities Data Manager”. The “Data Manager” window will appear with a list of data files in the “D:\pe\Default User\Results...” section. If not, click the “Library Category” button to ensure that “Results” appears in the box to its right. Then click the “Library Name” button to ensure that “D:\pe\Default User\Results...” appears in the box to its right.

12.6.3 Click on the appropriate “Results Data” set name.

12.6.4 Click the "Export" icon on the tool bar. The "Data Export Wizard" will appear.

12.6.5 In window "1.Select Export Design" click on the "Browse" button.

12.6.6 Select the "MARRS.xpt" by double clicking in it. Click "Next" after ensuring the MARRS.xpt path is in the window and the "Use Existing Design" choice is selected. This should happen automatically.

12.6.7 In window "2. Select Samples to Export" click the "Enable/Disable" button. Disable any samples not in the relevant batch/work order. This is done by clicking the boxes in the "Enabled" column, making the red check mark disappear from the grey box. **All Calibration and QC samples must be included in the export.** Click "OK" followed by "Next" once the "2. Select Samples to Export" window reopens.

12.6.8 In window "3. Select Analytes to Export" add or remove analytes as is appropriate for the batch/work order at hand. **Lu must be included in addition to any target analytes.** Click "Next".

12.6.9 In window "4. Select Export Options" type the batch number in the 'Exported File: Name:' box. The "Overwrite" choice should be selected for the "If File Already Exists:" selection.

12.6.10 For subsequent data files for reanalysis (e.g. in the case of all the required analysis not being valid as a result of failed QC, instrument failure or any other cause) the appropriate samples must be reanalyzed and re-exported. These data files will be labeled with the batch number followed by a letter designation starting with 'A' for the second analytical run ('B' for the third, etc.)

12.6.11 Click "Finish". From window "8. Export Data Set" click the "Export Data" Button. This exports the file to the "H:" drive. Click "Finish".

12.7 Uploading ICP data into Element.

12.7.1 Open Element, click on "Laboratory" and then select "Data Entry / Review".

12.7.2 Locate and select the batch number from the list on the left of the "Laboratory-Enter/Edit Data (Metals Batches)" Element window. Click "Create" followed by "Data Tool".

12.7.3 The "Select Data System Files" Data Tool window will open automatically. Select the file number by double clicking on the relevant file name (e.g. W701001.pm) from the "PE Winlab" window at the lower right. Sample ID numbers will appear in the 'File Name/Sample Information" window to the upper left. Click "Auto Select" and verify the necessary samples have moved down to the field directly below. If any samples didn't move down that are needed (primarily because of a labeling issue) highlight the sample numbers and click the "Include" button. Click the "Done" button.

12.7.4 From the "Data Tool – Main" window click on "Merge Files". Check that the "Merged Upload" and "Empty Upload" tabs should have matching sample ID numbers. If sample ID numbers need to be changed click the "Instrument Data" tab followed by selection of the "Lab_Number" column. To change the sample IDs to the correct number(s) right click on the highlighted "Lab_Number" column and select "Replace". Choose the incorrect sample label in the "Search for:" field then choose the correct label from the "Replace with:" field. Click "Replace" followed by "Done". Next click "Refresh" then "Save". A "Save As" box will pop up. Click on a file (e.g. AAA) and "Save". Return to "Data Entry / Review" screen and click "Save", "OK" in the "Element Data System – Data Post Results" pop-up then "Query".

12.7.5 The analyst shall perform all reviews on the "Data Entry/Review" page in Element and verify their data uploads.

12.7.6 If an input comes up color coded apply the appropriate data flags and/or undertake any corrective actions.

12.7.7 The analyst shall assign any qualifiers as necessary, which include but are not limited to: dilutions, RPD/RSD and/or spike recovery issues.

12.7.8 The analyst will then lock the results so that any future imports will not overwrite acceptable results.

12.7.9 The analyst will then update the status of the batch to "Analyzed".

12.7.10 The raw data is stored both on the instrument and on the network as a PDF file, which is located in a folder on the H: drive named for the respective instrument on which it was analyzed (H:\Optima1\PDF FILES for example).

12.7.11 Data review is outlined in SVL SOP 2009.

12.8 Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batching.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the samples began.

12.8.1 Indicate all reagents used in the batch by including them in the reagent section of the "Batch" screen.

12.9 Procedures for constructing sequences can be found at R:\Promium Stuff\How to's\Sequences.doc.

12.10 Corrective action is governed by SOP SVL 1019.

13.0 QUALITY CONTROL

Method	LCS	RPD	Spike	Prep Blank
200.7	Limits: 85 to 115%	Limit: 20%	Limits: 70 to 130%	Limit: less than half of the reporting limit[1]
	Action: re-run, then re-prep if outside limits	Action: flag if higher	Action: flag if outside recovery limits	Action: re-run, then re-prep if outside limits
6010C	Limits: 80 to 120%	Limit: 20%	Limits: 75% To 125%	Limit: less than half of the reporting limit
	Action: re-run, then re-prep if outside limits	Action: flag if higher	Action: flag, then run analytical (post) spike; failed post spike requires serial dilution	Action: re-run, then re-prep if outside limits

[1] **For California 200.7 samples, the method blank must be less than 2.2 x MDL or 10% of the lowest sample concentration.**

Method	ICV	ICB	CCV	CCB
200.7	Limit: within 5% of expected; 3% RSD between replicates	Limit: less than half of the reporting limit	Limit: within 10% of expected	Limit: less than half of the reporting limit
	Action: re-run then re-calibrate	Action: re-run, then re-calibrate and re-analyze	Action: re-run, then re-calibrate and re-analyze	Action: re-run, then re-calibrate and re-analyze
6010C	Limit: within 10% of expected; 5% RSD between replicates	Limit: less than half of the reporting limit	Limit: within 10% of expected	Limit: less than half of the reporting limit
	Action: re-run then re-calibrate	Action: re-run, then re-calibrate	Action: re-run, then re-calibrate and re-analyze	Action: re-run, then re-calibrate and re-analyze

13.1 For method 200.7, the recovery of the ICV (6.20) must be within 5% of the expected value for target analytes. For method 6010C, the recovery must be within 10% of the expected value for target analytes. In addition, the relative percent difference of the ICV replicate integrations must be 3% or less for method 200.7 and 5% or less for method 6010C. If the recovery falls outside these criteria, re-analyze the ICV. If the recovery still falls outside these criteria, re-calibrate the instrument before proceeding with the analysis. Additionally, for 200.7, a LLICV will be analyzed for silver at a concentration of 0.4 mg/L that must meet the same 200.7 criteria as above.

13.2 Recovery of the ICB (6.10) must be less than one-half the reporting limit, if the recovery exceeds this criterion, re-run the ICB. If the recovery still exceeds this limit, re-calibrate the instrument before proceeding with analysis. This is a deviation from method 200.7.

13.3 Analyze an RLCS**.** The acceptance limits are plus or minus 50% of the expected value." 13.9 changed to "Method 6010C requires an RLCS (6.21) be analyzed at the end of each analysis run (prior to the CCV and CCB) with an expected recovery between 50% and 150%. If the recovery exceeds these limits, one of two possibilities will occur. Samples with similar values (those that are less than 5 times the reporting limit) will be

re-analyzed with passing QC. Samples that are not similar (meaning greater than 5 times the reporting limit) shall be reported as run.

13.4 Analyze an ICSA (6.17) and an ICSAB (6.18) immediately after each CRI standard. For the ICSA and ICSAB, the recovery of the target analytes must be within 20% of the expected value. If the recovery of any analyte exceeds the 20% criteria, re-run the solution with the failed analytes. For the ICSA all non target analytes should be within ± 2x the EPA's CRQL; if not, adjust IECs to minimize interferences. If the recovery still exceeds the criteria, fix the problem and re-calibrate the instrument before proceeding with analysis**.**

13.4.1 For 200.7 Drinking Waters the ICSA and ICSAB must also be run at the end of the batch, before the last CCV and CCB.

13.5 Analyze a prep blank at a frequency of one per batch of 20 or fewer samples. The concentration of each target analyte in the prep blank must be less than half the reporting limit, or less than 10% of the concentration of the analyte in all samples. If the recovery of a target analyte in the prep blank exceeds these criteria, re-analyze the prep blank. If the recovery in the prep blank still exceeds the criteria, re-digest and re-analyze the samples associated with the prep blank.

13.5.1 For California method 200.7 samples, the prep blank must be less than 2.2xMDL or 10% of the lowest sample concentration.

13.6 Analyze an LCS (6.6) at a frequency of one per batch of 20 or fewer samples. For method 200.7, the recovery for the LCS must be between 85 and 115% of the expected value. The recovery of the LCS for method 6010C must be within 80 to 120% of the expected value, if the recovery falls outside the above criteria, re-run the LCS. If the recovery still falls outside these criteria, re-digest and re-analyze the samples associated with the LCS.

The expected concentration of the LCS will vary depending on the stock solutions used to prepare it. If several stock solutions are used, each may contribute to the final concentration. Make sure all spikes are accounted for on the benchsheet so that an accurate summation of the analytes spiked takes place.

13.6.1 If QC19 is used, the expected concentrations are:

As 1.0 mg/L
Be 1.0 mg/L
Ca 1.0 mg/L
Cd 1.0 mg/L
Co 1.0 mg/L

Cr 1.0 mg/L
Cu 1.0 mg/L
Fe 1.0 mg/L
Mg 1.0 mg/L
Mn 1.0 mg/L
Mo 1.0 mg/L
Ni 1.0 mg/L
Pb 1.0 mg/L
Sb 1.0 mg/L
Se 1.0 mg/L
Ti 1.0 mg/L
Tl 1.0 mg/L
V 1.0 mg/L
Zn 1.0 mg/L

13.6.2 If SVL 11 is used, the expected concentrations are:

Al 1.0 mg/L
B 1.0 mg/L
Ba 1.0 mg/L
Bi 1.0 mg/L
Ga 1.0 mg/L
La 1.0 mg/L
Li 1.0 mg/L
P 1.0 mg/L
Si 5.0 mg/L
Ag 0.05 mg/L
Sr 1.0 mg/L

13.6.3 If N5 is used, the expected concentrations are:

Ca 19 mg/L
Fe 9 mg/L
K 20 mg/L
Mg 19 mg/L
Na 19 mg/L

13.6.4 If QC-Sc is used, the expected concentration is:

Sc 0.5 mg/L

13.6.5 If QC-Sn is used, the expected concentration is:

Sn 1.0 mg/L

13.6.6 If TCLP7 is used, the expected concentration is:

Ag 1.0 mg/L
As 1.0 mg/L
Ba 20 mg/L
Cd 0.2 mg/L
Cr 1.0 mg/L
Pb 1.0 mg/L
Se 0.2 mg/L

13.6.7 For mercury see 10.22.5.

13.7 For method 200.7 analyze a matrix spike (MS) at a frequency of one per batch of 10 or fewer samples. Analyze a matrix spike duplicate (MSD) at a frequency of 1 per batch of 20 or fewer samples. Acceptance limits for spike recoveries for both the MS and MSD is 70 to 130% of the expected value. Recovery calculations are not required if the concentration added is less than 30% of the sample background concentration.

13.7.1 The spike concentration for the MS will mirror the LCS concentration (see 13.6).

13.7.2 The control limit for the relative percent difference (RPD) between the MS and MSD is 20%.

13.7.3 If the spike recovery or RPD exceed the above criterion, flag the data on the client's report.

13.8 For method 6010C analyze an MS and MSD at a frequency of 1 per batch of 20 or fewer samples. Acceptance limits for spike recoveries for both the MS and MSD is 75 to 125% of the expected value, if recovery is outside this range flag the client's report. The control limit for the relative percent difference (RPD) between the MS and MSD is 20%, if the RPD is outside the 20% criteria flag the clients' report. If the spike recovery is outside the 75 to 125% do the following before reporting results out to clients.

13.8.1 If the added analyte concentration is less than 30% of the sample concentration then a post spike will not be required. The results will be flagged accordingly.

13.8.2 Analyze a post spike (analyte spike) by spiking to a portion of a prepared sample, or its dilution. Acceptance limits for the post spike should be between 80 to 120%. The level of this spike will be between 10 and 100 times the reporting limit (post spikes will be

made from single analyte standards (6.5)). If the post spike fails then run a dilution test. Failure of the post spike will result in flagging the client's report.

13.8.3 If the failing analyte concentration is above 10 times the reporting limit, then a dilution test at a1:5 ratio of the original sample will be run. If the results of the dilution and the original sample don't agree within ± 10% then a matrix effect is confirmed and will be indicated via a case narrative or a qualifier on the report. If the dilution test passes then there is no confirmation of matrix interference and the qualifiers for the spikes indicate to the client the recovery problems.

13.9 Method 6010C requires a RLCS (6.21) be analyzed at the end of each analysis run (prior to the CCV and CCB) with a recovery limit of 50% to 150%. If the calibration cannot be verified within these specified limits, the analysis of samples containing the affected analytes at less than 5 times the reporting limit must be reanalyzed. Sample results greater than 5 times the reporting limit can be reported.

13.10 Analyze a CCV (6.20) at a frequency of one per 10 samples or fewer, and at the end of an analytical run. The recovery must be within 10% of the expected value for target analytes. Reportable analytes must be bracketed by acceptable CCVs, if the recovery falls outside these criteria, determine the cause, perform corrective action, and re-analyze it. If the recovery still falls outside the criteria, re-analyze all samples run since the last successful CCV.

13.11 Analyze a CCB (6.10) immediately after each CCV. The recovery must be less than one-half the reporting limit. Reportable analytes must be bracketed by acceptable CCBs, if the recovery exceeds this criterion, determine the cause, perform corrective action, and re-analyze the CCB. If the recovery still exceeds the limit, re-analyze all samples run since the last successful CCB. This is a deviation from method 200.7, which requires that the ICB be less than the IDL (section 9.3.4 of method 200.7).

13.12 Monitor the response from the internal standard throughout the sample set being analyzed. The ratio of the response of the internal standard in any sample to the response in the zero calibration standard must be between 60 and 125%. If the ratio lies outside this range, dilute the sample by a factor of two to five and re-analyze it.

13.13 Perform an aqueous and a soil MDL study annually. See SOP 1011 "Performing an MDL Study".

13.14 Determine the linear dynamic range every 12 months for all elements and every six months for Ca, Cu, Fe, Mg, Mn, Na, Pb, and Zn.

13.14.1 Calibrate the instrument in the normal manner.

13.14.2 Analyze three successively higher standards with the highest near the upper limit.

13.14.3 If the recovery of the higher standard is within 10% of the expected concentration, it is within the linear range of the instrument.

13.14.4 If the recovery of the higher standard deviates more than 10% from the expected value, analyze a lower-concentration standard to determine the linear range.

13.15 Determine inter-element correction factors for each element every quarter using single-element standards.

13.16 Trend analysis can be found in SOP SVL 1033.

13.17 Demonstration of capability requirements can be found in SOP SVL 1010.

14.0 REFERENCES

14.1 Method 6010C, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Third Edition, Update III, December 1996.

14.2 Method 200.7, Revision 4.4, Methods for the Determination of Metals in Environmental Samples—Supplement I, Method Update Rule, May, 18 2012.

14.3 Manual for the Certification of Laboratories Analyzing Drinking Water, Fifth Edition.

14.4 Perkin-Elmer Instruments, Optima 4000 Series Hardware Guide, Part No. 0993-6373, July 2000.

14.5 Perkin-Elmer Instruments, WinLab32 Instrument Control Software Guide, Part No. 0993-6335, January 2000.

15.0 POLLUTION PREVENTION

15.1 All standards are prepared and reagents used in volumes consistent with good laboratory practice to minimize the volume of disposable waste.

16.0 WASTE MANAGEMENT

16.1 Most chemicals used during digestion and/or analysis are neutralized and/or diluted prior to disposal by permit to the public sewer. Any hazardous chemicals and/or residues are disposed of through SVL's hazardous waste disposal system (see SOPs SVL 1001 & 1008).

17.0 CHANGE HISTORY

DATE	VER.	CHANGE
07/23/09	9.0	Due to number of changes made to this document please consult an archived version for comparisons.
08/26/10	10.0	6.9 changed to "Standard 1 Mix: Bi, Ga, Li, Sn and Sr at 500 µg/mL as well as P at 1000 µg/mL, in 10% HCl and Tr HNO_3. High-Purity Standards SM-150-060. Expiration date as stated by the manufacturer". 6.10 added "(Seq-Cal1@S0)". 6.11 added "(Seq-Cal 2@S)" and "Standard 1 Mix". 6.12 added "(Seq-Cal 3@S)". 6.13 added "(Seq-Cal 4@S)" and "10 mL of Standard 3 Mix (6.26**)** and 2.5 mL Si stock solution". 6.14 added "(Seq-Cal 5@S)". 6.26 added "Standard 3 Mix: La at 1000 ug/mL and Sc ug/mL at 200 in 2% HNO_3, High-Purity Standards SM-150-061. Expiration date as stated by the manufacturer". 9.1.1 added " Samples that have been put on hold due to the 24-hour desorb period after preservation, may not be removed for analysis prior to Sample Receiving releasing the container(s) as per SVL 2001 section 8.15". 12.8 Added "Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batching.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the samples began". 12.8.1 Added "Indicate all reagents used in the batch by including them in the reagent section of the "Batch" screen". 12.9 Added "Procedures for constructing sequences can be found at R:\PromiumStuff\Howto's\Sequences.doc". 13.4 changed to "For the ICSA all non target analytes should be within ± 2x the EPA's CRQL".
8/26/11	11.0	10.4.2 added "If difficulties are noticed with the recovery of antimony, barium, lead or silver an alternative

DATE	VER.	CHANGE
		preparation method following section 7.5 of EPA 3050B may be used".
03/01/13	12.0	2.0 added "6010B may also be run under this SOP." 6.20.1 added "Low Level Initial Check Verification (LLICV) solution: Add deionized water (6.25) to a 1000 mL volumetric flask. Carefully add 20 mL concentrated nitric acid (6.4) and 50 mL concentrated hydrochloric acid (6.3). Add 0.4 mL of 1000 ppm silver stock solution (6.5). Dilute to the mark with deionized water and mix well. Make sure to use a secondary source or a different lot number than was used for the calibration standards." 6.20.2 added " Note: The lower silver concentration (0.4 mg/L) is for the LLICV." 9.1 inserted "total recoverable." 9.1.2 changed to "Samples for dissolved analysis are to be filtered through a 0.45 µm filter upon collection or as soon thereafter as practically possible. After filtration preserve sample by acidification with nitric acid to a pH < 2." 10.2 inserted "acidify with nitric acid to a 1% (v/v)." 10.2.1 added "Each batch must be accompanied by a preparation blank, LCS, matrix spike and matrix spike duplicate. The preparation blank and LCS must also be filtered." 13.1 added "Additionally, for 200.7, a LLICV will be analyzed for silver at a concentration of 0.4 mg/L that must meet the same 200.7 criteria as above." 13.3 changed to "Analyze an RLCS (required for 200.7 drinking water and 6010C samples) (6.21) after the calibration. The acceptance limits are plus or minus 50% of the expected value for 200.7 and plus or minus 30% of the expected value for 6010C." 13.6 added "6010C must be within 80 to 120% of the expected value". Re-wrote 13.7 thru 13.9 please read the text of the document for current instructions.

DATE	VER.	CHANGE
03/27/13	12.1	13.3 changed to "The acceptance limits are plus or minus 50% of the expected value." 13.9 changed to "Method 6010C requires an RLCS (6.21) be analyzed at the end of each analysis run (prior to the CCV and CCB) with an expected recovery between 50% and 150%. If the recovery exceeds these limits, one of two possibilities will occur. Samples with similar values (those that are less than 5 times the reporting limit) will be re-analyzed with passing QC. Samples that are not similar (meaning greater than 5 times the reporting limit) shall be reported as run."
01/15/14	13.0	Added in all of the requirements for running mercury by 6010 C. 12.10 added "Corrective action is governed by SOP SVL 1019." 13.6 added "Trend analysis can be found in SOP SVL 1033." 13.7 added "Demonstration of capability requirements can be found in SOP SVL 1010."

ANALYSIS OF METALS BY PERKIN-ELMER ICP-MS (EPA METHOD 200.8)

Revised by: Michael Desmarais

Approved by: _____ Date: _____
Inorganic Instrumental Department Supervisor

Reviewed by: _____ Date: _____
Quality Assurance Manager

SVL Analytical, Inc.

I have read, understood and will comply with SOP (SVL 4111 Version 8.0)

Print Name	Signature	Date
Kevin Hathaway		
Dave Tryon		
Heather Crawford		
Heidi Barnes		

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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the daily operation, tuning, optimization and analysis procedures for the analysis of samples according to EPA Method 200.8 for the elements listed in method 200.8 using a Perkin-Elmer SCIEX ELAN 6100 DRC-e ICP-MS.

1.2 Method 200.8 provides procedures for the determination of dissolved elements in ground and surface waters, and drinking waters. It is also applicable for determination of total recoverable elements in these waters as well as waste waters, sludge and soil samples.

1.3 See Table 1 for elements applicable to method 200.8.

1.4 For the determination of elements in water samples with turbidity greater than 1 NTU, the digestion procedure cited in method 200.8 must be followed.

1.5 The ELAN 6100 method disk for method 200.8 must be used for this SOP.

1.6 The user of this SOP must generate all method performance data prior to analysis of samples, including an initial demonstration of performance.

1.7 Definitions for words used in this SOP may be found in SVL's Quality Manual.

1.8 This SOP is intended for the sole use of employees of SVL Analytical, Inc. who have intimate working knowledge of EPA Method 200.8, and have completed in-house training.

1.9 SVL uses a Laboratory Information Management System (LIMS) – Element, to manage client's samples. MDLs are updated annually and can be found in Element. Below are the current MDLs and reporting limits.

Metal	Aqueous MDLs (mg/L)	Aqueous Reporting Limits (mg/L)
Silver	0.000018	0.00008

Metal	Aqueous MDLs (mg/L)	Aqueous Reporting Limits (mg/L)
Arsenic	0.00031	0.0015
Barium	0.000034	0.0004
Beryllium	0.00005	0.00016
Boron	0.002	0.003
Cadmium	0.000031	0.0001
Cobalt	0.000021	0.0001
Chromium	0.00047	0.001
Copper	0.0001	0.0003
Manganese	0.000019	0.0001

Metal	Aqueous MDLs (mg/L)	Aqueous Reporting Limits (mg/L)
Molybdenum	0.000098	0.0005
Nickel	0.00011	0.0005
Lead	0.000035	0.0002
Antimony	0.00026	0.001
Selenium	0.00052	0.001
Thallium	0.000021	0.0002
Uranium	0.000028	0.0001
Vanadium	0.00078	0.001
Zinc	0.0004	0.004

2.0 SUMMARY OF METHOD

2.1 An aliquot of a well mixed, homogeneous aqueous or solid sample is accurately measured or weighed for sample processing. For total recoverable elements analysis of solid or aqueous samples containing particulates, analytes are soluble by refluxing with nitric and hydrochloric acids. After cooling, the digestate is brought to final volume, mixed and allowed to settle overnight prior to analysis. For the determination of dissolved elements in a filtered aqueous sample, the sample is readied for analysis by the addition of nitric acid coupled with mixing prior to analysis (see Section 9.2).

2.2 Aqueous samples, digestates, leachates, extracts, filtrates, etc. are nebulized into a spray chamber where a stream of argon gas carries the aerosol through a quartz torch and injects it into radiofrequency controlled plasma. While in the plasma, the sample aerosol is decomposed, desolvated, atomized and ionized. The ions produced by the plasma are entrained in the plasma gas and by means of a water-cooled, differentially pumped interface; they are introduced into a high-vacuum chamber that houses a quadrupole mass spectrometer. The ions are sorted according to their mass-to-charge ratio, measured by an analog and pulse height detector and the ion data processed by a data handling system. Instrument drift, matrix effects and interferences unique to ICP-MS are accounted for and corrected.

3.0 INTERFERENCES

3.1 Isobaric interferences are caused when isotopes of different elements have the same nominal mass-to-charge ratio. All elements determined by method 200.8 have at least one isotope free of isobaric interference. Of the isotopes recommended in method 200.8, only molybdenum-98 (ruthenium) and selenium-82 (krypton) have this interference. All data obtained under such conditions must be corrected by measuring the signal from other isotopes of potentially interfering elements and subtracting the appropriate signal ratio from the isotope of interest. The most commonly used corrections for isobaric interference are present in the ELAN 6100 method disk (see Section 1.6).

3.2 Care should be taken that the isotope measured for correction purposes does not overlap with other isotopes that may be present.

3.3 Molecular (isobaric polyatomic ion) interferences are caused by molecular species formed in the plasma with plasma or matrix ions. Examples of common molecular interferents include ArCl, ClO, nitrogen dimer, oxygen dimer, etc. Molecular interferences are corrected for in the same manner as isobaric interferences. For example, corrections for interferences of $Ar^{40}Cl^{35}$ on As at mass 75 may be made by measuring the intensity of $Ar^{40}Cl^{37}$ present at mass 77 and converting to the apparent intensity of ArCl at mass 75 by using

the isotopic ratio of $Cl^{37}$to Cl^{35}. Corrections for molecular interferences are present in the ELAN 6100 method disk.

3.4 The common Kr^{82} interference that affects the determination of both arsenic and selenium is greatly reduced by using high purity, krypton free argon.

4.0 SAFETY

4.1 The toxicity or carcinogenicity of reagents used in method 200.8 has not been fully established. The use of lab equipment and chemicals requires that good lab techniques and safety practices should be followed at all times. When using strong acids, e.g., nitric or hydrochloric, use a fume hood. If eye or skin contact occurs, flush with water for 15 minutes. These acids are toxic and extremely irritating to skin and mucus membranes. Observe proper mixing techniques and wear eye protection and protective clothing when using these acids. When in doubt about safe handling of a chemical, read the MSDS for the chemical in question.

4.2 The ICP plasma source emits radiofrequency (RF) radiation and intense UV radiation. The ELAN 6100 is fully interlocked to protect the analyst from high voltages and RF and UV radiation. At no time should the analyst attempt to disable these interlocks for any reason.

4.3 Spills should be contained immediately. A spill team member should be consulted before cleanup.

5.0 EQUIPMENT, INSTRUMENTATION AND MATERIALS

Equivalent equipment, instrumentation and materials may be used.

5.1 This SOP is for the operation of a complete Perkin-Elmer SCIEX ELAN 6100 DRC-e ICP-MS system.

5.1.1 This system includes an ELAN 6100 ICP-MS with a DRC-e detector, a computer and printer, Elan 200.8 method disk, and an auto sampler.

5.2 Gases that include: Argon gas having a 99.99% purity, methane having a 99.99% purity and oxygen having a 99.999% purity.

5.3 Peristaltic Pump Tubing:

5.3.1 Black/Black - 0.75 mm i.d. (for sample introduction)

5.3.2 Green/Orange - 0.38 mm i.d. (for internal standard introduction)

5.4 Calibrated micropipettes and metal-free disposable pipette tips.

5.4.1 10-100 µL

5.4.2 100 – 1000 µL

5.4.3 1000 – 5000 µL

5.4.4 10 mL fixed

5.5 Autosampler tubes; 15 and 50 mL capacity.

5.6 Analytical balance capable of weighing to 0.1 mg.

5.7 Miscellaneous glassware (volumetric flasks, graduated cylinders, etc.).

6.0 REAGENTS AND STANDARDS

Guidelines for the storage, tracking and expiration of chemicals and reagents can be found in SVL 1032. The procedure for purchasing chemicals and reagents can be found in SVL 1015. Any exceptions to the above mentioned SOPs will be found in this section: as well as, all of the preparatory steps needed to construct or prepare reagents, and standards. Equivalent chemicals and standards may be used. Equivalent materials may be used. Nitric acid is preferred in order to minimize molecular (polyatomic) interferences which occur when hydrochloric acid is used to stabilize solutions containing antimony and silver.

6.1 Nitric acid, concentrated, VWR Omni-Trace grade; catalog number EM-NX0407-2.

6.2 Nitric acid 1:1 (v/v) – Add 500 mL concentrated nitric acid to 400 mL reagent water and dilute to 1.0 L with deionized water (6.5). Mix well.

6.3 Hydrochloric acid, concentrated, VWR Omni-Trace grade; catalog number EM-HX0607-2.

6.4 Hydrochloric acid 1:1 (v/v) – Add 500 mL concentrated hydrochloric acid to 400 mL reagent water and dilute to 1.0 L with deionized water (6.5). Mix well.

6.5 Deionized water equivalent to ASTM Type I deionized water.

6.6 Tuning stock solution #1: 10 µg/mL Be, Co, Ba, Ce, In, Pb, Mg, and Rh in 2% nitric acid; (High Purity, catalog number ICP-MS Tuning Solution 6).

6.7 Uranium stock standard, 1000 µg/mL in 2% nitric acid (High Purity part number 100064-1).

6.8 Tuning stock solution #2, 10 µg/mL: Transfer about 40 mL deionized water (6.5) to a 100 mL volumetric flask. Add about 2 mL concentrated nitric acid (6.1), 1.0 mL uranium stock standard (6.7). Dilute to the mark. Mix well. Expiration date is six months after date prepared.

6.9 Tuning solution: 10 µg/L Be, Co, In, Pb, Mg, Ba, Rh, U and Ce. Transfer about 200 mL of deionized water (6.5) into a 500 mL volumetric flask. Add 20 mL 1:1 nitric acid (6.2). Add 0.5 mL of tuning stock solution #1 (6.6) and 0.5 mL of tuning stock solution #2 (6.8). Dilute to 500 mL with reagent water. Mix well. Expiration date is six months after date prepared.

6.10 Internal standard stock solution (10 µg/mL): Li^6, Sc, Rh, Y, In, Bi, Ho and 30 µg/mL Ga. High Purity part # SM-150-074.

6.11 Internal standard working solution: Transfer about 400 mL of deionized water (6.5) to a 1 L volumetric flask. Add 20 mL concentrated nitric acid (6.1). Add 10 mL internal standard stock solution (6.10). Dilute to the mark with deionized water. Mix well. Expiration date is six months after date prepared.

6.12 QC26 stock solution for ICV Stock: Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Ag, Na, Tl, Ti, V, and Zn at 100 µg/mL, K at 1000 µg/mL, and Si at 50 µg/mL, in 4% HNO_3, (High-Purity catalog number QCS-26, or equivalent). A separate lot number from the QC26 Stock is used for calibration stock solution.

6.13 ICV stock solution: Transfer about 100 mL of deionized water (6.5) to a 200 mL volumetric flask. Add 4.0 mL concentrated nitric acid (6.1). Then add 20.0 mL of the QC26 stock solution (6.12) and 2.0 mL of the uranium stock solution (6.7). Dilute to the mark with deionized water and mix well. Record the preparation in the Reagent Logbook. Expiration date is six months after date prepared. This will result in a solution with the following concentrations: Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, Tl, Ti, U, V, and Zn at 10 µg/mL and Si at 5 µg/mL. A secondary source or different lot numbers are used for calibration stock solution.

6.14 ICV solution (used as the QCS solution): Transfer about 20 mL of deionized water (6.5) to a 100 mL volumetric flask. Add 2.0 mL concentrated nitric acid (6.1). Add 0.4 mL of 1:1 hydrochloric acid (6.4). Then add 0.25 mL of the ICV stock solution (6.13). Dilute to the mark with deionized water and mix well. This will result in a solution with the following concentrations: Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, Tl, Ti, U, V, and Zn at 25 µg/L and Si at 12.5 µg/L.

6.15 QC26 stock solution for calibration stock: Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Se, Ag, Na, Tl, Ti, V, and Zn at 100 µg/mL, K at 1000 µg/mL, and Si at 50 µg/mL, in 4% HNO_3, (High-Purity catalog number QC-26). A separate lot number from the QC26 Stock is used for ICV stock solution.

6.16 Calibration stock solution: Transfer about 100 mL of deionized water (6.5) to a 200 mL volumetric flask. Add 4.0 mL concentrated nitric acid (6.1). Then add 20.0 mL of the QC26 stock solution (6.15) and 2.0 mL of the uranium stock solution (6.7). Dilute to the mark with deionized water and mix well. Record the preparation in the Reagent Logbook. Expiration date is six months after date prepared. This will result in a solution with the following concentrations: Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, Tl, Ti, U, V, and Zn at 10 µg/mL and Si at 5 µg/mL. A secondary source or different lot numbers are used for the ICV stock solution.

6.17 Multi-element calibration standards are prepared fresh daily as appropriate for the analysis. All calibration blanks, calibration standards, and quality control standards and samples are spiked by direct on-line additions with the internal standard working solution prior to analysis.

6.17.1 Calibration blank: A solution containing 2% (v/v) nitric acid (6.1) and 0.2% hydrochloric acid (6.3) in deionized water (6.5). Prepare fresh daily.

6.17.2 Calibration standard 1: Add 20 mL deionized water (6.5) to a 100 mL volumetric flask. Carefully add 2 mL concentrated nitric acid (6.1) and 0.8 mL 1:1 hydrochloric acid (6.4). Add 0.1 mL of the reporting limit stock solution (6.19). Dilute to volume with deionized water and mix. Prepare fresh daily. The final concentrations of the elements in this solution are:

Analyte	Final Conc. (mg/L)
Ag	0.00008
As	0.00150
B	0.00300
Ba	0.00010
Be	0.00010
Cd	0.00010
Co	0.00010
Cr	0.00100
Cu	0.00030
Mn	0.00010
Mo	0.00050
Ni	0.00050

Analyte	Final Conc. (mg/L)
Pb	0.00020
Sb	0.00100
Se	0.00100
Tl	0.00020
U	0.00010
V	0.00100
Zn	0.00400

6.17.3 Calibration standard 2: Add 20 mL deionized water (6.5) to a 100 mL volumetric flask. Carefully add 2 mL concentrated nitric acid (6.1) and 0.8 mL 1:1 hydrochloric acid (6.4). Add 0.5 mL of the reporting limit stock solution (6.19). Dilute to volume with deionized water and mix. Prepare fresh daily. The final concentrations of the elements in this solution are:

Analyte	Final Conc. (mg/L)
Ag	0.0004
As	0.0075
B	0.015
Ba	0.0005
Be	0.0005
Cd	0.0005
Co	0.0005
Cr	0.005
Cu	0.0015
Mn	0.0005
Mo	0.0025
Ni	0.0025
Pb	0.001
Sb	0.005
Se	0.005
Tl	0.001
U	0.0005
V	0.005
Zn	0.02

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6.17.4 Calibration standard 3: Add 2.0 mL of concentrated nitric acid (6.1) and 0.8 mL of 1:1 hydrochloric acid (6.4) to 20 mL of deionized water in a 100 mL volumetric flask add 250 µL of calibration standard stock

solution (6.16), dilute to volume with deionized water (6.5) and mix. Prepare fresh daily. All analytes at 0.025 ug/mL.

6.17.5 Calibration standard 4: Add 2.0 mL of concentrated nitric acid (6.1) and 0.8 mL of 1:1 hydrochloric acid (6.4) to 20 mL of deionized water (6.5) in a 100 mL volumetric flask add 500 µL of calibration standard stock solution (6.16), dilute to volume with deionized water (6.5) and mix. Prepare fresh daily. All analytes at 0.050 ug/mL.

6.17.6 Calibration standard 5: Add 2.0 mL of concentrated nitric acid (6.1) and 0.8 mL of 1:1 hydrochloric acid (6.4) to 20 mL of deionized water (6.5) in a 100 mL volumetric flask, add 750 µL of calibration standard stock solution (6.16), dilute to volume with deionized water and mix . Prepare fresh daily. All analytes at 0.075 ug/mL.

6.18 Use calibration standard 4 (6.17.5) as the CCV.

6.19 Reporting limit stock solution: Add deionized water (6.5) to a 1000 mL volumetric flask. Add 20 mL of concentrated nitric acid (6.1) and 50 mL of concentrated hydrochloric acid (6.3). Add the following amounts of single-element stock solutions. Preparation of intermediate solutions of the single-element stock solutions is permissible. Then dilute to the mark with deionized water and mix well. The final concentrations of the elements in this solution are:

Analyte	Volume (mL)	Stock Solution (Mg/L)	Final Conc. (mg/L)	High Purity Catalog #
Ag	0.080	1000	0.080	100051-1
As	1.50	1000	1.50	10003-1
Be	0.10	1000	0.10	10005-1
Cd	0.10	1000	0.10	10008-1
Co	0.10	1000	0.10	100013-1
Cr	1.00	1000	1.00	100012-1
Cu	0.30	1000	0.30	100014-1
Mn	0.10	1000	0.10	100032-1
Mo	0.50	1000	0.50	100034-1
Ni	0.50	1000	0.50	100036-1
Pb	0.20	1000	0.20	100028-1
Sb	1.00	1000	1.00	10002-3
Se	1.00	1000	1.00	100049-1
Tl	0.20	1000	0.20	100058-1
U	0.10	1000	0.10	100064-1
V	1.00	1000	1.00	100065-1
Zn	4.00	1000	4.00	100068-1
B	0.60	5000	3.00	5M7-4
Ba	0.01	10000	0.10	10M4-1

6.20 Reporting limit check standard: Add deionized water (6.5) to a 100 mL volumetric flask. Carefully add 2 mL concentrated nitric acid (6.2) and 0.8 mL 1:1 hydrochloric acid (6.4). Add 0.1 mL of the reporting limit stock solution (6.19). Store in a brown bottle, or away from light. The final concentrations of the elements in this solution are:

Analyte	Volume (mL)	Stock Solution (mg/L)	Final Conc. (mg/L)
Ag	0.10	0.080	0.00008
As	0.10	1.50	0.00150
B	0.10	3.00	0.00300
Ba	0.10	0.10	0.00010
Be	0.10	0.10	0.00010
Cd	0.10	0.10	0.00010
Co	0.10	0.10	0.00010
Cr	0.10	1.00	0.00100
Cu	0.10	0.30	0.00030
Mn	0.10	0.10	0.00010
Mo	0.10	0.50	0.00050
Ni	0.10	0.50	0.00050
Pb	0.10	0.20	0.00020
Sb	0.10	1.00	0.00100
Se	0.10	1.00	0.00100
Tl	0.10	0.20	0.00020
U	0.10	0.10	0.00010
V	0.10	1.00	0.00100
Zn	0.10	4.00	0.00400

6.21 Rinse blank – Consists of 1% (v/v) nitric acid (6.1) and 0.5% hydrochloric acid (6.3) in deionized water (6.5).

6.22 Carrier Solution – 1% HNO_3 (6.1) and 0.5% HCL (6.3) in deionized water (6.5).

6.23 ICB/CCB solution same as 6.17.1.

6.24 F26 Spiking Solution: Transfer about 400 mL of deionized water (6.5) to a 1000 mL volumetric flask. Add 20.0 mL concentrated nitric acid (6.1). Then add 25.0 mL of the QC26 stock solution (6.14). Add 2.5 mL of uranium stock standard (6.7). Dilute to the mark with deionized water (6.5) and mix well. Expiration date is six months after date prepared, but no later than the expiration dates of the stock solutions. This will result in a solution with the following concentrations: Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Ag, Tl, Ti, V, and Zn at 2.5. Si at 1.25 µg/mL. Store in a brown bottle, or away from light.

6.25 Dual detector cross - Calibration solution contains 250 µg/L of Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Se, Tl, U, V, Zn, Sc, Y, Rh, Tb, Ho, Ga and Bi, and 1 mg/L Mg, K, and Fe, and 0.5 mg/L Na and Ca, in 2% nitric acid and 0.5% hydrochloric acid. Note that Hg is not added to this solution.

7.0 INSTRUMENT SETTINGS

Method 200.8 advises to follow the recommended operating conditions provided by the instrument manufacturer. This SOP follows the recommendations of Perkin-Elmer for the operational procedures of the ELAN6100 DRC-e ICP-MS. Appendices 1 and 2 show typical daily tuning reports.

7.1 Initiate the plasma and allow a 30 minutes warm-up. The tuning procedures are carried out during this time.

7.1.1 Calibrate the dual detectors quarterly or when there has been a change in the instrumentation to ensure the linearity between the pulse and analog modes.

7.2 Open the “SVL DAILY FAST.WRK”. Click on “File”, “print setup”, “reports” change the printer to pdfFactory Pro.

7.2.1 Aspirate the 10 µg/L tuning solution (6.9).

7.2.2 Click on the “Analyze” button in the manual sample window to acquire.

7.2.2.1 Data will print to a pdf file. Click on the “Doc info” tab in the pdfFactory Pro window and change the file name to the current file.

7.2.3 Ensure that the RSDs of the five replicates for all of the tuning solution analytes are all less than 5%.

7.2.4 Monitor daily performance measures of In sensitivity, background, % double charged and % oxide levels.

7.2.4.1 In greater than 200,000 cps for 10 µg/L.

7.2.4.2 Background at mass 220 about 30 cps.

7.2.4.3 % double charged less than 3 to 5 %.

7.2.4.4 % oxides less than 3 to 5 %. Note that double charged and oxide levels can be reduced by slightly decreasing nebulizer flow rate.

7.3 Open the “SVL TUNING FAST.WRK”.

7.3.1 Aspirate the 10 μg/L tuning solution (6.9).

7.3.2 Click on the “Calibrate” button in the tuning window.

7.3.3 Ensure that the resolution for Be, C, Mg, ^{76}Ar, Co, Rh, In, Ce, Pb, U is 0.7 amu +/- 0.1 amu as measured at 10% peak height. Correct as needed. Note that it has been shown that 0.65 amu at 10% peak height is equivalent to 0.75 amu at 5% peak height.

7.3.4 Ensure that the measured mass is within 0.1 amu of the true mass. Correct as needed.

7.3.5 Save the tuning file. Print the tuning window if documentation is required.

7.4 If either “SVL DAILY FAST.WRK” or “SVL TUNING FAST.WRK” fails, open the “SVL OPTIMIZE NEBULIZER GAS FLOW.WRK” and optimize the following parameters using the 10 μg/L tuning solution (6.9) containing Be, Mg, Co, Rh, In, Ba, Ce, U and Pb.

7.4.1 Set RF power to 1400 watts.

7.4.2 Optimize the nebulizer argon flow.

7.4.3 Optimize the static lens voltage.

7.4.4 Save the optimization file.

7.5 Open the “SVL AUTOLENS.WRK” and perform the autoLens calibration using the 10 μg/L tuning solution (6.9).

7.5.1 Clear any old calibration.

7.5.2 Click on “Get Analytes”.

7.5.3 Click on “Optimize”.

7.5.4 Save the optimization file.

7.6 If steps 8.5 or 8.6 fail, perform a full optimization according to the flow chart in the software manual.

7.7 If the detector voltages are changed, or a new detector is installed, open the "SVL DUAL DETECTOR CALIB FAST. WRK" method and aspirate the dual detector cross calibration solution (6.25).

7.7.1 Run the detector cross-calibration routine.

7.7.1.1 Clear any old calibration.

7.7.1.2 Click on "Get Analytes".

7.7.1.3 Click on "Optimize".

7.7.1.4 Save the optimization file and print.

7.8 Open the "SVL DAILY FAST.WRK".

7.8.1 Aspirate the 10 μg/L tuning solution (6.9).

7.8.2 Click on the "Analyze" button in the manual sample window to acquire.

7.8.3 Ensure that the RSDs of the five replicates for all of the tuning solution analytes are less than 5%.

7.8.4 Monitor daily performance measures of In sensitivity, background, % double charged and % oxide levels.

7.8.4.1 In more than 200,000 cps for 10 μg/L.

7.8.4.2 Background at mass 220 about 30 cps.

7.8.4.3 % double charged less than 3 to 5%.

7.8.4.4 % oxides less than 3 to 5 %. Note that double charged and oxide levels can be reduced by slightly decreasing nebulizer flow rate.

7.9 An example of a Tuning Report is located in Appendix 3.

7.10 Close the PDF file.

8.0 CALIBRATION

8.1 Open the "SVL SAMPLE ANALYSIS FAST.WRK".

8.2 Prepare the calibration standards. Move tubes from the tuning solution to the internal standard and carrier solutions.

8.2.1 See sections 6.21.1 through 6.21.7.

8.3 Enter the concentrations of the standards into the calibration page of the analytical method in the ELAN software.

8.3.1 Select a “Linear Through Zero” curve type for all analytes.

8.3.2 Run the calibration blank before the analysis of any calibration standards.

8.3.3 Analyze the lowest level standard, followed by standards of increasing concentration in order to minimize cross-contamination and carryover.

8.4 Make any desired changes to the method and save under a different name. Note that the EPA200.mth method is write protected.

8.4.1 Load the calibration blank and calibration standards into the auto sampler positions specified in the autosampler page of the analytical method.

8.5 Load the QC samples defined in the QC checking part of the method into the autosampler according to the positions entered in the QC autosampler page of the method (see Section 13 of the ELAN software manual for more information on setting up QC protocols).

8.5.1 Load the RLCS solution (6.20) and place in its auto sampler position.

8.5.1.1 If the analytical run is for drinking water the RLCS must go through the same digestive procedure as the analytical batch.

8.5.2 Load the ICV solution (6.14) and place in its auto sampler position.

8.5.3 Load the ICB/CCB solution (6.17.1) and place in its auto sampler position.

8.5.4 Load the CCV solution (6.17.5) and place in its auto sampler position.

8.6 Digestive procedures for standards and samples are found in the digestive SOPs as well as in 10.2.1 and 10.3.1.

8.7 Edit the sample window for batch analysis to update with new sample information. Note: Only enter sample, QC spike, QC duplicate, QC dilution or

reagent blank information in the batch sample page. Calibration standards and QC standards are defined in the relevant sections of the method.

8.7.1 Load the applicable method for the sample batch (i.e., 200.8). Note that if automatic QC checking is used the method must be the same for all samples.

8.7.2 The calibration action for the first sample for which concentration results are desired must be “Analyze Blank, Standards and Sample”.

8.7.3 The calibration action for all other samples is usually “Analyze Sample”, unless periodic re-calibration is desired.

8.7.4 Enter the appropriate pump speeds for all samples.

8.7.5 Save sample file.

8.7.6 Re-open the sample file. Note that this must be done for the batch QC to run properly.

8.7.7 Load the samples into the autosampler positions specified in the sample file.

8.7.8 Select the samples to be analyzed by highlighting the row number with the mouse.

8.7.9 Select “Analyze Batch”. Note: Aspirate the rinse blank for 5-10 minutes before beginning a batch run to avoid carry-over and contamination.

9.0 SAMPLE HANDLING AND PRESERVATION

9.1 Prior to collection of aqueous samples, the type of data required (dissolved or total recoverable), must be known to ensure appropriate preservation and pretreatment. The pH of all aqueous samples must be checked immediately upon receipt by SVL. Any preservation by SVL will follow the protocols outlined in SVL SOP 2001. If properly preserved, samples can be held for 6 months before analysis.

9.2 Samples for dissolved elements must have been filtered through a 0.45 μm filter and then preserved with (1+1) nitric (6.2) acid to a pH of < 2 at time of sample collection.

9.3 For determination of total recoverable elements in aqueous samples, samples are not filtered, but are preserved with (1+1) nitric acid (6.2) to pH of < 2.

Preservation should be done at the time of collection or if preserved at the laboratory the sample must wait 24 hours before being prepped or analyzed. After 24 hours, verify that the pH of < 2 prior to withdrawing an aliquot for digestion or direct analysis (see SVL 2001).

9.4 Solid samples require no preservation prior to analysis other than storage between 0 – 6°C upon request. There is no established holding time limitation for solid samples that are properly stored.

10.0 SAMPLE PREPARATION AND ANALYSIS

10.1 Aqueous sample preparation for dissolved analytes in ground and surface waters.

10.1.1 Transfer an aliquot (at least 20 mL) into a 50 mL polypropylene snap cap vial. Add an approximate volume of (1+1) nitric acid (6.2) to adjust the acid concentration to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 mL (1+1) nitric acid to a 20 mL aliquot of sample). The sample is ready for analysis. The sample value(s) must be corrected for dilution.

10.2 Aqueous sample preparation for total recoverable analytes.

10.2.1 ICP-MS aqueous samples and batch QC are digested according to SVL SOP 4106.

10.2.2 Let the digestate set over night to allow any undissolved material to settle.

10.2.3 Prior to analysis, adjust the chloride concentration by pipetting 20 mL of digestate into a 50 mL volumetric flask, dilute to volume with deionized water (6.5) and mix. Note that if the dissolved solids in this solution are >0.2%, additional dilution may be required to prevent clogging of the extraction and/or skimmer cones. Correct the sample value for dilutions.

10.2.4 For aqueous samples containing silver at concentrations ≥ 0.1 mg/L the sample will need to be re-digested to a level below 0.1 mg/L and re-analyzed. The diluted silver sample results shall be reported.

10.3 Solid sample preparation for total recoverable analytes.

10.3.1 ICP-MS solid samples and batch QC are digested according to SVL SOP 4094.

10.3.2 Let the digestate set over night to allow any undissolved material to settle.

10.3.3 Prior to analysis, adjust the chloride concentration by pipetting 10 mL of digestate into a 50 mL volumetric flask, dilute to volume with deionized water and mix. Note that if the dissolved solids in this solution are >0.2%, additional dilution may be required to prevent clogging of the extraction and/or skimmer cones. Correct the sample value for dilutions.

10.4 The preparation and use of quality control samples is described in Sections 6.0 and 13.0.

10.5 Soil samples containing > 50 mg/kg of silver will also need to be diluted and re-digested below 50 mg/kg and re-ran on the ICP. The diluted silver sample results shall be reported.

11.0 DATA REDUCTION

11.1 The ELAN software performs all calculations necessary to convert raw data (ion counts/second). The calculated quantities are selected by choosing the desired options in “Report Options” screen. The default option for the ELAN 200.8 method is “EPA200 QCReport.rop”. This format can be edited and saved under a new name.

11.2 The software will create a linear calibration curve. The correlation coefficient must be at least 0.995. If the correlation coefficient is less than 0.995, re-calibrate the instrument prior to analyzing any samples.

11.2.1 Calibration standards are reprocessed as they run; the software provides side by side columns for concentration as made and the actual concentration after calibration. The analyst will edit the PDF and insert “The calibration was verified” followed by their initials and date. SVL’s criteria for a passing calibration curve is ± 30% for the first standard and ± 10% for the remaining standards. Failure to meet the criteria will result in not using the failed analyte or re-calibrating.

11.3 All calculations performed by the ELAN ICP-MS software are based on the ratio of the analyte intensity (cps) to internal standard intensity (cps). In all calculations, the ratio of the analyte intensity to internal standard intensity is determined before any other calculation is performed.

11.4 The QC Checking feature in the ELAN software checks the results of QC Samples. All values entered in the default ELAN 200.8 method should be checked and edited to match the true values being used. The modified method can then be saved under a different name.

11.5 Report sample results for aqueous samples in mg/L. Results for solids are reported on an "as received" basis unless otherwise requested.

11.6 See SVL 1028 for equations used in this SOP.

12.0 DATA AND RECORDS MANAGEMENT

12.1 Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batching.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the samples began.

12.1.1 Indicate all reagents used in the batch by including them in the reagent section of the "Batch" screen.

12.2 Procedures for constructing sequences can be found at R:\Promium Stuff\How to's\Sequences.doc.

12.3 Print "SVL Analytical Daily Performance Reports 1 and 2", and the "Instrument Tuning Report" (see Appendix 1, 2, and 3, respectively). Place copies of these reports (located in H:ICPMS/PDF) in the Daily Performance Check logbook.

12.4 After analysis is complete, the analyst will reprocess the data and print to a pdf using pdfFactory Pro.

12.4.1 Open "Methods/Reports" and uncheck "Report to File".

12.4.2 In ELAN click "File", "Print setup", "Reports". Change the printer name to pdfFactory Pro. Click "Analysis" then select "Clear calibration".

12.4.3 Highlight data set on the Data Set page and click on "Reprocess". The data will be converted to a pdf.

12.4.4 Click on the "Doc Info" tab located inside the pdfFactory Pro window. Change the file name to the current data file.

12.4.5 When the reprocessing is complete add the Data Set Report, Calibration file and the current Standards page to the file. Close the pdf file.

12.4.6 Print a hard copy of the Data Set file for the log book.

12.4.7 Open H:ICPMS/PDF and move the pdf file to the corresponding month's folder.

12.5 The analyst will upload the data to Element via Data Tool or manually.

12.5.1 Open Element, click on “Laboratory” and select “Data Entry / Review”.

12.5.2 Locate batch number and click on it, select “Create” and then “Data Tool”.

12.5.3 A box will pop up for the PE Elan raw data, select a file number (e.g. 222A.Raw), and click on “Auto Select”. Verify numbers. Click on “Done”.

12.5.4 Click on “Merge Files”. Check that the Merged Upload and the Empty Upload are the same. Click “Save”. Return to the “Data Entry / Review” screen and “Save”.

12.6 The analyst shall perform all reviews on the “Data Entry/Review” page in Element and verify their data uploads.

12.7 If an input comes up color coded, apply the appropriate data flags or undertake corrective actions.

12.8 The analyst shall assign any qualifiers.

12.9 The analyst will then update the status of the batch to “Analyzed”.

12.10 The analyst will then lock the results so that any future imports will not overwrite acceptable results.

12.11 Data review is governed by SVL SOP 2009.

12.12 Corrective action is governed by SVL 1019.

13.0 QUALITY CONTROL

Method	LCS	RPD	Spike	Prep Blank
200.8	Limits: 85 to 115%	Limit: 20%	Limits: 70 to 130%	Limit: less than half of the reporting limit[1]
	Action: re-run, then re-prep if outside limits	Action: flag if higher	Action: flag if outside	Action: re-run, then re-prep if outside limits

Method	ICV	ICB	CCV	CCB
200.8	Limit: within 10% of expected	Limit: less than half of the reporting limit	Limit: within 10% of expected	Limit: less than half of the reporting limit
	Action: re-run then re-calibrate	Action: re-run, then re-calibrate	Action: re-run, then re-calibrate and re-analyze	Action: re-run, then re-calibrate and re-analyze

13.1 Analyze an ICV (6.14). This doubles as a QCS. The acceptance limits are 90 to 110% of the expected value. If the recovery falls outside these criteria, re-analyze the ICV/QCS. If the recovery still falls outside these criteria, re-calibrate the instrument before proceeding with the analysis.

13.2 Analyze an ICB (6.17.1) after the ICV. The ICB must be less than half the reporting limit for each analyte. If the recovery falls outside the criteria, re-analyze the CCB. If the CCB still exceeds the reporting limit, discontinue analysis and recalibrate the instrument. The exception to this rule is: when the analyte that is out is not being analyzed for, then the run can continue.

13.3 Analyze a RLCS (6.20) after the ICB. The acceptance limits are 50 to 150% of the expected value. If the recovery falls outside these limits, re-analyze the RLCS. If the recovery still falls outside the limits, re-calibrate the instrument.

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[1] **For California 200.8 samples, the method blank must be less than 2.2 x MDL or 10% of the lowest sample concentration.**

The exception to this rule is: when the analyte that is out is not being analyzed for, then the run can continue.

13.4 Analyze a prep blank (10.2.1) (10.3.1) at a frequency of one per batch of 20 or fewer samples. The concentration of each target analyte in the prep blank must be less than half the reporting limit, or less than 10% of the concentration of the analyte in all samples. If the recovery of a target analyte in the prep blank exceeds these criteria, re-analyze the prep blank. If the recovery in the prep blank still exceeds the criteria, re-digest and re-analyze the samples associated with the prep blank.

13.4.1 For California method 200.8 samples, the prep blank must be less than 2.2 x MDL or 10% of the lowest sample concentration.

13.5 Analyze a LCS (10.2.1) (10.3.1) at a frequency of one per batch of 20 or fewer samples. The recovery for the LCS must be between 85 and 115% of the expected value. If the recovery falls outside the above criteria, re-run the LCS. If the recovery still falls outside these criteria, re-digest and re-analyze the samples associated with the LCS. The F26 spike (6.24) will result in the following concentrations:

Analyte	Spike Volume (mL)	Stock Solution (mg/L)	Final Conc. (mg/L)
Ag	0.50	2.5	0.025
As	0.50	2.5	0.025
B	0.50	2.5	0.025
Ba	0.50	2.5	0.025
Be	0.50	2.5	0.025
Cd	0.50	2.5	0.025
Co	0.50	2.5	0.025
Cr	0.50	2.5	0.025
Cu	0.50	2.5	0.025
Mn	0.50	2.5	0.025
Mo	0.50	2.5	0.025
Ni	0.50	2.5	0.025
Pb	0.50	2.5	0.025
Sb	0.50	2.5	0.025
Se	0.50	2.5	0.025
Tl	0.50	2.5	0.025
U	0.50	2.5	0.025
V	0.50	2.5	0.025
Zn	0.50	2.5	0.025

13.6 Analyze a matrix spike (10.2.1) (10.3.1) at a frequency of at least one per batch of 10 or fewer samples. The acceptance limits for spike recoveries are 70 to 130% of the expected value if the spike added is greater than 30% of the concentration in the un-spiked sample There are no acceptance limits if the

spike added is less than 30% of the concentration in the un-spiked sample. If the recovery is not within this range and the LCS recovery is acceptable, the recovery failure is judged to be matrix related, not system related. Flag the client report. The expected concentrations of the matrix spike are the same as for the LCS (see 13.6).

13.7 Analyze a matrix spike duplicate (10.2.1) (10.3.1) at a frequency of 1 per batch of 20 or fewer samples. Acceptance limits for the spike recovery are 70 to 130%. The control limit for the RPD between MS and MSD is 20%. If the MSD fails the recovery range or the RPD exceeds the control limit, flag the client report.

13.8 Analyze a CCV (6.17.5) at a frequency of one per 10 samples or fewer and at the end of an analytical run. The recovery must be within 10% of the expected value for target analytes. Reportable analytes must be bracketed by acceptable CCVs, if the recovery falls outside these criteria, determine the cause, perform corrective action, and re-analyze it. If the recovery still falls outside the criteria, re-analyze all samples run since the last successful CCV. The exception to the 10% rule is when the recovery for an analyte(s) is within 15%, the results may be reported out but the analyte(s) is finished for the remainder of the analytical run.

13.9 Analyze a CCB (6.17.1) immediately after each CCV. The recovery must be less than one-half the reporting limit. Reportable analytes must be bracketed by acceptable CCBs, if the recovery exceeds this criterion, determine the cause, perform corrective action, and re-analyze the CCB. If the recovery still exceeds the limit, re-analyze all samples run since the last successful CCB.

13.10 Export the RLCS recoveries into an SRM batch so that trending of the RLCS can occur.

13.11 Analyze a method detection limit study annually, when a new analyst is trained, when changes occur to the sample preparation procedure, when there is a change to the instrument (e.g., new detector) or a change in operating conditions.

13.12 Monitor the responses from the internal standards throughout the sample batch being analyzed. Ratios of the internal standards responses should also be routinely monitored. This information may be useful detecting mass dependent drift, errors in adding internal standards or increased internal standards concentrations due to contributions from samples.

13.12.1 The intensities of internal standards in all samples, QC, and continuing calibration checks should be within 60 – 125% of the original response in the calibration blank.

13.12.2 If deviations greater than these occur, flush the instrument with rinse blank and monitor the intensities of internal standards in the calibration blank.

13.12.3 If the intensities are now within limits, take a fresh aliquot of sample, dilute by a factor of two, add appropriate internal standard and reanalyze.

13.12.4 If after flushing, the response is still out of control, terminate the analysis and determine the cause of the drift. An irreversible blockage of the sample cones may have occurred or the tuning condition of the instrument may have changed.

13.13 Annual Linear Dynamic Range (LDR) studies are not conducted, LDRs should be verified during initial training or whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be re-determined.

13.13.1 Samples having concentrations higher than the established linear dynamic range will be diluted back into calibration range and reanalyzed (unless sample matrix is such that dilutions are unwarranted).

13.14 Trend analyses can be found in SVL 1033.

13.15 Demonstrations of capability requirements can be found in SVL 1010.

14.0 REFERENCES

14.1 “Method 200.8, Revision 5.5: Determination Of Trace Elements In Waters And Wastes By Inductively Coupled Plasma-Mass Spectrometry”, EPA-821-R-99-017, October 1999.

14.2 “Methods For The Determination Of Metals In Environmental Samples – Supplement 1”, EPA-600/R-94-111, May, 1994.

14.3 Manual for the Certification of Laboratories Analyzing Drinking Water, Fifth Edition.

14.4 ELAN ICP-MS Hardware Manual, 1995, Perkin-Elmer, Inc.

14.5 ELAN ICP-MS Software Manual, 1995, Perkin-Elmer, Inc.

14.6 “EPA Method 200.8 Using the ELAN 6000/6100/9000 ICP-MS”, Perkin-Elmer, Inc.

14.7 "EPA Method 200.8 Turnkey Method for the ELAN 6000", Perkin-Elmer, Inc.

15.0 POLLUTION PREVENTION

15.1 All standards are prepared and reagents used in volumes consistent with good laboratory practice, which is used to minimize the volume of disposable waste.

15.2 Efficient laboratory practices that reduce the need for re-digestions and/or re-extractions minimize contributions to pollution.

16.0 WASTE MANAGEMENT

16.1 Waste generated by this method includes plastic-ware, chemicals used in the digestion and/or analysis, and paper.

16.2 Plastic-ware is emptied, rinsed, and discarded to a sanitary landfill.

16.3 Most chemicals used during digestion and/or analysis are neutralized and/or diluted prior to disposal by permit to the public sewer. Any hazardous chemicals and/or residues are disposed of through SVL's hazardous waste disposal system (see SOP's SVL 1001 & 1008).

17.0 CHANGE HISTORY

Date	Version	Change
07/29/09	4.0	Due to number of changes made to this document please consult an archived version for comparisons
10/11/10	5.0	5.4.4 added "10 mL fixed". Solutions in 6.0 were modified to reflect current solutions in use. 7.2 added "Click on "File", "print setup", "reports" change the printer to pdfFactory Pro". 7.2.2.1 added "Data will print to a pdf file. Click on the "Doc info" tab in the pdfFactory Pro window and change the file name to the current file". 7.10 added "Close the pdf file". Section 12.0 was completely revised to reflect the processes under taken from setting up bench sheet to sequencing to using pdfFactory Pro to create pdfs.

01/18/12	6.0	Updated Section 6.0. 11.2.1 added "Calibration standards are reprocessed as they run; the software provides side by side columns for concentration as made and the actual concentration after calibration. The analyst will edit the PDF and insert "The calibration was verified" followed by their initials and date. SVL's criteria for a passing calibration curve is ± 30% for the first standard and ± 10% for the remaining standards. Failure to meet the criteria will result in not using the failed analyte or re-calibrating". 13.13.1 added "(unless sample matrix is such that dilutions are unwarranted)". 13.5 adjusted LCS chart.
02/20/13	7.0	Removed all references to running cations. 13.7 added "Analyze a matrix spike duplicate (10.2.1) (10.3.1) at a frequency of 1 per batch of 20 or fewer samples. Acceptance limits for the spike recovery are 70 to 130%. The control limit for the RPD between MS and MSD is 20%. If the MSD fails the recovery range or the RPD exceeds the control limit, flag the client report". 13.8 changed to "The exception to the 10% rule is when the recovery for an analyte(s) is within 15%, the results may be reported out but the analyte(s) is finished for the remainder of the analytical run".
02/26/14	8.0	SW-846 digestive methods were removed. 12.12 added "Corrective action is governed by SVL 1019." 13.14 added "Trend analyses can be found in SVL 1033." 13.15 added "Demonstrations of capability requirements can be found in SVL 1010."

Table 1 Table of the Isotopes Monitored and Equations Used

Analyte	Symbol	Isotopes Monitored	Correction Equations
Aluminum	Al	27	
Antimony	Sb	121, 123	Sb 123 = Sb 123 - 0.127189 * Te 125
Arsenic	As	75	As 75 = As 75 - 3.127 * [ArCl 77 - (0.815*Se 82)]
Barium	Ba	135, 137	
Beryllium	Be	9	
Cadmium	Cd	106, 108, 111, 114	Cd 111 = Cd 111 - 1.073 * [MoO 108 -(0.712*Pd 106)] Cd 114 = Cd 114 - 0.026826 * Sn 118
Chromium	Cr	52,53	
Cobalt	Co	59	
Copper	Cu	63,65	
Lead	Pb	206,207,208	Pb 208 = Pb 208 + 1* Pb 206 + 1* Pb 207
Manganese	Mn	55	
Mercury	Hg	202	
Molybdenum	Mo	95,97,98	Mo 98 = Mo 98 - 0.110588 * Ru 101
Nickel	Ni	60,62	
Selenium	Se	77,82	Se 82 = Se 82 - 1.008696 * Kr 83
Silver	Ag	107,109	
Thallium	Tl	203,205	
Thorium	Th	232	
Uranium	U	238	
Vanadium	V	51	V 51 = V 51 - 3.127*[ClO 53 - (0.113*Cr 52)]
Zinc	Zn	66,67,68	
Internal Standards			
Lithium	Li	6	
Scandium	Sc	45	
Yttrium	Y	89	
Rhodium	Rh	103	
Indium	In	115	
Terbium	Tb	159	
Bismuth	Bi	209	
Holmium	Ho	165	
Calcium	Ca	44	
Magnesium	Mg	24	
Sodium	Na	23	
Potassium	K	39	
Iron	Fe	54	Fe 54 = Fe 54 - 0.028226 * Cr 52

APPENDIX 1 Daily Report 1

SVL Analytical Daily Performance Report

Sample ID: DAILY I
Sample Date/Time: 06:39:34 Mon 02-Aug-xx
Sample Description:
Method File: C:\elandata\Method\SVL Daily.mth
Dataset File: C:\elandata\Dataset\Daily Performance\DAILY 1.278
Tuning File: C:~elandata\Tuning\default.tUfl
Optimization File: C:\elandata\Optimize\defaUlt.daC
Dual Detector Mode: Pulse
Acq. Dead Time(ns): 55
Current Dead Time (ns): 55

Analysis Summary

Analyte	Mass	Meas. Intens.	Mean Net Intens.	Mean Net Intens.	SD Net Intens.	RSD
Be	9.0	5041.9	5041 .868	266.617	5.3
Mg	24.0	70868.6	70868.555	3024.982	4.3
Rh	102.9	270125.5	270125.489	7140.969	2.6
In	114.9	318363.7	318363.688	7480.046	2.3
Pb	208.0	115385.3	115385.276	3414.673	3.0
-> Ce	139.9	289137.9	289137.871	7362.710	2.5
LCeO	155.9	8588.7	0.030	0.000	0.9
1>Ba	137.9	230800.7	230800.716	6909.189	3.0
LBa++	69.0	6717.5	0.029	0.000	1.6
220	220.0	0.7	0.667	0.333	50.0
8.5	8.5	1.1	1.067	0.450	42.2

Current Optimization File Data

Current Value	Description
0.88	Nebulizer Gas Flow [NEB]
1.20	Auxiliary Gas Flow
15.00	Plasma Gas Flow
5.50	Lens Voltage
1400.00	ICP RE Power
-1725.00	Analog Stage Voltage
1050.00	Pulse Stage Voltage
0.00	Quadrupole Rod Offset Std (QRO]
-15.00	Cell Rod Offset Std (CR0]
70.00	Discriminator Threshold
-19.00	Cell Path Voltage Std [CPV]
0.00	RPa
0.25	RPq
0.91	DRC Mode NEB
-6.50	DRC Mode QRO
-1.00	DRC Mode CR0
-15.00	DRC Mode CPV
0.00	Cell Gas A

0.00Cell Gas B

Current Autolens Data

Analyte	Mass	Num of Pts	DAC Value	Maximum Intensity
Be	9	53	4.8	4371.1
Co	59	53	5.5	133836.0
In	115	53	5.8	288628.2

Base Vac _____ Run Vac _____ DRC Vac _____

APPENDIX 2 **Daily Report 2**

SVL Analytical~ Daily Performance Report

Sample ID: DAILY 2
Sample Date/Time: 06:53:34 Mon 02-Aug-xx
Sample Description:
Method File: C:\elandata\Method\SVL Daily.mth
Dataset File: C:\eIandata\Dataset~Daily Performance\DAILY 2.279
Tuning File: C:\elandata\Tuning\default.tun
Optimization File: C:\elandata\Optimize\default.dac
Dual Detector Mode: Pulse
Acq. Dead Time(ns): 55
Current Dead Time (ns): 55

Analysis Summary

Analyte	Mass	Meas. Intens.	Mean Net Intens.	Mean Net Intens. SD	Net Intens. RSD
Be	9.0	4530.7	4530.729	84.787	1.9
Mg	24.0	62795.2	62795.160	805.158	1.3
Rh	102.9	256024.1	256024.100	2521.336	1.0
In	114.9	301210.8	301210.821	2974.341	1.0
Pb	208.0	108537.9	108537.947	1229.000	1.1
1>	Ce	139.9	272879.2	272879.200	2623.314
1.0					
LCeO	155.9	8051.8	0.030	0.001	2.0
1>	Ba	137.9	217617.9	217617.936	2290.789
1.1					
LBa÷+	69.0	6203.2	0.029	0.000	0.7
220	220.0	0.6	0.633	0.342	53.9
8.5	8.5	0.9	0.900	0.253	28.1

Current Optimization File Data

Current Value	Description
0.88	Nebulizer Gas Flow [NEB]
1.20	Auxiliary Gas Flow
15.00	Plasma Gas Flow
5.50	Lens Voltage
1400.00	ICP RF Power
-1725.00	Analog Stage Voltage
1050.00	Pulse Stage Voltage
0.00	Quadrupole Rod Offset Std [QRO]
-15.00	Cell Rod Offset Std [CR0]
70.00	Discriminator Threshold
-19.00	Cell Path Voltage Std [CPV]
0.00	RPa
0.25	RPq
0.91	DRC Mode NEB

-6.50	DRC Mode QRO
-1.00	ORG Mode CR0
-15.00	DRC Mode CPV
0.00	Cell Gas A
0.00	Cell Gas B

Current Autolens Data

Analyte	Mass	Num of Pts	DAC Value	Maximum Intensity
Be	9	53	4.8	4803.3
Co	59	53	5.5	148308.0
In	115	53	5.8	312185.8

Base Vac ____ Run Vac ____ DRC Vac ____

APPENDIX 3

Instrument Tuning Report

File Name: 239.tun
File Path. C:\Elandata\Tuning

Analyte	Exact Mass	Meas. Mass	Mass DAC	Res. DAC	Meas. Pk. Width	Custom Res.
Be	9.012	9.026	2028	2054	0.665	
C	12.000	12.028	2780	2058	0.661	
Mg	23.985	23.979	5688	2061	0.686	
Mg	24.986	24.979	5919	2044	0.686	
Mg	25.983	25.929	6170	2071	0.675	
78Ar2	75.880	75.879	16317	2074	0.680	
Co	58.933	58.928	14182	2065	0.681	
Rh	102.905	102.929	24876	2089	0.674	
In	112.904	112.879	27315	2098	0.690	
In	114.904	114.929	27802	2100	0.675	
Ce	139.905	139.929	33885	2110	0.675	
Pb	205.975	206.027	49956	2143	0.650	
Pb	206.976	206.979	50199	2131	0.709	
Pb	207.977	207.979	50430	2147	0.698	
U	238.050	238.026	57746	2164	0.673	

Report Date/Time: Monday, August 27, 2007 05:44:44
Page 1

INORGANIC ANIONS BY EPA 300.0 USING THE DIONEX ICS-90 AND ICS-900

Revised by: Andy Waters and Michael Desmarais

Approved by: _____ Date: _____
Inorganic Instrument Department Supervisor

Reviewed by: _____ Date: _____
Quality Assurance Manager

SVL Analytical, Inc.

I have read, understood and will comply with SOP (SVL 4122 Version 7.0)

Print Name	Signature	Date
Andrew Waters		
Dave Tryon		
Justin Walker		

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1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedure used for the determination of inorganic anions by Ion Chromatography (IC) according to EPA Method 300.0. The anions which may be determined under this method include bromide, chloride, fluoride, nitrate-N, nitrite-N, and sulfate.

This method is applicable to drinking water, surface water, mixed domestic and industrial wastewaters, ground waters, reagent waters, soil extracts, and leachates (when no acetic acid is used). The reporting limits and typical MDLs are shown in the table below. Definitions found in this SOP may be found the SVL Quality Manual. The holding time is 28 days for chloride, fluoride, sulfate, and bromide. The holding time for nitrate and nitrite is 48 hours.

Analyte	Reporting Limit Aq. (mg/L)	Reporting Limit Soil (mg/L)	Aq. MDLs (mg/L)	Soil MDLs (mg/L)
Br	0.1	1.0	0.017	0.51
Cl	0.2	2.0	0.047	0.93
F	0.1	1.0	0.027	0.49
NO_2 (N)	0.05	0.5	0.0095	0.25
NO_3 (N)	0.05	0.5	0.016	0.27
SO_4	0.3	3.0	0.055	1.5

2.0 SUMMARY OF METHOD

A small aliquot of sample is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

2.1 An extraction procedure must be performed on soils before analysis.

3.0 INTERFERENCES

3.1 High concentrations of anions may interfere by creating peak overlaps (dilution of the sample may resolve the problem).

3.2 A negative peak, or water dip, may interfere with fluoride recovery (the addition of 50 µL of concentrated eluent to 5 mL of each sample and standard helps with this problem).

3.3 Particles larger than 0.45 µm will damage the columns. Samples that can't be decanted without particulates should be filtered prior to analysis.

3.4 Carbonate and other small organic anions may elute in the fluoride region and interfere.

3.5 Acetate ion may change the retention times of other anions.

3.6 High cation concentrations elute early and may interfere with fluoride analysis.

4.0 SAFETY

Sulfuric acid can cause severe burns if it comes into contact with skin or eyes. Wear safety glasses or goggles, gloves and lab coat or apron. In the case of exposure, flush with water for at least fifteen minutes.

5.0 EQUIPMENT, INSTRUMENTATION AND MATERIALS

Equivalent equipment, instrumentation and materials may be substituted.

5.1 Analytical balance, capable of weighing to 0.0001 grams, OHAUS AR2140.

5.2 Ion Chromatograph (IC), Model ICS-90 or Model ICS-900.

5.3 Chromatographic Control/Processing Software Chromeleon 6.60 for the ICS-90 and Chromeleon 6.80 for the ICS-900.

5.4 Analytical column, Dionex AS4A-SC, 4mm.

5.5 Guard column, Dionex AG4A-SC, 4mm.

5.6 Suppressor, Dionex AMMS 111, 4mm.

5.7 Conductivity detector, Dionex DS5.

5.8 Volumetric flasks, 25mL, 100mL, 200mL, 250mL, 500mL, 1L.

5.9 BD syringe, Luer-Lock, 10 ml.

5.10 0.45µm syringe filter, Whatman Puradisc 25, PVDF type, PN 6749250K.

5.11 Dionex Automated Sampler with sample racks, Dionex Model AS40.

5.12 Dionex Automated Sampler, Dionex Model AS-DV.

5.13 Dionex 5mL Polyvials and Caps, PN 038141.

5.14 Micropipets, 10, 20, 25, 50, 100, 500, 1000µL, 5mL fixed volume, 0.5-5 µL variable volume, Lambda, Wheaton, Eppendorf, VWR, accurate to within 3%.

5.15 Centrifuge vials, 50 mL screw top, Evergreen Scientific, PN 220-3550-080.

5.16 Centrifuge, Beckman GS-6.

5.17 Shaker, SVL Custom.

6.0 REAGENTS AND STANDARDS

Guidelines for the storage, tracking and expiration of chemicals and reagents can be found in SVL 1032. The procedure for purchasing chemicals and reagents can be found in SVL 1015. Any exceptions to the above mentioned SOPs will be found in this section, as well as all of the preparatory steps needed to construct or prepare reagents and standards. Equivalent standards or reagents may be used.

6.1 AS4A eluent concentrate (Matrix Matching Solution (MMS)), Dionex, 500mL, 180mM sodium carbonate, 170mM sodium bicarbonate, PN 039513.

6.2 Sulfuric acid, H_2SO_4, Fisher, tracemetal grade, PN A510SK-212.

6.3 Sodium fluoride solution, HPS, 250mL, 1000 mg/L solution. PN IC-FF-M-250.

6.4 Sodium chloride solution, HPS, 250mL, 1000 mg/L solution. PN IC-CL-M-250.

6.5 Nitrogen from sodium nitrite solution, HPS, 250mL, 1000 mg/L solution. PN IC-NO2-M-250.

6.6 Sodium bromide solution, HPS, 250mL, 1000 mg/L solution. PN IC-BR-M-250.

6.7 Nitrogen from sodium nitrate solution, HPS, 250mL, 1000 mg/L solution. PN IC-NO3-M-250.

6.8 Sodium sulfate solution, HPS, 250mL, 1000 mg/L solution. PN IC-SS-M-250.

6.9 IC nitrite spike mix, HPS, 250mL, 1000mg/L, PN IC-NO2-M.

6.10 IC custom spike mix, HPS, 125mL, PN SM-150-062. Concentrations are as follows (mg/L); Br 4000, Cl 3000, F 2000, NO3 2000 and SO4 10,000.

6.11 Eluent: Pipet 30mL of Dionex eluent concentrate (6.1) into a 3L vacuum flask and fill to the 3L mark with deionized water (6.19). Degas the solution for 15-30 minutes. Prepare daily.

6.12 Calibration standard 1: Use prepared eluent (6.11).

6.13 Calibration standard 2 through 7: Mix the following volumes (µL) of stock standards to 20 mL of deionized water (6.19), in a 100 mL volumetric flask. Bulk the standard to 100 mL with deionized water. Use a separate flask for each standard:

Analyte	F	Cl	NO2	Br	NO3	SO4	MMS
Std #	6.3	6.4	6.5	6.6	6.7	6.8	6.1
Cal Std 2	10	20	5	10	5	30	1000
Cal Std 3	50	100	20	50	20	200	1000
Cal Std 4	100	200	50	200	50	500	1000
Cal Std 5	200	500	100	500	200	1000	1000
Cal Std 6	500	1000	200	1000	500	2500	1000
Cal Std 7	700	1200	500	2000	700	5000	1000

The final concentrations (mg/L) of calibration standards 2 through 7 are shown in the table below:

Analyte	F	Cl	NO2	Br	NO3	SO4	MMS
Std #	6.3	6.4	6.5	6.6	6.7	6.8	6.1
Cal Std 2	0.1	0.2	0.05	0.1	0.05	0.3	1%
Cal Std 3	0.5	1.0	0.2	0.5	0.2	2.0	1%
Cal Std 4	1.0	2.0	0.5	2.0	0.5	5.0	1%
Cal Std 5	2.0	5.0	1.0	5.0	2.0	10.0	1%
Cal Std 6	5.0	10.0	3.0	10.0	5.0	25.0	1%
Cal Std 7	7.0	12.0	5.0	20.0	7.0	50.0	1%

6.14 Working ICV, CCV, and LCS solution: Transfer 200 µL of IC custom spike mix (6.10), 500 µL of IC nitrite spike mix (6.9), and 2.0 mL MMS (6.1) to 50 mL of deionized water (6.19) in a 200 mL volumetric flask. Bulk the standard to 200 mL with deionized water. Prepare fresh daily for NO2/NO3 and weekly for all other analytes. Concentrations are listed below.

Anion	Concentration (mg/L)
Br	4.0
Cl	3.0
F	2.0
NO_3 (N)	2.0
NO_2 (N)	2.5
SO_4	10.0

6.15 Regenerate solution: Dilute 4.2 mL concentrated sulfuric acid (6.2) to 2 L with deionized water (6.19). Final concentration is 75 mN H_2SO_4.

6.16 Matrix spike working solution: Transfer 5.0 mL IC nitrite spike mix (6.9) and 2.5 mL of IC custom spike mix (6.10) to 10 mL of deionized water (6.19) in a 25 mL volumetric flask. Bulk the standard to 25 mL with deionized water. Mix well. Prepare fresh daily for NO2/NO3 and weekly for all other analytes. Concentrations are listed below.

Anion	Concentration (mg/L)
Br	400
Cl	300
F	200
NO_3 (N)	200
NO_2 (N)	250
SO_4	1000

6.17 Diluent: Use eluent (6.11).

6.18 Chemware Ultra Pure PTFE Boiling Stones, catalog # D-1069103.

6.19 Type I deionized water.

6.20 Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB) and prep blank: use eluent (6.11).

6.21 RLCS Stock 1: IC custom spike mix, HPS, 125mL, PN XX-XXX-XXX. Concentrations are as follows (in mg/L); Br 100, Cl 200, F 100, NO3 50 and SO4 300.

6.22 RLCS Stock 2: 50 mg/L nitrite standard, HPS, 125mL, PN XX-XXX-XXX.

6.23 RLCS working standard: Transfer 50 µL of RLCS Stock 1 (6.21), 50 µL of RLCS Stock 2 (6.22) and 0.5 mL MMS (6.1) into a 50 mL volumetric containing 20 mL of deionized water (6.19). Bulk the standard to 50 mL with deionized water. Make fresh daily. Concentrations are listed below.

Anion	Concentration (mg/L)
Br	0.1
Cl	0.2
F	0.1
NO_3 (N)	0.05
NO_2 (N)	0.05
SO_4	0.3

7.0 INSTRUMENT SETTINGS (FOR DIONEX ICS-90 and ICS-900)

ICS-90 and ICS-900 are interchangeable unless otherwise noted.

7.1 Empty the eluent reservoir and fill it to the top with freshly prepared eluent.

7.2 Empty, thoroughly rinse and refill regenerate reservoir. The reservoir must be completely filled (no headspace) for it to function properly.

7.3 Turn on the nitrogen gas (ICS-90 only).

7.4 Start the Chromeleon program by double-clicking the Chromeleon icon on the desktop or from the start menu.

7.5 From the Browser, open the ICS-90 control panel by double-clicking the “ICS-90_System_AS40.pan” file from the “Control Panel” sub-directory of the ICS-90 directory.

7.6 Start the pump by clicking the “On” button in the control panel. Let the instrument equilibrate for 20-30 minutes. For ICS-900 open the pump valve and then click “prime”. A pop up will prompt you to open the pump

valve, select “ok”. Allow the pump to prime for 2-3 minutes, watching for air bubbles in the system. Click “off” to stop the prime cycle, close the pump valve and then turn the pump back on using the “on” button. Allow to equilibrate for 20-30 minutes.

8.0 CALIBRATION

Calibration is performed using a quadratic regression and seven calibration standards. The high calibration standard varies from 7-50 mg/L, depending on the anion.

8.1 Create a new sequence.

8.1.1 Open the browser.

8.1.2 Select the most recent sequence, and click “Save As…” from the File menu.

8.1.3 Name the new sequence as the four digit year, then the Julian day of the year, and “A, B or C” (dependent upon instrument used) at the end, e.g. 2005 365B. Click “Save.

8.1.4 When the new sequence is created, all samples are reset to “Single” status, which means they will be processed when the sequence is started.

8.1.5 The new sequence should start with seven AUTOCAL standards (“AUTOCAL1”, “AUTOCAL2”, etc.), followed by two retention time tests, one ICV, one ICB and one RLCS.

8.2 Initiate the calibration sequence:

8.2.1 Transfer 3-5 mL of each calibration standard to separate vials. Place the vials into the racks and load them on the auto sampler. Press the hold/run button on the auto sampler (A & B only) to load the standards. (For ICS-900C move the standards from the racks to the auto sampler carousel. Be sure that the carousel numbers match the injection number of each standard in the Chromeleon sequence list.)

8.2.2 Verify that all calibration standards in the sequence are the proper type (e.g. unknown, standard, etc.). Disable any samples that won’t be used by deleting them or changing their status to “Finished”.

8.2.3 Start the calibration by clicking “batch” on the Chromeleon menu. Select “start” and then “ok”.

8.2.4 After the calibration standards have been analyzed, double-click on the name of the first standard to open the report window.

8.2.5 Click on the “Integration” tab, and inspect the chromatograms for all seven standards for proper integration and make sure the peaks for the seven anions are identified with the correct names.

8.2.6 Verify the calibration curve by using the following excel worksheet “Calibration Curve Check (IC) short” found at H:/Templates.

8.2.6.1 Take values from the Chromeleon generated curve and enter them into the above worksheet.

8.2.6.2 The worksheet will fit each calibration standard back into the newly derived calibration curve.

8.2.6.3 If the curve is validated, save the worksheet in H:/Cal Checks. You must name it with the calibration date and place it in the corresponding instrument file.

8.2.7 Select the appropriate PDF printer from the drop down box. Reporting to PDF should be turned off until after all of the calibration standards have been analyzed. Calibration values will now be based upon the entire calibration curve.

8.2.7.1 Highlight all calibration standards and right click, check both “Export” and “Printout” boxes. Under “Printer” choose the correct PDF printer then select “OK”.

8.2.7.2 Name the PDF file with the same two digit year, three digit Julian date and instrument letter as the Chromeleon file.

8.2.8 Turn printing and exporting on by clicking “batch” on the Chromeleon menu. Select “batch report” and check the box next to “print/export”.

8.3 After every calibration (and on every day that samples are run) initial QC must be run to verify the calibration.

8.3.1 Fill three vials with ICV/CCV solution (6.14) (two retention time tests and one ICV). Fill one vial with ICB/CCB solution (6.20). Fill one vial with RLCS solution (6.23).

8.3.2 Type the names of the initial QC into the sequence after the calibration standards in the following order:

RT TEST 1
RT TEST 2
ICV
ICB
RLCS

8.3.3 Set all of the QC standards to single status and disable all other samples by setting them to “finished”.

8.3.4 Start the initial QC by clicking “batch”, then “start” and then “ok”.

8.3.5 The program will run the five QC samples and print chromatograms to the PDF file.

8.4 Retention Time Tests

8.4.1 The two retention time tests (RT TEST 1 & 2) are used to verify that the retention times for each analyte have not changed since the instrument was calibrated. The retention times of both tests must be within 10% of the original elution times, if the standards are not within 10% remake the eluent and regenerate and re-prepare the ICV/CCV solution (6.14) and run it again. If the standard is still not within the established limits, the method requires that the IC be re-calibrated.

8.4.2 The IC operator will use RT TEST 2 to manually update the instrument’s retention times.

9.0 SAMPLE HANDLING AND PRESERVATION

9.1 Store samples between 0-6°C prior to analysis. The holding time is 28 days for chloride, fluoride, sulfate, and bromide. For nitrate and nitrite the holding time is 48 hours.

10.0 SAMPLE PREPARATION AND ANALYSIS

10.1 Start the instruments as described in section 7.0.

10.2 Create a new sequence as described in 8.1

10.3 Copy the previous day's calibration to the new sequence

10.3.1 Select all seven AUTOCAL standards from the old sequence by highlighting them.

10.3.2 Right click; select "copy" to copy the old calibration.

10.3.3 Go to the new sequence; right click and select paste (be sure to select "paste all" (including raw data)).

10.4 Allow the instruments to equilibrate. Run retention tests.

10.5 After the retention time test is completed and has passed the 10% requirement (8.4.1), update the retention times (if needed).

10.5.1 Double click "90C_AnionsM.qnt."

10.5.2 From the peak table use the next chromatograph arrow to find the RT Tests.

10.5.3 Select all analytes in the table at the bottom of the screen.

10.5.4 Right click and select "Get current retention times."

10.5.5 Close the qnt window with the smaller x in the upper right hand corner.

10.5.6 Click "Yes" on the pop up window to save the changes to the qnt file.

10.6 If operating under an existing calibration continuing QC consists of analyzing a CCV followed by a CCB after every ten injections. (Note: The RLCS counts as an injection).

10.6.1 CCV: Transfer 3-5 mL of the working ICV/CCV solution (6.14) into a vial and place in the correct position in the rack.

10.6.2 CCB: Transfer 3-5 mL of ICB/CCB solution (6.20) to a vial and place in the correct rack position.

10.7 In the sample list, after the initial QC, type the names of the samples to be analyzed (with associated QC) in the order to be loaded in the auto sampler. If a sample is prepared at a dilution type the sample ID immediately followed by the "@" symbol and the required dilution. (i.e. W0H0001@10X).

10.8 Place the racks of vials on the automated sampler and push the "Run" button (on A and B only, for C be sure the carousel numbers match the injection numbers).

10.9 Verify that all samples in the sequence are the proper type (e.g. Unknown) and using the proper program (Anion). Disable any samples that won't be used by deleting them or changing their status to "Finished".

10.10 Start analyzing samples by clicking batch on the Chromeleon menu. Select start and then ok.

10.11 To prepare aqueous samples

10.11.1 Prepare a method blank for every batch of 20 or less samples: Transfer 3-5 mL of eluent (6.11) into a vial.

10.11.2 Prepare an LCS for every batch of 20 or less samples: Transfer 3- 5 mL of ICV/CCV solution (6.14) into a vial.

10.11.3 Transfer 5 mL of each well-mixed sample into a vial, and add 50 µL of MMS (6.1).

10.11.3.1 Samples which contain particles larger in diameter than 45 µm must be filtered with a 45 µm syringe filter to prevent damage to the analytical column.

10.11.4 Prepare a matrix spike (one for every batch of ten samples or less) by transferring 5 mL of sample into a vial. Add 50 µL of the matrix spike working solution (6.16) and 50 µL of MMS (6.1) to the vial. Mix well. If the batch exceeds ten samples an additional matrix spike must be prepared.

10.11.5 Prepare a matrix spike duplicate following procedure outlined above in 10.11.4.

10.11.6 Place the vials into racks and load them on the automated sampler.

10.11.7 If the concentration of an anion in any sample exceeds the highest standard in the calibration curve, dilute the sample with eluent (6.11) and re-analyze it.

10.11.8 The last sample of a sequence should be called “Shut Down” and should use the “90_Shutdown.pgm” program.

10.12 To analyze soils for extractable anions, extract them as follows:

10.12.1 Prepare a prep blank (one for every 20 or fewer samples): add 40 mL of diluent (6.17) to a centrifuge vial containing 4g of PTFE boiling stones (6.18). Add 400 µL of MMS (6.1) to the vial. Mix well.

10.12.1.1 Pipet a 5 mL aliquot of the prep blank and add it to a Dionex poly vial then add 50 µL of MMS (6.1) to the vial. Mix well.

10.12.2 Prepare an LCS (one for every batch of 20 or fewer samples): add 40 mL of working ICV/CCV/LCS solution (6.14) to 4 g of PTFE boiling stones (6.18). Add 400 µL of MMS (6.1) to the vial. Mix well.

10.12.2.1 Pipet a 5 mL aliquot of the LCS and add it to a Dionex poly vial then add 50 µL of MMS (6.1) to the vial. Mix well. The final concentrations are as follows:

Analyte	LCS Conc. (mg/L)
F	3.32
Cl	7.23
Br	1.72
NO_3 (N)	3.32
PO_4 (P)	2.50
SO_4	6.12

10.12.3 Soil extractions of solid samples will be performed on an “as received” basis (any other preparation instructions will be placed in a work order memo).

10.12.4 For sample extractions weigh 4.0 g of sample to the nearest 0.01 g in a centrifuge vial. Add 40 mL of deionized water.

10.12.4.1 Pipet a 5 mL aliquot of the extraction and add it to a Dionex poly vial then add 50 µL of MMS (6.1) to the vial. Mix well.

10.12.5 Prepare a matrix spike (one for every batch of 10 or fewer): weigh another 4.0 g of sample to the nearest 0.01 g in a centrifuge vial. Add 40 mL of deionized water (6.20). Mix well. Spike additions are as below:

Analyte	MS Conc. (mg/L)
F	2.0
Cl	3.0
NO_2 (N)	2.0
Br	4.0
NO_3 (N)	2.0
SO_4	10.0

10.12.5.1 Pipet a 5 mL aliquot of the matrix spike and add it to a Dionex poly vial then add 50 µL of MMS (6.1) to the vial. Mix well.

10.12.6 Prepare a matrix spike duplicate following procedure outlined above in 10.12.5 and 10.12.5.1.

10.12.7 Place vials in shaker and shake vigorously for about 10 minutes.

10.12.8 Centrifuge after shaking for 15-20 minutes.

10.12.9 Filter the extract through a 45 µm syringe filter. Analyze the extract as a sample.

11.0 DATA REDUCTION

11.1 The software will generate a calibration curve of peak area versus concentration using a quadratic regression (see SVL SOP 1020 on quadratic and linear regression).

11.2 The analyst will visually check the peak integrations on each report.

11.2.1 If peaks are manually integrated for any reason, the original chromatogram will remain in the data package and expanded chromatograms of before and after a manual integration will be included. On the expanded chromatograms explanations for the manual integration must be notated. The manual integration must be dated and initialed by the analyst (see SVL 1021 on manual integrations). Secondary review is required for all manual integrations; after review the reviewer will date and initial all manual integrations.

12.0 DATA AND RECORDS MANAGEMENT

12.1 Procedures for constructing bench sheets can be found at R:\Promium Stuff\How to's\Batching.doc. Make sure that the bench sheet is initialed and dated when the actual preparation of the sample(s) began.

12.1.1 Indicate all reagents used in the batch by including them in the reagent section of the "Batch" screen.

12.2 Procedures for constructing sequences can be found at R:\Promium Stuff\How to's\Sequences.doc.

12.3 The raw data will print to a PDF file (pdfFactory Pro is set as the default printer) and be exported via a data tool compatible file as the run proceeds.

12.4 If sequencing is required, go to the "Sequence" page, highlight all of the applicable samples, and click the print icon to print a runlog to the same PDF as the chromatograms. Perform this function upon completion of the run.

12.5 Instructions on including data in PDF format.

12.5.1 The run file should begin with PDF formatted copies of the original autocal standards from most recent calibration curve followed by the current day's QC standards; the run file will include every chromatogram up to the last useable CCV/CCB. The run file should end with an IC Control Sheet and a runlog.

12.5.2 Insertion of chromatograms in pdf format is necessary whenever a manual integration has been performed. The analyst must print to PDF an expanded chromatogram of the manually integrated area

both prior to the manual integration and after the integration has been made.

12.5.2.1 These printouts should be placed in the run file so that they are the pages immediately preceding the original full scale chromatogram (Note: pages can only be re-arranged before closing the original pdfFactory Pro file. After the pdfFactory Pro file is closed secondary files or pages must be attached using the Foxit Reader editing software).

12.5.3 Verify that all of the criteria presented in 11.2.1 is included in the run file; if not, use Foxit Reader to modify the chromatograms before saving the run file.

12.6 Use data tool to upload results into Element.

12.7 In Element, the analyst shall perform all reviews on the "Data Entry/Review" page and verify their data uploads.

12.8 If input comes up color coded, apply the appropriate qualifiers or undertake any corrective actions. Also, add qualifiers for all dilutions.

12.9 The analyst shall update the status of the batch to "Analyzed", and lock the results so that any future imports will not overwrite acceptable results.

12.10 The data review process is outlined in SVL 2009.

12.11 Corrective action is governed by SOP SVL 1019.

13.0 QUALITY CONTROL

Method	ICV	ICB	RLCS	CCV	CCB
300.0	Limit: within 10% of expected	Limit: less than the reporting limit	Limit: within 50% of expected	Limit: within 10% of expected	Limit: less than the reporting limit
	Action: re-run then re-calibrate	Action: re-run then re-calibrate	Action: re-run, then re-calibrate	Action: re-run, then re-calibrate and re-analyze the previous ten samples	Action: re-run, then re-calibrate and re-analyze the previous ten samples.

Method	LCS	MS Dup. RPD	Matrix Spike	Method Blank
300.0	Limits: 90 to 110% for aqueous samples and 80-120% for soils	Limit: 20%	Limits: 90 to 110% for aqueous and 75-125% for soils.	Limit: less than the reporting limit
	Action: re-run, then re-calibrate if outside established limits.	Action: flag if higher	Action: flag if out	Action: re-run, then re-calibrate if outside established limits.

13.1 Analyze an ICV (10.6.1). This doubles as an Instrument Performance Check Solution (IPC). The acceptance limits are 90 to 110% of the expected value. If the ICV/IPC falls outside the acceptance limits, reanalyze it. If the second analysis is within the acceptance limits, the analysis of the sample batch may continue. If the results of the second analysis confirm calibration to be outside the limits, stop sample analysis and determine the cause.

13.2 Analyze an ICB (10.6.2) after the ICV. The blank must be less than the reporting limit for each analyte. If the blank exceeds the reporting limit for any anion of interest, re-run the ICB. If the ICB still exceeds the reporting limit, discontinue analysis and recalibrate the instrument. The exception to this rule is: when the analyte that is out is not being analyzed for, then the run can continue.

13.3 Analyze a RLCS (8.3.1) after the ICB. The acceptance limits are 50 to 150% of the expected value. If the recovery falls outside these limits, re-analyze the RLCS. If the recovery still falls outside the limits, re-calibrate the instrument.

13.4 Re-analyze the working ICB/CCB (6.20) and ICV/CCV (6.14) solution as a method blank (10.11.1 and 10.12.1) and LCS (10.11.2). Run them once per batch of 20 or fewer samples. The method blank must read less than the reporting limit. The LCS acceptance limits are 90 to 110% of the expected value. If the recovery falls outside these limits, re-analyze the method blank or LCS. If the recovery still falls outside these limits, re-calibrate the instrument prior to analysis of any samples.

13.4.1 For soils, analyze the soil LCS extract (10.12.2) at a frequency of one per batch of 20 or fewer samples. The LCS acceptance limits are 80 to 120% of the expected value. If the recovery falls outside the limits, re-run the LCS, if it fails again re-extract and analyze the batch.

13.5 Analyze a matrix spike (10.11.4) at a frequency of 1 per batch of 10 or fewer samples. If the batch exceeds ten samples an additional matrix spike must be prepared. The acceptance limits are 90 to 110% of the expected value, if the spike added is greater than 25% of the concentration of the un-spiked sample. There are no acceptance limits if the spike added is less than 25% of the concentration in the un-spiked sample. If the MS recovery falls outside of these limits, and the following CCV and CCB pass then the recovery failure is judged to be either matrix or solution related. Flag the client report with the appropriate data qualifier.

13.5.1 For soils analyze a matrix spike (10.12.5) at a frequency of 1 per batch of 10 or fewer samples. The acceptance limits are 75 to 125% except for fluoride where the limit is 50 to 150% of the expected value, if the spike added is greater than 25% of the concentration of the un-spiked sample. There are no acceptance limits if the spike added is less than 25% of the concentration in the un-spiked sample. If the MS recovery falls outside of these limits, and the following CCV and CCB pass then the recovery failure is judged to be either matrix or solution related. Flag the client report with the appropriate data qualifier.

13.6 Analyze a matrix spike duplicate (10.11.5) (10.12.6) once per follow the guidelines and recoveries above. The control limit for RPD between matrix spike and matrix spike duplicates is 20%.

13.7 For the CCV (6.14) analyze the working ICV/CCV solution. The acceptance limits are 90 to 110% of the expected value. If the CCV falls outside the acceptance limits, reanalyze it. If it fails again stop the run, determine the cause for the failure, recalibrate and re-analyze all samples run since the last successful CCV/CCB.

13.8 Analyze a CCB (6.20) after each CCV. The CCB must be less than the reporting limit for each analyte. If the CCB results exceed the reporting limit for any anion of interest, then re-run the CCB. If the CCB still exceeds the reporting limit and the failed anion is required, discontinue the analysis. Re-analyze all samples run since the last successful CCV/CCB. If the anion is not required continue with the run.

13.9 Perform an aqueous MDL study every six months and a soil MDL annually, when a new analyst begins work, or when there is a significant change in background or in instrument response.

13.10 LCR studies are conducted initially, or whenever a significant change is noted in the instrument response and when a new analyst is trained.

13.10.1 Since SVL does not report above its calibration range, twice a year the analyst will use the linear calibration verification template mentioned in 8.2.6 to verify that the quadratic curve is linear over a portion of the curve. Any three points from the quadratic curve may be fitted into the linear template in order to prove linearity. Copies of these runs will be placed in an electronic folder titled "H:/Linearities."

13.12 Trend analysis can be found in SOP SVL 1033.

13.13 Demonstration of capability requirements can be found in SOP SVL 1010.

14.0 REFERENCES

14.1 Method 300.0, "Determination of Inorganic Ions by Ion Chromatography", Methods for the Determination of Inorganic Substances in Environmental Samples, EPA/600/R-93/100, August 1993.

14.2 Manual for the Certification of Laboratories Analyzing Drinking Water, Fifth Edition.

14.3 ICS-90 Ion Chromatograph Operator's Manual. Dionex Corporation, Document No. 031851, December 2004.

14.4 Chromeleon Tutorial and User Manual, version 6.60. Dionex Corporation, March 2004.

14.5 ICS-900 Ion Chromatograph Operator's Manual. Dionex Corporation, Document No. 031851, December 2004.

14.6 Chromeleon Tutorial and User Manual, version 6.80. Dionex Corporation, March 2004.

15.0 POLLUTION PREVENTION

15.1 The chemicals used in this method pose no threat to the environment. All standards are prepared and reagents used in volumes consistent with laboratory use to minimize the volume of disposable waste.

15.2 All standards are prepared and reagents used in volumes consistent with good laboratory practice to minimize the volume of disposable waste.

16.0 WASTE MANAGEMENT

16.1 Waste generated by this method includes plastic-ware, chemicals used in digestion and/or analysis, and paper.

16.2 Most chemicals used during digestion and/or analysis are neutralized and/or diluted prior to disposal by permit to the public sewer. Any hazardous chemicals and/or residues are disposed of through SVL's hazardous waste disposal system (see SOPs SVL 1001 & 1008).

17.0 CHANGE HISTORY

Date	Version	Change
07/21/09	2.0	SOP was completely re-worked please see archived versions for any comparisons that need to be made. 6.24 added "Chemware Ultra Pure PTFE Boiling Stones, catalog # D-1069103". 10.12.1 changed to "centrifuge vial containing 4g of PTFE boiling stones (6.24)".

10/07/10	3.0	3.6 added “High cation concentrations elute early and may interfere with fluoride analysis”. 5.7 added “Conductivity detector, Dionex DS5”. 5.16 added “Shaker, SVL Custom”. Re-wrote Section 6.0. 7.2 added “thoroughly rinse”. 7.3 added “(ICS-90 only)”. Cropped Section 7.0 to only include instrument set-up not standard verifications. 11.2.1 changed to “If peaks are manually integrated for any reason, the original chromatogram will remain in the data package and expanded chromatograms of before and after a manual integration will be included. On the expanded chromatograms explanations for the manual integration must be notated. The manual integration must be dated and initialed by the analyst (see SVL 1021 on manual integrations). Secondary review is necessary for all manual integrations; after review the supervisor will date and initial all manual integrations”. Re-wrote the majority of Section 12.0. 13.11 changed to “Perform a Linear Calibration Range (LCR) study every 6 months, whenever there is a new analyst, during the initial set-up of the instrument or when there is a significant change in background or instrument response. The study will consist of a minimum of a blank and three standards. The recovery of the standards must be within 10% of the true value. If a standard fails then the calibration curve must be adjusted to meet the new LCR”. 13.12 added “Annually, reprocess a quadratic calibration curve using a linear regression. A correlation coefficient of 0.995 will provide a suitable comparison of the two studies. The study will be turned into the QA office and placed with the MDLs. This study will satisfy Idaho requirements.

10/28/11	4.0	6.14 and 6.16 changed to "Prepare fresh daily for NO2/NO3 and weekly for all other analytes. Concentrations are listed below". 6.15 changed to "Dilute 4.2 mL concentrated sulfuric acid (6.2) to 2 L". Added 6.21, 6.22 and 6.23. Re-wrote Section 8.2. 8.4.1 changed to "The two retention time tests (RT TEST 1 & 2) are used to verify that the retention times for each analyte have not changed since the instrument was calibrated. The retention times of both tests must be within 10% of the original elution times, if the standards are not within 10% remake the eluent and regenerate and re-prepare the ICV/CCV solution (6.14) and run it again. If the standard is still not within the established limits, the method requires that the IC to be re-calibrated". 8.4.2 added "The IC operator will use RT TEST 2 to manually update the instrument's retention times". 10.11.6 added "If the batch exceeds ten samples an additional matrix spike must be prepared". 13.6 added "If the batch exceeds ten samples an additional matrix spike must be prepared". 13.9 added "and a soil MDL annually".
11/16/12	5.0	6.13 adjusted curve concentrations. 10.11.5 added "Prepare a matrix spike duplicate following procedure outlined above in 10.11.4". 10.12.3 changed to "Soil extractions will be performed on an as received basis (any other instructions will be placed in a Work Order memo)". Throughout section 10.12 the following was added for all sample types "Pipet a 5 mL aliquot of the _____ and add it to a Dionex poly vial then add 50 µL of MMS (6.1) to the vial. Mix well". 13.6 added "Analyze a matrix spike duplicate (10.11.5) (10.12.6) once per follow the guidelines and recoveries above. The control limit for RPD between matrix spike and matrix spike duplicates is 20%". 13.10 changed to "SVL does not report results above its calibration curve. Samples are diluted to fit back within the curve parameters. If possible, aim for a response between the two highest standards. A secondary source verifies the curve and linearity is verified using the calibration curve check". 13.10.1 added "LCR studies are conducted upon instrument setup, when a significant change is noted in the instrument response and when a new analyst is trained".

10/11/13	6.0	10.12.2 changed to “add 40 mL of working ICV/CCV/LCS solution (6.14) to 4 g of PTFE boiling stones (6.18). Add 400 µL of MMS (6.1) to the vial. Mix well.” 10.12.7 changed to “10.” 13.10 changed to “13.11 LCR studies are conducted initially, or whenever a significant change is noted in the instrument response and when a new analyst is trained.” 13.11.1 changed to “Since SVL does not report above its calibration range, twice a year the analyst will use the linear calibration verification template mentioned in 8.2.6 to verify that the quadratic curve is linear over a portion of the curve. Any three points from the quadratic curve may be fitted into the linear template in order to prove linearity. Copies of these runs will be placed in an electronic folder titled “H:/Linearities”.”
08/13/14		6.13 changed calibration standard 6 for nitrite from 2.0 to 3.0. 12.11 added “Corrective action is governed by SOP SVL 1019.” 13.12 added “Trend analysis can be found in SOP SVL 1033.” 13.13 added “Demonstration of capability requirements can be found in SOP SVL 1010.”

Attachment B

EQuIS Standard Operating Procedure

INTRODUCTION

ARCADIS manages and verifies/validates analytical data generated by commercial analytical laboratories in the EQuIS database (product of Earthsoft, Inc.). All laboratories contracted by ARCADIS or their clients, on a site-by-site basis, may be required to submit electronic data deliverables (EDDs) in addition to the hard copy report. This Standard Operating Procedure (SOP) describes the structure, format, and submission requirements for electronic data deliverables (EDDs) in the EQuIS EFWEDD (Sample, Test, Result, Batch) format.

This document is a general guidance for preparation of the required electronic data and associated quality control information. The structure of the EDD as defined in this document will remain constant unless Earthsoft modifies the database structure. Reference values and requirements for population of additional fields with specific information will not change from project to project.

Modification to reference value lists may NOT be made by the laboratory without authorization from ARCADIS.

Section I provides ARCADIS contact information and the procedure to submit electronic deliverables directly via e-mail. However, all EDDs will be required to be submitted in a final CD compilation for each specific sampling event or as directed by the ARCADIS Project Manager (PM).

Section II outlines the table structures and general requirements of the EDDs. The EDD structure is based on EarthSoft's EFWEDD EDD format. EarthSoft's EDD format has not been changed; however, some 'optional' fields identified in the EarthSoft EDD have been modified to be 'required' in this EDD format. Additional information regarding the EarthSoft products can be found at http://www.earthsoft.com/.

Section III presents some additional explanation and requirements for populating the table structure and population set forth in Section II.

Section IV summarizes the use of the EDP. Each laboratory **MUST** use EDP to check each EDD file set prior to submission to ARCADIS. The EDP Error Report must be submitted with the EDD. ***All errors identified by the EDP routine must be corrected prior to forwarding the files for entry into the EQuIS database. Or approval for submittal with errors must be authorized by ARCADIS.***

I. CONTACT INFORMATION

Laboratories should contact the ARCADIS National Program Lab Managers with questions regarding this document. The contact info is as follows:

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ELECTRONIC LABORATORY DATA CHECKER EDP

Prior to submitting an EDD to ARCADIS, the EarthSoft EDP must be run to check and verify the EDD structure, format and reference value compliance. The EDP report must be submitted for each file with each EDD set. The Data Checker error report, which demonstrates that the EDD files were successfully checked, must be electronically submitted with the four EDD files to ARCADIS.

REFERENCE VALUES

A specific set of values is required to be utilized in populating certain key fields of the EDD. The Reference Value Lists for the EDP will be provided for each ARCADIS subcontracted laboratory. The Reference Value Lists must be utilized as provided. Alterations or additions to the Reference Values are **NOT** allowed **without prior** written authorization by the ARCADIS Data Manager. Electronic mail may be considered written authorization.

ELECTRONIC DATA DELIVERABLE (EDD) SUBMISSION

Prior to submission to ARCADIS, each data file must also be reviewed by the laboratory to ensure that the sample IDs, dates, times and other inter-related information is consistent between all four (4) files and the EDD is complete. All parameters that are subcontracted to other laboratories must be included in the EDD for a specific SDG or Laboratory Project Number. It is not acceptable to submit separate EDDs for subcontract parameters. Manual review of the files may be necessary to complete this review.

It is **IMPERATIVE** that the EDD results match the hard copy results. If the results do not match the lab will correct the error ASAP at no additional charge. This includes issues involving various rounding routines for different electronic data management programs within the laboratory (i.e. LIMS vs. EPA CLP). Significant figures must also match hard copy and be consistent from one sampling event to the next. Reporting limits must be consistent between events as well and must be in compliance with the Laboratory Task Order or Project Statement of Work. There may be instances where diluted surrogates and unrecovered spike compounds will require population of the EDD with numeric values in lieu of data flags in the hard copy report. The ARCADIS Data Manager will provide project specific guidance for these conditions. Adherence to the SOP requirements for population of spike/surrogate recovery and RPD fields is required to allow electronic validation of the data.

The EDP Reports for each file must be submitted with the 4 files of the actual EDD.

Laboratories must submit EDDs via e-mail for verification of compatibility and completeness to the assigned ARCADIS Data Manager for the project.

The subject line of this e-mail must include the following text:

[Facility-Code] [Laboratory Project/Log/SDG Number] - EDD Submission

The e-mail should also include the laboratory contact name and phone number.

EDDs must be submitted via e-mail prior to or at the same time the final hard copy document is delivered. ARCADIS may review the EDDs prior to requesting final submittal on CD. EDDs will be returned to the laboratory for modifications until the files can be successfully imported into the EQuIS Project Database and Electronic Data Validation can be performed without field population errors. Any revisions to the EDD will be required within 24 hours of notification to the laboratory regarding observed problems with the EDD. When the EDD is acceptable to the ARCADIS Data Manager and Project Manager, a CD containing all final versions of the EDD should be submitted to ARCADIS for archiving.

Invoices for analytical work will not be approved for payment until the final EDD revisions are acceptable.

II. ELECTRONIC DELIVERABLE DATA FORMAT

This section identifies the structure and format requirements for EQuIS EFWEDD EDDs submitted by all laboratories to ARCADIS. Specific field definitions are presented for each of the four files. Laboratories should review the unique requirements for these fields. The format population and adherence to the criteria are mandatory. Data are electronically validated and errors are quickly identifiable if the EDD is incorrect.

GENERAL FORMAT REQUIREMENTS

All laboratory data must be saved as an ASCII file format using the following standard format. Each subcontracting laboratory's data must be incorporated into the primary laboratory's EDD.

Each data field must be either separated by tabs or enclosed in double quotes (") and separated by commas. Data fields that do not contain information may be represented by two commas. Maximum length of text fields is indicated in the parentheses. If the input information is less than the maximum field length, **DO NOT ADD** spaces to account for the difference.

Each record must be terminated with a carriage return/line feed (i.e., standard DOS text file). The file can be produced using any software with the capability to create ASCII files.

THE LABORATORY SHALL LEAVE THE HEADERS IN EACH ASCII FILE TO ASSIST IN REVIEW AND RESOLUTION OF ERRORS.

Four files are required for each SDG or Laboratory Project Number: one each for samples, tests, results, and batches. Each file must be saved as a Tab Delimited or Comma Separated file.

Enterprise EDD File Naming Conventions
EDD packages must be named using a specific naming convention. An EDD Package consists of a .zip file containing the text (.txt) EDDs and a User Certificate. The zip file and text file names must contain the specific elements listed below under file naming conventions, separated by a period. A User Certificate file will be supplied to the lab by Arcadis for inclusion in the zip file. Please include in the subject line of emailed EDD submissions the facility code and Sample Delivery Group (SDG) number.

File Naming Conventions:
ZIP File Name = Unique ID.Facility Code.Format Name.zip
Text File EDDs Name = Unique ID.EDD Section Name.txt

Unique ID = SDG number.
Facility Code = The facility code (i.e., Site Name from ENFOS)
Format Name = The EQuIS EDD format name (e.g., ESBasic, EFWEDD, etc.).
EDD Section Name = The name of the section within the EDD (e.g. EFW2FSample, EFW2LabTST, etc.).

For example, ZIP File Name = "2009001.BP-99999.EFWEDD.zip" will contain the following files: "2009001.EFW2FSample.txt", "2009001.EFW2LabTST.txt", “2009001.EFW2LabRES.txt", '2009001.EFW2LabBCH.txt' and "pfoos.usr".

Package re-submittal
In order to re-submit corrected EDDs, the .zip file and text (.txt) EDDs must each be renamed. If the example EDD package above were to be re-submitted it would have ZIP File Name = "2009001B.BP-99999.EFWEDD.zip" containing "2009001B.EFW2FSample.txt", "2009001B.EFW2LabTST.txt", “2009001B.EFW2LabRES.txt", '2009001B.EFW2LabBCH.txt' and "pfoos.usr". Note that a “B” has been appended to the SDG name in both the zip file name and each of the text file names. A subsequent re-submittal of the same SDG would require that a C be appended and so on.

Referential integrity is enforced between tables (e.g. sys_sample_code present in the result, batch, and test tables must also be present in the sample table). For example, a data record with a specific sys_sample_code found in the result table, but not in the sample table, will cause and error in the Data Import Module and the file will not be allowed to be entered into the database. Dates and times associated with each test must match in the “Test” and “Result” files or the database will not allow entry of the entire file.

Reference values must be adhered to for a variety of fields as identified in the Reference Value list and described in the following table format requirements.

FORMAT DETAILS

The following four sections provide a detailed summary and the specific layout for each field required in each of the four (4) tables of the EDD. The ARCADIS EDD has been derived from the EarthSoft EFWEDD EDD.

Date is reported as MM/DD/YY (month/day/year) and time as HH:MM (hour:minute). Time must be reported in 24-hour (military) format (3:30 p.m. = 15:30 and 8:30 AM = 08:30 not 8:30). **NOTE:** Make certain that the LIMS systems format the date and time the same way for all files.

The columns in the following 4 tables relate to:

“Number” Column in Tables = Column of EDD table

“Attribute Name” = Column Name
PK after attribute indicates this is a primary key within Access for the table.

"Column Data" Type = Text or Numeric values required. Parenthetical number indicates total allowable number of characters in the field.

"Required" Column:

The column titled 'Required' will contain the text 'Yes' if the field is required to be populated by the laboratory. In addition, a "condition" is added to indicate additional information applying to population of the associated field. The first number of the condition relates to the table in which the condition applies, i.e. 1 is the Sample File, 2 is the Test File, 3 is the Result File, and 4 is the Batch File. Conditions apply as follows:

Condition	Table	Description
0	ALL	Field always required
1-1	SAMPLE	Field required for field samples only not required for laboratory samples
1-2	SAMPLE	Field required (parent_sample_code) for **laboratory** QC samples that have 'parents'
1-3	SAMPLE	Field not required for field samples
2-1	TEST	Field required if applicable for specific test
3-1	RESULT	Field required (result_value) for detected analytes only (TRG or TICs). Must be NULL if non-detect or surrogates, internal standards or spiked compounds
3-2	RESULT	Field required if available or appropriate for result
3-3	RESULT	Field required for matrix spikes or matrix spike duplicates (NOT required for surrogate compounds or LCS samples where the original concentration is assumed to be zero).
3-4	RESULT	Field required for surrogate compounds, LCS, Blank Spikes, Matrix Spikes, and Internal Standards.
3-5	RESULT	Field required for LCS duplicates, Blank Spike Duplicates, Matrix Spike Duplicates, Lab Replicates
3-6	RESULT	Field required for LCSD, BSD, MSD, and Lab duplicate samples
3-7	RESULT	Field required for surrogates and spike compounds
4-1	BATCH	Field required if available or appropriate for result

"REQUIRED":

"YES" = Required data if applicable

"NO" = Optional information unless otherwise directed by ARCADIS Data Manager or preferred for insertion by lab except where lab is specifically directed to leave the field Null.

Parent Sample Definition

Parent Samples are base samples for duplicates or spikes. i.e. original field samples used for matrix spikes or field sample used for Lab Duplicate/Replicate. A Matrix Spike is not the Parent Sample of the Matrix Spike Duplicate.

POPULATING SPIKE FIELDS

SURROGATES: surrogate recoveries are to be populated in qc_spike_added, qc_spike_measure, and qc_spike_recovery fields. Surrogates are analyte type = SUR. Control limits for surrogate recoveries must also be populated.

INTERNAL STANDARDS: internal standard values are to be populated in qc_spike_added, qc_spike_measure, and qc_spike_recovery fields. Internal Standards are analyte type = IS.

LCS, BS, and MS COMPOUNDS: recoveries are to be populated in qc_spike_added, qc_spike_measured, and qc_spike_recovery fields. Compounds spiked to evaluate method accuracy are analyte type = SC. Control limits for spike recoveries must also be populated.

LCSD, BD, AND MSD COMPOUNDS: recoveries are to be populated in qc_dup_spike_added, qc_dup_spike_measured, and qc_dup_spike_recovery fields. The Compounds spiked to evaluate method accuracy are analyte type = SC. Control limits for spike recoveries must also be populated. Additionally, the qc_rpd and qc_rpd_cl fields must be populated for these samples.

LAB REPLICATE SAMPLE DATA: values for lab duplicates/replicates are to be populated in qc_dup_spike_measured field. The qc_rpd and qc_rpd_cl fields must be populated for these samples.

III. ADDITIONAL REQUIREMENTS

SAMPLE TABLE				
Num	**Attribute Name**	**Column Data Type**	**Required**	**Attribute Definition**
1	sys_sample_code	Text(40)	Yes (0)	Unique sample identifier (COC Sample ID). Each sample must have a unique value, including spikes and duplicates. Unique sample identifiers **throughout** the database are an **ABSOLUTE** restriction enforced by EQuIS Chemistry. This unique identifier also carries through to each subsequent sampling event where the samples IDs must be unique for EVERY event of the project (continuing years). Laboratory QC samples must also have unique identifiers between sampling event and from 1 year to the next and between laboratories in the event subcontractors are used. For Matrix Spike, Matrix Spike Duplicate, and Laboratory Duplicates of Field Samples, add the suffix **MS, MSD, and LR**, respectively to create unique identifiers for these types of Lab QC samples.
2	sample_name	Text(30)	No	Additional sample identification information as necessary. Is not required to be unique (i.e., duplicates are OK).

SAMPLE TABLE				
Num	**Attribute Name**	**Column Data Type**	**Required**	**Attribute Definition**
3	sample_matrix_code	Text(10)	Yes (0)	Code, which distinguishes between different types of sample matrix. **Examples**: Soil samples =“SO” , groundwater samples = “WG”. Field Blanks, Trip Blanks, and Rinsate Blanks = “WQ”. Water Method Blanks and liquid matrix spikes = “WQ” Soil Method Blanks and soil/sludge/sediment matrix spikes = “SQ’ This field refers to the sample matrix not the matrix after preparation or extraction. See rt_matrix for the list of valid values.
4	sample_type_code	Text(10)	Yes (0)	Code that distinguishes between different types of samples. **For example**, normal field samples = “N” and laboratory method blank =“LB”. Field QC sample types are Field Duplicates = “FD”, Field Blanks = “FB”, Trip Blanks = “TB”. Lab QC sample types are LCS or Blank Spikes = “BS”, LCSD or BS Duplicates = “BD” and Matrix Spikes = “MS” and Matrix Spike Duplicates = “SD”. See rt_sample_type in Reference Values list of valid values.
5	sample_source	Text(10)	Yes (0)	Must be either "Field" for field samples **or** "Lab" for laboratory QC samples. No other values are allowed. Matrix spikes and lab duplicate/replicate are "Lab" samples, even though the parent is a "Field" and the base sample came from the field. The spiking or splitting for duplication is done in the lab. Field duplicates as submitted to the lab by field sampling teams are “Field”
6	parent_sample_code	Text(40)	Yes (1-2)	The value in the "sys_sample_code" that identifies the sample that was the source of this sample. *For example*, the Matrix Spike and the Matrix Spike Duplicate or Lab Replicates parent_sample_code is the sys_sample_code for the originating field sample that is spiked to generate the MS/MSD or split by the lab for use as the laboratory duplicate. This field is only required in the EDD for laboratory "clone" samples (e.g., matrix spikes and duplicates). Field duplicates are submitted blind to the laboratory, so this field cannot be completed by the laboratory. This field must be blank for samples that have no parent (e.g., normal field samples, method blanks, etc.).
7	sample_delivery_group	Text(10)	Yes (0)	Sample delivery group or laboratory Project/Log Number. All deliverables must reference the SDG or Lab Log-in Number. **This field MUST BE POPULATED**
8	sample_date	Date	Yes (1-1)	Date of sample collection in **MM/DD/YY** format including trip blanks. Must be blank for laboratory samples.
9	sample_time	Time	Yes (1-1)	Time of sample collection in 24-hour (military) **HH:MM** format. 8:45 AM = 08:45 and 3:30 PM = 15:30. Must be blank for laboratory samples.

SAMPLE TABLE				
Num	**Attribute Name**	**Column Data Type**	**Required**	**Attribute Definition**
10	sys_loc_code	Text(20)	No	Sample collection location. To be populated by ARCADIS unless otherwise directed at project initiation.
11	start_depth	Double	No	Beginning depth (top) of soil sample. To be populated by ARCADIS unless otherwise directed at project initiation.
12	end_depth	Double	No	Ending depth (bottom) of soil sample. To be populated by ARCADIS unless otherwise directed at project initiation.
13	depth_unit	Text(15)	No	Unit of measurement for the sample begin and end depths. IRPIMS-style unit of measurement codes (see table X03) are recognized by Chem; other codes may be allowed by the Chem project manager. To be populated by ARCADIS unless otherwise directed at project initiation.
14	chain_of_custody	Text(15)	Yes (1-1)	Chain of custody identifier or number. A single sample may be assigned to only one chain of custody. The COC identifier will be provided by the field sampling team based on conventions established for a specific project.
15	sent_to_lab_date	Date	No	Date sample was sent to lab (in MM/DD/YY format for EDD).
16	sample_receipt_date	Date	Yes (1-1)	Date that sample was received at laboratory in **MM/DD/YY** format. Must be blank for laboratory samples.
17	sampler	Text(30)	No	Name or initials of sampler.
18	sampling_company_ code	Text(10)	Yes (1-1)	Name or initials of sampling company (no controlled vocabulary). "ARCADIS" should be entered into this field unless otherwise directed at project initiation.
19	sampling_reason	Text(30)	No	Optional reason for sampling. No controlled vocabulary is enforced.
20	sampling_technique	Text(40)	No (1-1)	To be populated by ARCADIS unless otherwise directed at project initiation. Sampling technique. **For example**, low flow, bailing, MIP, etc… Must be blank for laboratory samples.
21	task_code	Text(10)	No	Code used to identify the task under which the field sample was retrieved.
22	collection_quarter	Text(5)	No	Quarter of the year sample was collected (e.g., "1Q96")
23	composite_yn	Text(1)	No	Boolean field used to indicate whether a sample is a composite sample.
24	composite_desc	Text(255)	No	Description of composite sample (if composite_yn is YES).

SAMPLE TABLE				
Num	**Attribute Name**	**Column Data Type**	**Required**	**Attribute Definition**
25	sample_class	Text(10)	No	Navy sample class code.
26	custom_field_1	Text(255)	No	Custom sample field
27	custom_field_2	Text(255)	No	Custom sample field
28	custom_field_3	Text(255)	No	Custom sample field
29	comment	Text(255)	Yes (0)	Field required to contain the full sample ID code.
30	sample_receipt_time	Text(5)	Yes (1-1)	Time of sample receipt by laboratory in 24-hour (military) **HH:MM** format. 8:45 AM = 08:45 and 3:30 PM = 15:30

TEST TABLE				
Num	**Attribute Name**	**Column Data Type**	**Required**	**Attribute Definition**
1	sys_sample_code (PK)	Text (40)	Yes (0)	SAME AS #1 IN SAMPLE TABLE. This value is used in enforcing referential integrity between tables. Must match sys_sample_code in Sample Table.
2	lab_anl_method_name (PK)	Text (35)	Yes (0)	Laboratory analytic method name or description. See rt_analytic_method in reference value tables for list of valid values.
3	analysis_date (PK)	Date/ Time	Yes (0)	Date of sample analysis in MM/DD/YY format. Refers to initiation of the analysis not prep method date.
4	analysis_time (PK)	Text (5)	Yes (0)	Time of sample analysis in 24-hour (military) HH:MM format. Note that this field, combined with the "analysis_date" field is used to distinguish between reextractions, reanalyses, and dilutions. Please ensure that retests have "analysis_date" and/or analysis_time" different from the original test event (and complete test_type field as appropriate).
5	total_or_dissolved (PK)	Text (1)	Yes (0)	"T" for total metal organic carbon concentration, "D" for dissolved or filtered metal or organic carbon concentration ONLY. USE "N" for organic (or other) constituents for which neither "total" nor "dissolved" is applicable including TDS.
6	column_number (PK)	Text (2)	Yes (2-1)	Applicable for GC or HPLC methods. "1C" for first column analyses, "2C" for second column analyses, or "NA" for analyses where not applicable. If any "2C" tests are listed, then there must be corresponding "1C" tests present also. Laboratories must indicate which of the two columns is to be considered "primary" by entering “Y” in the "reportable_result" field of the result table for the result presented in hard copy reports. It is NOT acceptable to identify both “1C” and “2C” reportable_result as “Y:; one must be “N” if” “1C” and “2C” are provided in the EDD.

TEST TABLE				
Num	**Attribute Name**	**Column Data Type**	**Required**	**Attribute Definition**
7	test_type (PK)	Text (10)	Yes (0)	Type of test. Valid values include "initial", "reextract", and "reanalysis", "dilution" are acceptable. See rt_test_type for al valid values.
8	lab_matrix_code	Text (10)	Yes (0)	Code that distinguishes between different types of matrix analyzed. Soil = "SO"; groundwater = "GW" and TCLP = TCLP as a lab matrix. See rt_matrix for valid values
9	analysis_location	Text (2)	Yes (0)	"LB" for fixed-based laboratory analysis, "FI" for field instrument, "FL" for mobile field laboratory analysis, or.
10	basis	Text (10)	Yes (0)	"Wet" for wet-weight basis; or "Dry" for dry-weight basis. For tests for which this distinction is not applicable use Wet
11	container_id	Text (30)	No	Sample container identifier.
12	dilution_factor	Single	Yes (0)	Test or analytical run dilution factor. **Must** be "1'" if no dilution.
13	Prep_method	Text (35)	Yes (2-1)	Laboratory sample preparation method name. See rt_std_prep_method for valid values.
14	prep_date	Date/ Time	Yes (2-1)	Date of sample preparation in MM/DD/YY format.
15	prep_time	Text (5)	Yes (2-1)	Time of sample preparation in 24-hour (military) HH:MM format
16	leachate_method	Text (15)	Yes (2-1)	Method name, e.g., SW1311 or SW1312. See rt_analytic_method for valid values.
17	leachate_date	Date/ Time	Yes (2-1)	Date of leachate preparation in MM/DD/YY format.
18	leachate_time	Text (5)	Yes (2-1)	Time of leachate preparation in 24-hour (military) HH:MM format.
19	lab_name_code	Text (10)	Yes (0)	Unique identifier of the laboratory reporting results. See rt_subcontractor for valid values.
20	qc_level	Text (10)	NO	Not populated by Lab.
21	lab_sample_ id	Text (20)	Yes (0)	Laboratory sample identifier. A field sample may have more than one laboratory lab_sample_id; however it is limited to only ONE lab_sample_id per method).
22	percent_moisture	Text (5)	Yes (2-1)	Percent moisture of the sample portion used in the specific lab_anl_methd_name test; this value may vary from test to test for any sample. The value must be NUMERIC as "NN.MM", e.g., 70.1% could be reported as "70.1" but not as 70.1%". The database assumes that the number is a "%" and units of measure are not necessary. **NOTE: This field MUST be populated for all soil, sludge, and sediment samples whether or not the value is reported in the hard copy. Use "0" for lab soil QC samples.**
23	subsample_amount	Text (14)	Yes 0)	Amount of sample used for the test. THIS FIELD MUST BE POPULATED
24	subsample_amount_unit	Text (15)	Yes (0)	Unit of measurement for subsample amount. See rt_unit for valid values.

TEST TABLE				
Num	**Attribute Name**	**Column Data Type**	**Required**	**Attribute Definition**
25	analyst_name	Text (30)	Yes (0)	Name or initials of laboratory analyst.
26	instrument_lab	Text (50)	Yes (0)	Instrument identifier.
27	comment	Text (255)	NO	Comments about the test as necessary (Optional).
28	preservative	Text (50)	Yes (2-1)	Indicate preservative or leave blank, if none. **THIS FIELD MUST BE POPULATED IF A PRESERVATIVE WAS IN THE SAMPLE AS RECEIVED FROM THE FIELD OR IF THE SAMPLE WAS PRESERVED BY THE LABORATORY BEFORE PREPARATION AND ANALYSIS.**
29	final_volume	Text (15)	Yes (2-1)	Final amount of extract or digestate.
30	final_volume_unit	Text (15)	Yes (2-1)	Unit of measure for final_volume. See rt_unit for valid values.

RESULT TABLE				
Num	**Attribute Name**	**Column Data Type**	**Required**	**Attribute Definition**
1	sys_sample_code (PK)	Text (40)	Yes (0)	SAME AS #1 IN SAMPLE & TEST TABLES. This value is used in enforcing referential integrity between tables.
2	lab_anl_method_name (PK)	Text (35)	Yes (0)	Laboratory analytic method name. Must be same as lab_anl_method_name in Test File. See rt _analytic_method for valid values.
3	analysis_date (PK)	Date/Time	Yes (0)	Must be the SAME AS #3 IN THE TEST TABLE. This value is used in enforcing referential integrity between tables. Date of sample analysis in MM/DD/YY format.
4	analysis_time (PK)	Text (5)	Yes (0)	Must be the SAME AS #4 IN THE TEST TABLE. This value is used in enforcing referential integrity between tables.
5	total_or_dissolved_ (PK)	Text (1)	Yes (0)	Must be the SAME AS #5 IN THE TEST FILE.
6	column_number (PK)	Text (2)	Yes (3-2)	Must be the SAME AS #6 IN THE TEST FILE
7	test_type (PK)	Text (10)	Yes (0)	Must be the SAME AS #7 IN THE TEST FILE
8	cas_rn (PK)	Text (15)	Yes (0)	Chemical Abstracts Number for the parameter if available. This must be the true CAS # and "not made up". Where CAS #s are not available, i.e. wet chem. Parameters, identifiers will be provided by ARCADIS project requirements. See notes at end of section for TIC management. See rt_analyte for valid values. The lab is not authorized to add internally developed "CAS #s" for general chemistry parameters, surrogates, internal standards, TICs. CAS#s used for TICs must be available through an outside source such as "Chemfinder".
9	chemical_name	Text (60)	Yes (0)	Chemical name associated with CAS # in #8. The cas_rn field is the only chemical identifier information actually imported in EQuIS Chemistry.

RESULT TABLE				
Num	**Attribute Name**	**Column Data Type**	**Required**	**Attribute Definition**
10	result_value	Text (20)	Yes (3-1)	Analytical result reported for **"TRG" or "TIC"** result_type **ONLY**. Appropriate and consistent number of significant digits must be entered. **MUST BE BLANK FOR NON-DETECTS.** "SUR", "IS", and "SC" results do **NOT** populate this field (populate the QC fields).
11	result_error_delta	Text (20)	Yes (3-2) [Radiochem)	Error range applicable to the result value for radiochemistry results.
12	result_type_code	Text (10)	Yes (0)	Must be either "TRG" for a target or regular results, "TIC" for tentatively identified compounds, "SUR" for surrogates, "IS" for internal standards, or "SC" for spiked compounds.[**LCS, LCSD, MS, MSD, BS, BSD]**
13	reportable_result	Text (10)	Yes (0)	Must be either "**Yes**" for results, which are considered to be reportable, **or** "**No**" for other results. Used to distinguish between multiple results where a sample is retested after dilution or to indicate which of the first or second column result should be considered primary. For re-analyses and dilutions all results must be entered into the database if hard copy data is provided **BUT ONLY ONE RESULT FOR EACH COMPOUND/ANALYTE MAY BE FLAGGED AS REPORTABLE**.
14	detect_flag	Text (2)	Yes (0)	Either "Y" for detected analytes or "N" for non-detects**. MUST be "N" for NON-DETECTS**.
15	lab_qualifiers	Text (7)	Yes (3-2)	Qualifier flags assigned by the laboratory. See rt_qualifier for valid qualifiers that may be used.
16	Organic_ yn	Yes/No	Yes (0)	Must be either "Y" for organic constituents or "N" for inorganic constituents.
17	method_detection_ limit	Text (20)	Yes (0)	Laboratory determined MDL per 40 CFR Part 136, adjusted for dilutions and percent moisture (if it applies).
18	reporting_detection_ limit	Text (20)	Yes (0)	Detection limit that reflects sample analysis conditions including analysis volumes and dilution factors. This should be the laboratory PQL or standard reporting limits
19	quantitation_limit	Text (20)	No	NOT Currently used unless specifically defined for the project.
20	Result_unit	Text (15)	Yes (0)	Units of measure relates to **ALL** results including result_value, qc_original_concentration, qc_spike added, qc_spike_measured, qc_dup_orginal_conc, qc_dup_spike_added, qc_dup_spike_measured. See rt_unit for valid values.
21	detection_limit_unit	Text (15)	Yes (0)	Units of measure for detection limit(s). See rt_unit for valid values.
22	tic_retention_time	Text (8)	Yes (3-2)	Retention time in minutes for tentatively identified compounds (TICs). Populated only for TIC result_type
23	result_comment	Text (255)	NO	MUST BE LEFT BLANK BY THE LAB

RESULT TABLE				
Num	**Attribute Name**	**Column Data Type**	**Required**	**Attribute Definition**
24	qc_original_conc	Text (14)	Yes (3-3)	The concentration of the analyte in the original (unspiked) sample. Populated for matrix spike samples. Not populated where original concentration is assumed to be zero, i.e. LCS or BS samples.
25	qc_spike_added	Text (14)	Yes (3-4)	The concentration of the analyte added to the original sample. Populated for **ALL** Surrogates, and LCS, BS, and MS samples
26	qc_spike_measured	Text (14)	Yes (3-4)	The measured concentration of the analyte. Use zero for spiked compounds that were not detected in the sample. **MUST BE NUMBERIC** even if diluted out or not recovered (use “0” if diluted, matrix interference, elevated concentrations of target compounds, etc.) Populated for **ALL** Surrogates, and LCS, BS, and MS samples
27	qc_spike_recovery	Text (14)	Yes (3-4)	The percent recovery for “SUR” and “SC” results. **MUST BE NUMERIC** even if diluted out or not recovered (use “0” if diluted, matrix interference, elevated concentrations of target compounds, etc.) Report as percentage (e.g., report "120%" as "120"); DO NOT include “%” sign in field. Populated for **ALL** Surrogates, and LCS, BS, and MS samples
28	qc_dup_original conc	Text (14)	Yes (3-5)	The concentration of the analyte in the original (unspiked) sample. Populated for matrix spike duplicate samples. Not populated where original concentration is assumed to be zero, i.e. LCSD or BSD samples.
29	qc_dup_spike_added	Text (14)	Yes (3-5)	The concentration of the analyte added to the original sample. Populated for **ALL** LCSD, BSD, and MSD samples.
30	qc_dup_spike_measured	Text (14)	Yes (3-5)	The measured concentration of the analyte in the duplicate. Populated for **ALL** LCSD, BSD, and MSD samples. MUST be NUMERIC. Use zero for spiked compounds that were not recovered due to dilution, matrix interference, elevated concentrations of target compounds, etc..
31	qc_dup_spike_recovery	Text (14)	Yes (3-5)	The duplicate percent recovery. Populated for **ALL** LCSD, BSD, and MSD samples. **MUST be NUMERIC.** Use zero for spiked compounds that were not recovered due to dilution, matrix interference, elevated concentrations of target compounds, etc Report as percentage (e.g., report "120%" as "120").
32	qc_rpd	Text (8)	Yes (3-6)	The relative percent difference between MS and MSD, LCS and LCSD, BS and BSD, & primary field sample result and Lab Replicate. Populated for **ALL** LCSD, BSD, MSD, and LR samples. **MUST be NUMERIC**. Use zero for RPDs that were not calculated due to elevated concentrations of target compounds, dilution, matrix interference, etc Report as percentage (e.g., report "120%" as 120").
33	qc_spike_lcl	Text (8)	Yes (3-7)	Lower control limit for spike recovery. Required for spikes, spike duplicates, surrogate compounds, LCS and any spiked sample. Report as

RESULT TABLE				
Num	**Attribute Name**	**Column Data Type**	**Required**	**Attribute Definition**
				percentage (e.g., report "120%" as "120").
34	qc_spike_ucl	Text (8)	Yes (3-7)	Upper control limit for spike recovery. Required for spikes, spike duplicates, surrogate compounds, LCS and any spiked sample. Report as percentage (e.g., report "120%" as "120").
35	qc_rpd_cl	Text (8)	Yes (3-6)	Relative percent difference control limit. Required for any duplicated sample. Report as percentage (e.g., report "120%" as "120").
36	qc_spike_status	Text (10)	Yes (3-4)	Used to indicate whether the spike recovery was within control limits. Use the "+" character to indicate failure, otherwise leave blank.
37	qc_dup_spike_status	Text (10)	Yes (3-5)	Used to indicate whether the duplicate spike recovery was within control limits. Use the "+" character to indicate failure, otherwise leave blank.
38	qc_rpd_status	Text (10)	Yes (3-6)	Used to indicate whether the relative percent difference was within control limits. Use the "+" character to indicate failure, otherwise leave blank. Required for any duplicated sample.

BATCH TABLE				
Num	**Attribute Name**	**Column Datatype**	**Required**	**Attribute Definition**
1	sys_sample_code (PK)	Text (40)	Yes (0)	SAME AS #1 IN SAMPLE , TEST TABLE. This value is used in enforcing referential integrity between tables.
2	lab_anl_method_name (PK)	Text (35)	Yes (0)	SAME AS #2 IN TEST TABLE. See rt _analytic_method for valid values.
3	analysis_date (PK)	Date	Yes (0)	SAME AS #3 IN TEST TABLE. This value is used in enforcing referential integrity between tables. Date of sample analysis in MM/DD/YY format. May refer to either beginning or end of the analysis as required by EQuIS Chemistry project manager.
4	analysis_time (PK)	Text (5)	Yes (0)	SAME AS #4 IN TEST, AND RESULT TABLES. This value is used in enforcing referential integrity between tables.
5	total_or_dissolved (PK)	Text (1)	Yes (0)	SAME AS #5 IN TEST TABLE. This value is used in enforcing referential integrity between tables.
6	column_number (PK)	Text (2)	Yes (4-1)	SAME AS #6 IN TEST TABLE. This value is used in enforcing referential integrity between tables.
7	test_type (PK)	Text (10)	Yes (0)	SAME AS #7 IN TEST TABLE. This value is used in enforcing referential integrity between tables.
8	test_batch_type (PK)	Text (10)	Yes (0)	Lab batch type. Valid values include "Prep", "Analysis", and "Leach". Additional valid values may optionally be provided by the EQuIS Chemistry project manager. This is a required field for all batches.
9	test_batch_id	Text (20)	Yes (0)	Unique identifier for all and each lab batches. Must be unique within EQuIS Chemistry database. For example, the same identifier cannot be used for a prep batch and an analysis batch and the values must be different from one sampling event to another. THIS IDENTIFIER CANNOT BE USED FROM ONE YEAR TO THE NEXT.

ADDITIONAL INFORMATION FOR PREPARING THE 4-FILE EDD

SAMPLE FILE AND SYS_SAMPLE_CODE

1. The sys_sample_code is the unique sample ID as supplied on the Chain of Custody form with the same spacing as identified on the COC or on a supplemental Sample ID list submitted to the laboratory with the Laboratory Task Order or prior to submission of samples.

2. In order to uniquely identify MS/MSD, laboratory duplicates, TCLP, and SPLP samples, the laboratory shall add a suffix to the original sample ID listed on the chain of custody:

   Matrix Spike Sample = xxxxx MS
   Matrix Spike Duplicate Sample = xxxxx MSD
   Lab Duplicate/Replicate = xxxxx LR
   TCLP Extract Sample = xxxxx TCLP
   SPLP Extract Sample = xxxxx SPLP

   These are the only characters that are allowed to be amended to ANY sample ID as listed on the COC or the sample ID list referred to above.
   The parent_sample_code shall be entered into the parent_sample_code field of the Sample File.

3. If the sample_name field is provided it must contain the full sample ID from the chain of custody.

4. Sample_Type_Code must be appropriately applied as follows:
   "N" = normal field samples
   "FD" = field duplicates samples submitted blind to the laboratory
   "TB" = trip blanks
   "FB" = field blanks
   "EB" = rinsate or equipment blanks
   "BS" = laboratory control samples or blank spikes
   "BD" = laboratory control sample duplicates or blank spike duplicates
   "MS" = matrix spikes
   "SD" = matrix spike duplicates
   "LR" = laboratory duplicates or laboratory replicates

5. The following "**matrix_type**" codes must be used ("**SQ**" = soil QC sample and "**WQ"** = water QC sample):
   Method Blank = "SQ" or "WQ"
   MS/MSDs = "SQ" or "WQ"
   LCS/LCSDs = "SQ" or "WQ"
   BS/BSDs = "SQ" or "WQ"

6. SDG Numbers or laboratory Log Numbers (per ARCADIS PM direction) **MUST** be populated in "**sample_delivery_group**" field of the **Sample File.**

QUALITY CONTROL SAMPLES AND DATA

7. The source of Lab Duplicates, Lab Replicates, Matrix Spikes, and Matrix Spike Duplicates is the Lab not the Field even if the MS/MSD are identified on the COC by the field sampling team. The samples are spiked in the laboratory not in the field.

8. Laboratory QC data, which span more than one SDG may be submitted with each appropriate SDG.

9. Laboratory LCS and LCSD should be reported as two separate samples.

10. **Matrix Spike and Matrix Spike Duplicate recoveries must be reported as "0" if the value is not calculated due to concentrations of the spiked analyte in the sample at concentrations above the 4X factor.**

11. **All laboratory method performance site-specific and batch Quality Control sample results (i.e. Method Blanks, LCS/LCSDs, Blank Spikes, Leachate Blanks as method appropriate) must be included in the EDD.** For most projects, this does **NOT** include **non-site-specific** matrix spikes and laboratory duplicates/replicates.

12. Laboratory batch sample duplicate/replicate and MS/MSD results from **non-project specific** samples (i.e. batch QC samples) shall **NOT** be included in the EDD.

13. Surrogates populate the qc_spike fields not qc_dup_spike fields or the result_value field even if the surrogates are reported for MSD, BSD, or LCSD samples.

14. QC_Spike_Added values for Spike, IS and Surrogate compounds are REQUIRED.

15. QC_Spike_Measured values for Spike, IS and Surrogate compounds are REQUIRED.

16. RPDs for LCSDs, BSDs, MSDs, and Laboratory Duplicates must be populated in the "**qc_rpd"** field. A value of "0" or "100" must be reported, as appropriate, if the RPD is not calculated due to excessive concentrations or interference present in the sample. The "**qc_rpd**" must be a numeric entry.

17. The RPD control limit must be listed in the "**rpd_cl"** field for all parameters where an RPD is reported. This includes lab duplicate/replicate samples.

SAMPLE FILE

18. The following "**matrix_type**" codes must be used for QC samples ("**SQ**" = soil QC sample and "**WQ"** = water QC sample):

    Method Blank = "SQ" of "WQ"
    MS/MSDs = "SQ" or "WQ"
    LCS/LCSDs = "SQ" or "WQ"
    BS/BSDs = "SQ" or "WQ"

19. SDG or Laboratory Project numbers must be populated in "sample_delivery_group" field.

TEST FILE

20. Percent moisture must be reported in the "**percent_moisture**" field in the **Test File** for all solid samples (i.e., soil, sediment, and sludge).

21. Subsample weights and final volumes must be listed for all parameters as appropriate.

RESULTS FILE

22. Result_value is only populated with data for "TRG" and "TIC" detections. All other data is entered in the "qc_" fields. The field must be "NULL" for non-detects and other analyte_types. The Reporting Limit must not be entered in this field.

23. Non-detected data shall have a lab_qualifier of "U" in addition to other qualifiers deemed applicable. The Detect_Flag shall be "N" and the Result_value field shall be blank.

24. The Reporting Limit must be provided for all parameters. The RL MUST be adjusted for dilutions made during analysis.

25. Surrogate recoveries MUST BE REPORTED in the qc_spike_measured and qc_spike_recovery fields, even if the surrogate had been diluted out. List “0” as the measured and recovered amount. Control Limits must also be entered for surrogates. Surrogates are “SUR” analyte_type not “TRG”.

26. Surrogate, LCS, LCSD, BS, BSD, MS, and MSD detected concentrations, and percent recoveries must be populated with a numeric value. A value of “0” **must** be entered if the Spiked Compound is diluted out or not recovered. An “+” is unacceptable as this is a numeric field.

27. “**QC_original_concentration**” must be populated for matrix spikes and matrix spike duplicates

28. Valid entries for the reportable_result field are "Yes" or "No” only.

29. ONLY report compounds of interest for any method blank, sample, and sample duplicate, trip blank.

30. Laboratory Qualifier designation must be consistent. For an estimated concentration with blank contamination “BJ” must be used. Note that “JB”, “B J” or “J B” cannot be used.

31. Explanation of Duplicate Qualifiers:

B	Analyte found in associated blank	Organic Analysis
B	<CRDL but >= Instrument Detection Limit	Inorganic Analysis
N	Presumptive evidence of a compound	Organic Analysis
N	Sample recovery not within control limits	Inorganic Analysis

It is preferred by ARCADIS that the laboratory not qualifiers with multiple explanations. **Any qualifiers utilized in the hard copy report or the electronic report must be defined in the hard copy report. There is no exception to this requirement for explanation of qualifiers applied to electronic data.**

32. Nomenclature for tentatively identified compounds (TIC):

Use the CAS # if it is available and **REAL** **(outside verifiable source)** for TICs and enter the chemical name in the chemical_name field.

For UNKNOWN TICs follow the following protocol:

cas_rn for unkown VOA TIC = VTIC 1 through VTIC 10
cas_rn for unkown SVOA TIC = SVTIC 1 through SVTIC 20

Enter “UNKNOWN”, “UNKNOWN Hydrocarbon”, “UNKNOWN Aliphatic”, or other identifier as appropriate or applicable in “chemical_name” field.

TICs will produce errors in the ELDC/EDDP that cannot be corrected by the laboratory. These are the only acceptable errors in the data checker report unless otherwise authorized by ARCADIS.

33. TCLP or SPLP results must be submitted in units of mg/L or appropriate liquid units. **(Make sure that moisture correction is not automatically enforced).**

BATCH FILE

34. The laboratory must use unique Batch File Names for each analytical department/method and for continuing years. Electronic validation utilizes Batch IDs to link field samples with quality control data. Overlapping Batch IDs are not acceptable.

GENERAL ISSUES

35. Incomplete chain-of-custody (C-O-C) forms must be immediately communicated to the project manager. Some of the C-O-C information is used for completion of the Sample_Matrix_Code and Sample_Delivery_Group. These discrepancies must be rectified upon receipt of samples at the laboratory prior to log in.

36. **Duplicate sample IDs are not acceptable within the EQuIS database. It is imperative that samples including field blanks, trip blanks, equipment blanks, field duplicates have unique sample IDs for projects including ongoing sampling events such as quarterly groundwater monitoring.**

SUBCONTRACTED PARAMETERS

37. The EDD must be populated with **ALL** appropriate and applicable fields, including **ALL** QC data for any subcontracted parameters.

PLEASE CONTACT THE ARCADIS PROJECT CHEMIST, DATA MANAGER or PROJECT MANAGER IF THERE ARE ANY QUESTIONS REGARDING PREPARATION OR GENERATION OF THE EDD.

EXAMPLE EDD REPORTS

The following subsections provide examples of how the EQuIS EDD should be populated for QC data.

RESULT FILE FIELDS FOR A NORMAL FIELD SAMPLE, TRG AND TIC RESULTS

The table below shows some of the fields in the Result File for a normal field sample (i.e., Sample_type_code = N, TB, FD, etc.) and "TRG" or "TIC" analyte_type_code. NOTE: all QC fields are blank.

cas_rn	result value	qc original conc	qc spike added	qc spike measured	qc spike recovery	qc dup. original conc	qc dupl. spike added	qc dup. spike measured	qc dup. spike recovery
93-76-5 94-75-7 94-82-6	3.17 1.56 2.31								

RESULT FILE FIELDS FOR A NORMAL FIELD SAMPLE WITH SURROGATES

The following table shows some of the fields in the result file for a normal field sample (i.e., Sample_type_code = N, TB, etc.). Note that QC fields are blank except on surrogate Rows.

cas_rn	result value	result unit	result type code	qc original conc	qc spike added	qc spike measured	qc spike recovery
93-76-5	1.56	mg/L	TRG				
94-75-7	3.17	mg/L	TRG				
PHEN2F		mg/L	SUR		12.5	12.9	103

RESULT FILE FIELDS FOR A MATRIX SPIKE

The following table shows some of the fields in the result file for a matrix spike sample (i.e., Sample_type_code = MS). Note that all "dup" QC fields are blank, and that the result_value field is NULL. Also, the qc_rpd field would be blank for these rows. The parent_sample_code must contain the contents of the sys_sample_code of the original (parent) sample.

cas_rn	result value	qc original conc	qc spike added	qc spike measured	qc spike recovery	qc dup. original conc	qc dupl. Spike added	qc dup. spike measured	qc dup. spike recovery
93-76-5		1.56	4.18	5.36	90.9				
94-75-7		3.17	4.18	7.15	95.2				
94-82-6		2.31	4.22	5.66	79.3				

RESULT FILE FIELDS FOR A MATRIX SPIKE DUPLICATE

The following table shows some of the fields in the result file for a matrix spike/matrix spike duplicate considered as a single sample (i.e., Sample_type_code = MSD). Note that all QC fields are completed, and that the result_value field is not needed. Also, the qc_rpd field would be completed for these rows. The parent_sample_code must contain the contents of the sys_sample_code of the original (parent) sample.

cas_rn	result value	qc original conc	qc spike added	qc spike measured	qc spike recovery	qc dup original conc	qc dup. spike added	qc dup spike measured	qc dup spike recovery
93-76-5						1.56	4.23	5.70	97.8
94-75-7						3.17	4.23	7.62	105
94-82-6						2.31	4.13	5.33	73.1

**RESULT FILE FIELDS FOR A LCS or BS **

The following table shows some of the fields in the result file for an LCS sample (i.e., laboratory control sample, blank spike, Sample_type_code = BS). The qc_rpd field is left blank for these rows.

cas_rn	result value	qc original conc	qc spike added	qc spike measured	qc spike recovery	qc dup original conc	qc dup spike added	qc dup spike measured	qc dup spike recovery
93-76-5		1.5	5.00	5.26	105				
94-75-7		10.2	1.00	1.02	102				
94-82-6		3.4	12.5	12.9	103				

RESULT FILE FIELDS FOR A LCS DUPLICATE OR BS DUPLICATE

The following table shows some of the fields in the result file for a laboratory control sample duplicate (i.e., Sample_type_code = BD). Note that the result_value field is not required. Also, the qc_rpd field must be completed for these rows.

cas_rn	result value	qc original conc	qc spike added	qc spike measured	qc spike recovery	qc dup original conc	qc dup spike added	qc dup spike measured	qc dup spike recovery	qc_rpd
93-76-5							5.00	4.92	98	2.0
94-75-7							1.00	0.95	95	6.6
94-82-6							12.5	11.8	94	12.3

REANALYSES, REEXTRACTIONS, DILUTIONS

The following table shows how to report retests for three different circumstances. The first example, the sample was retested (for 75-25-2) because the initial result required reanalysis due to QC failure. For the second example, the initial sample result (for 95-95-4) required dilution. The third example (for 67-66-3) required both reanalysis and dilution (reanalysis supercedes dilution). The fourth example (87-86-5) shows an initial result that require re-extraction due to QC failure or elevated concentrations that could not be diluted based on the original extraction. The other results are "turned off" by setting the reportable_result field to "No".

test_type	cas_rn	result_value	reportable_result
initial	75-25-2	1.2	No
reanalysis	75-25-2	1.1	Yes
initial	95-95-4	250E	No
dilution	95-95-4	328	Yes
initial	67-66-3	3.4	No
reanalysis	67-66-3	3.3	Yes
initial	87-86-5	980E	No
reextraction	87-86-5	1500	Yes

ANALYSES REQUIRING SECOND COLUMN CONFIRMATION

Analyte identification requiring confirmation by a second analytical technique is required by certain gas chromatography (GC) methods. A common technique used to confirm the identity of an analyte is to analyze the sample using a second GC column that is dissimilar from the GC column used for the first analysis. This confirmation technique is used routinely when analyzing samples for pesticides, herbicides, and certain volatile organic compounds (e.g., BTEX), and the two analyses often are performed simultaneously using an instrument equipped with dual GC columns connected to common injection port.

The method for reporting data from dual column GC analyses is not standard throughout the environmental laboratory industry. ARCADIS recommends that laboratories use the method described in SW-846 Method 8000B, unless project-specific requirements or the method used for analysis dictate otherwise. The following table illustrates the proper format to be used to report first and second column results. The results for the first and third constituents (75-25-2 and 95-95-4) are being reported from column 1, and the result for the second constituent (67-66-3) is being reported from column 2. The other results are "turned off" by setting the reportable_result field to "No".

column_number	cas_rn	result_value	reportable_result
1C	75-25-2	6.2	Yes
1C	67-66-3	3.4	No
1C	95-95-4	5.6	Yes
2C	75-25-2	1.3	No
2C	67-66-3	33.7	Yes
2C	95-95-4	5.4	No

REFERENCE TABLES

A number of fields in each of the EDD files must be entered to correspond exactly with reference values standardized by ARCADIS. These reference values will be updated from time to time. Each laboratory will be supplied a copy of the updated document. It is the laboratory's responsibility to submit EDDs using the most current reference tables as defined by a specific project.

The following table summarizes the EDD fields where standard reference values must be used:

EDD File	EDD Field	Reference Table
Sample	sample_type_code	rt_sample_type
	sample_matrix_code	rt_matrix
Test	lab_anl_method_name	rt_anl_mthd
	lab_matrix_code	rt_matrix
	prep_method	rt_std_prep_mthd
	subsample_amount_unit	rt_unit
	final_volume_unit	rt_unit
Result	lab_anl_method_name	rt_anl_mthd
	cas_rn	rt_analyte
	chemical_name	rt_analyte
	result_type_code	rt_result_type
	lab_qualifier	rt_qualifier
	result_unit	rt_unit
	detection_limit_unit	rt_unit
Batch	lab_anl_method_name	rt_anl_mthd

IV. EDP

The EDP data checker assists the **LABORATORY** in checking EDD files to ensure that they are error-free prior to submission to ARCADIS. All laboratories providing data to ARCADIS **must use** the EDP program to verify that EDDs are without error. The EDP error reports for each file **must be** submitted with each EDD.

The use of the EDDP helps to solve common data population problems including duplicate data, incorrectly populated fields, and incorrect methods, CAS #s, and other acceptable reference values. If an EDD is received by ARCADIS containing errors it will be rejected until the EDD report is acceptable for import into the EQuIS database. Invoice payment will not be made until the EDD is acceptable.

ARCADIS will provide laboratories with the most recent version of the EDP.

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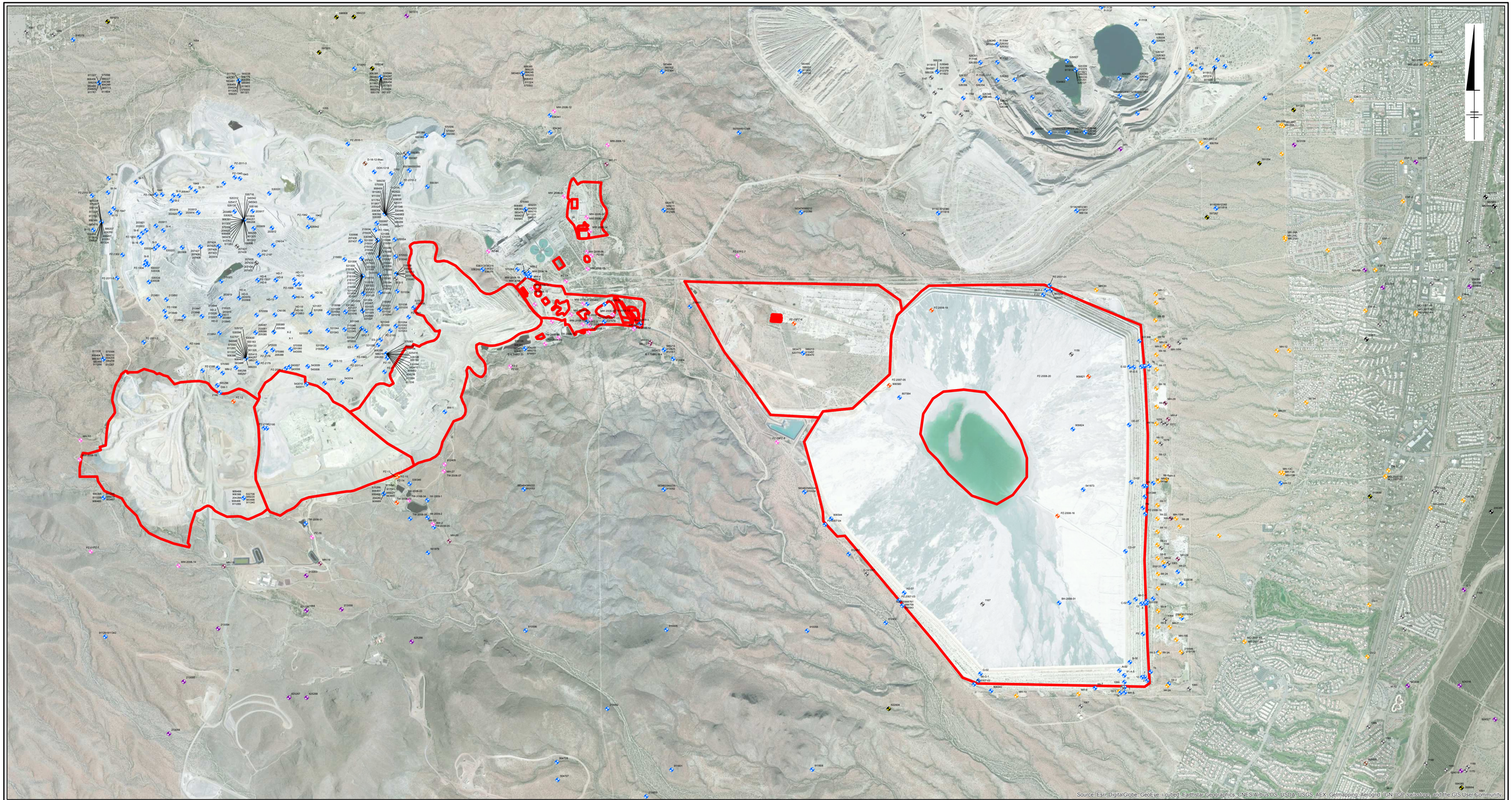
Appendix C

Well Location Map for the Sierrita Mine



Legend

Well Category

- APP
- Abandoned
- Commercial
- MOC
- Mine
- Municipal/Utility
- No-Owner Defined
- Private
- State
- VRP

0 1,800 3,600 5,400 7,200

SCALE IN FEET

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA
VOLUNTARY REMEDIATION PROGRAM
DATA GAPS WORKPLAN

VRP, APP and MOC wells

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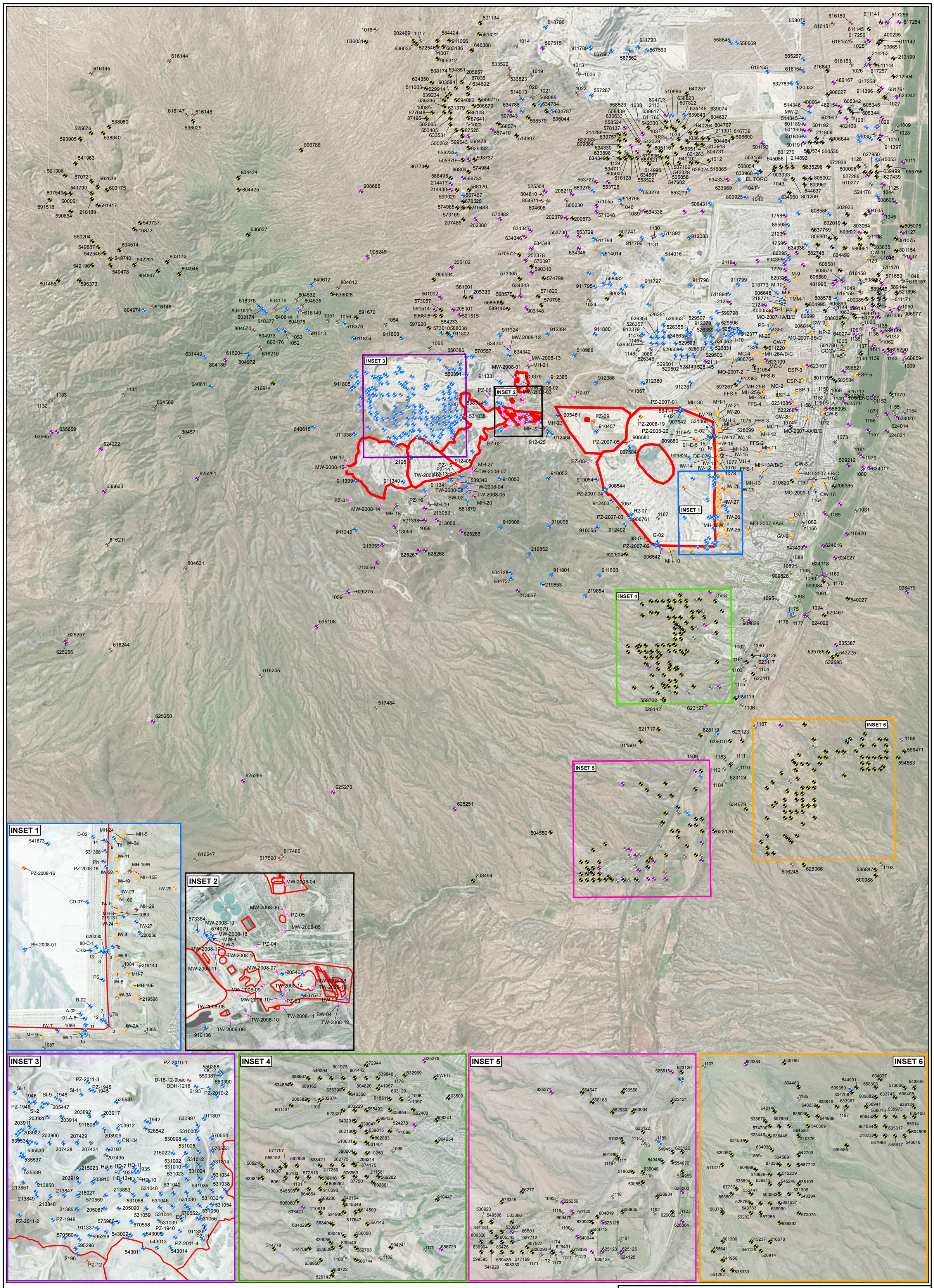
FIGURE
C-1

CITY:(HIGHLANDS RANCH) DIV/GROUP:(ENV/GIS) DB:gmckinney LD: PIC: PM: TM:
PROJECT: PATH:Z:\GISPROJECTS_ENV\Sierrita\GIS\ArcMap_MXD\2014\FigC1_All_Wells_Dsize.mxd

CITY: (DENTECH) DIV/GROUP:(ENV) DB:GMCKINNEY LD: PIC: PM: TM: DATE: 11/10/2014
PROJECT: PATH: Z:\GISPROJECTS_ENV\Sierrita\GIS\ArcMap_MXD\2014\FigC2_All_Wells_Dsize_fullextent.mxd



Legend

AllWells20141110

Well Category

- APP
- Abandoned
- Commercial
- MOC
- Mine
- Municipal/Utility
- No-Owner Defined
- Private
- State
- VRP

Site Features

0 5,000 10,000 15,000 20,000

SCALE IN FEET

FREEPORT-MCMORAN SIERRITA INC.
GREEN VALLEY, ARIZONA
VOLUNTARY REMEDIATION PROGRAM
DATA GAPS WORKPLAN

All Wells in the Site Vicinity

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FIGURE
C-2

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Appendix E

Anticipated Well Construction Diagrams

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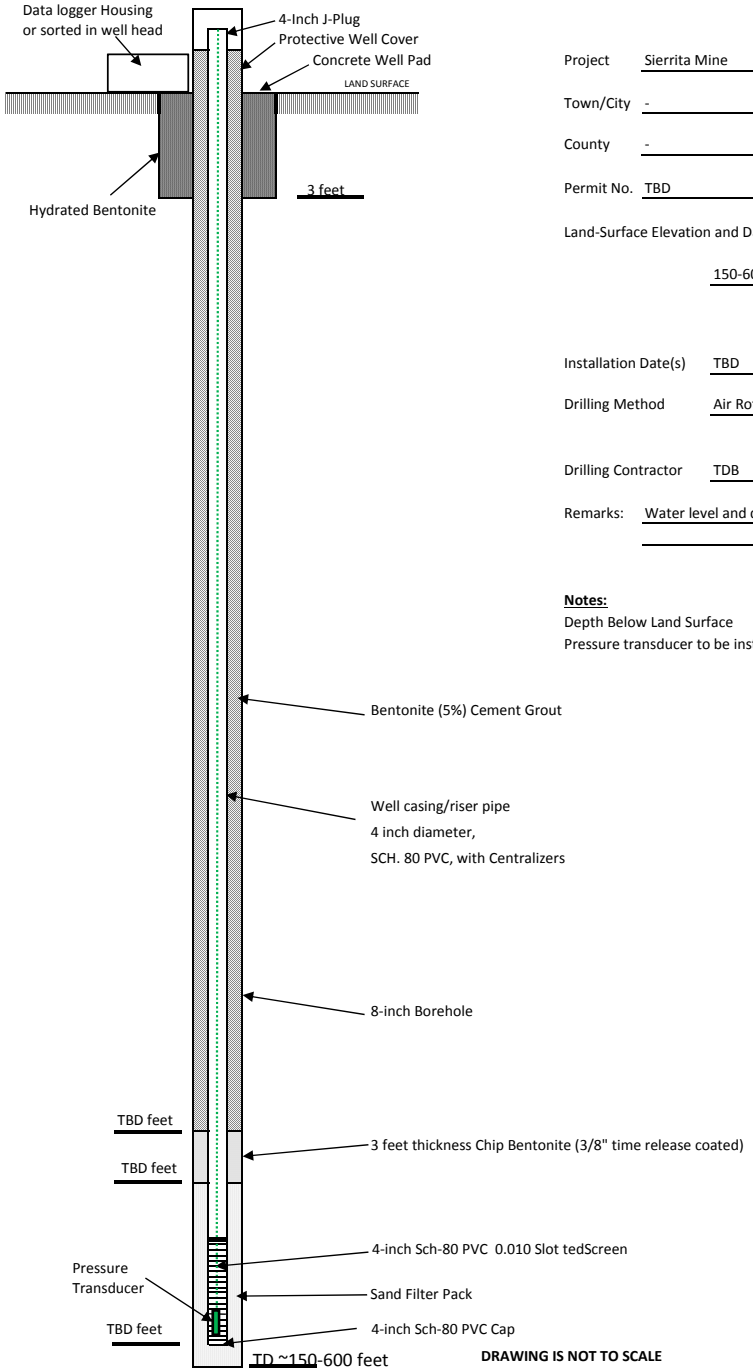
Infrastructure, environment, facilities

Figure E2 - Bedrock Monitoring Well Construction (Depth ~150-600 feet)



Project Sierrita Mine Wells Monitoring

Town/City -

County - State Arizona

Permit No. TBD

Land-Surface Elevation and Datum:

150-600 feet ☐ Surveyed

☒ Estimated

Installation Date(s) TBD

Drilling Method Air Rotary Casing Hammer (ARCH)

Drilling Contractor TDB

Remarks: Water level and quality monitoring wells

Notes:

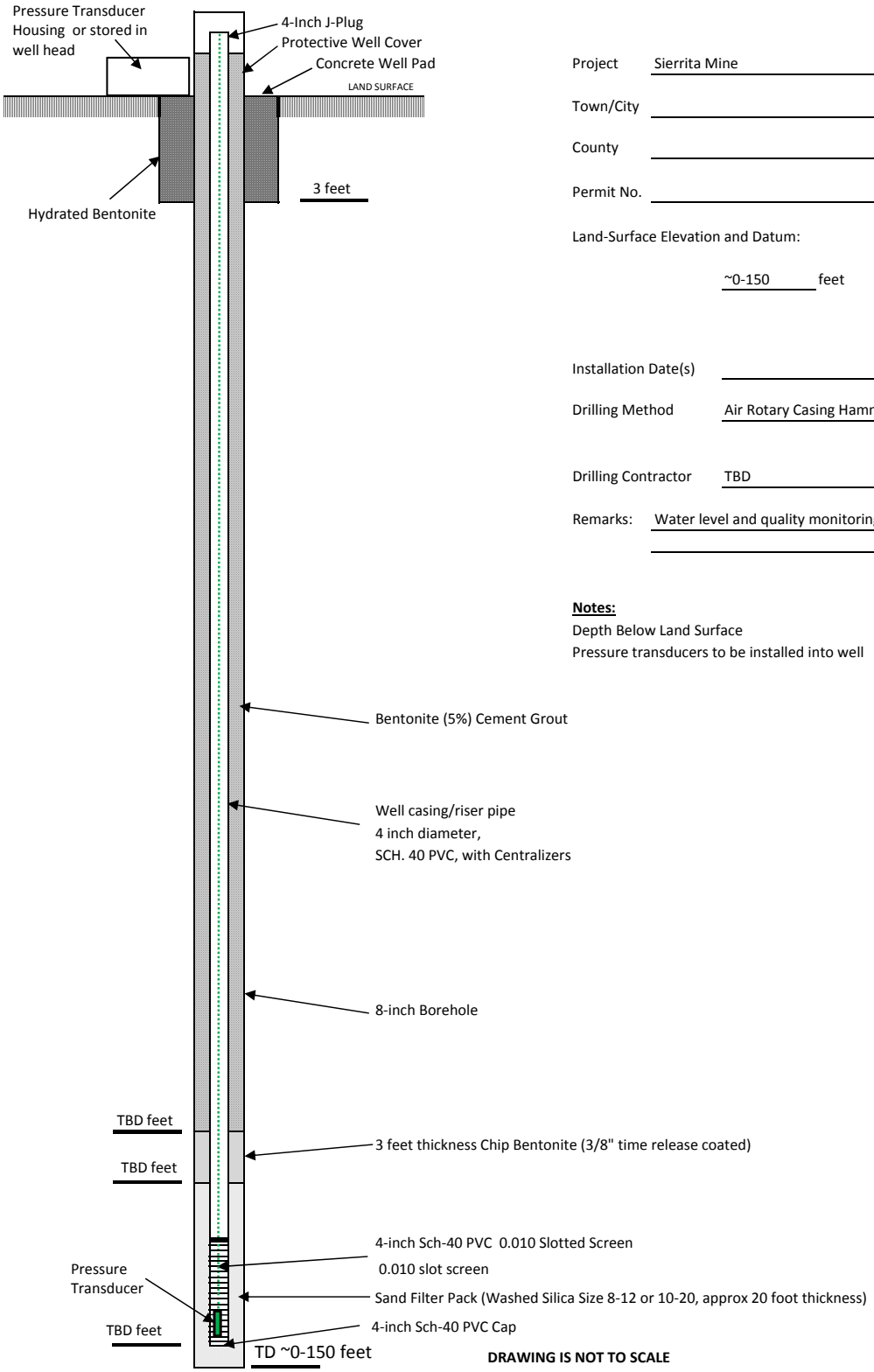
Depth Below Land Surface

Pressure transducer to be installed into one well

DRAWING IS NOT TO SCALE

ARCADIS
Infrastructure, environment, facilities

Figure E1- Alluvial or Bedrock Monitoring Well Construction (Depth ~0-150 feet)



Project Sierrita Mine Wells Monitoring

Town/City

County State Arizona

Permit No.

Land-Surface Elevation and Datum:

~0-150 feet ☐ Surveyed

☒ Estimated

Installation Date(s)

Drilling Method Air Rotary Casing Hammer (ARCH)

Drilling Contractor TBD

Remarks: Water level and quality monitoring wells

Notes:
Depth Below Land Surface
Pressure transducers to be installed into well

DRAWING IS NOT TO SCALE