

Bonita Peak Mining District

2018 High-Flow Seeps, Springs, and Draining Adits Investigation Field Sampling Plan



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Acronyms

BLM	Bureau of Land Management
BPMD	Bonita Peak Mining District
CDM Smith	CDM Federal Programs Corporation
DI	Dissolved ion
DO	Dissolved oxygen
DQA	Data Quality Assessment
DQO	Data Quality Objectives
DRMS	Colorado Department of Mining, Reclamation, and Safety
EPA	United States Environmental Protection Agency
ESAT	Environmental Services Assistance Team
FSP	Field Sampling Plan
GIS	Geographic information system
GPS	Geographic positioning system
ID	Identification
l	liter
LIMS	Laboratory Information System
m	Meters
mL	Milliliter
mL/s	Milliliters per second
MS	Matrix spikes
MSD	Matrix spike duplicates
MSI	Mountain Studies Institute
QA/QC	Quality Assurance/ Quality Control
QAPP	Quality Assurance Project Plan
RI	Remedial Investigation
RPD	Relative Percent Difference
RPM	Remedial Project Manager
s	second
SAP	Sampling and Analysis Plan
SCRIBE	EPA environmental database software
SOP	Standard Operating Procedures
USFS	United States Forest Service
WQP	Water Quality Parameters

1.0 Introduction

This field sampling plan (FSP) is for technical support services to be provided by the Mountain Studies Institute (MSI) for the investigation of seeps and springs within the Bonita Peak Mining District (BPMD) Superfund Site in San Juan County, Colorado, with a specific focus on the vicinity of Bonita Peak and the Sunnyside Mine Pool. The work will be completed by MSI as a sub-contractor to CDM Federal Programs Corporation (CDM Smith) who is under contract to the U.S. Environmental Protection Agency (EPA) (Contract No. EP-W-05-049) to prepare a remedial investigation (RI) at the BPMD site.

MSI has prepared the following FSP that describes the implementation of seeps, springs, and draining adit sampling at the BPMD site during high-flow conditions in 2018. This FSP follows the Quality Assurance Project Plan (QAPP) [CDM Smith 2018]. This FSP presents information specific to a seeps and springs investigation while the QAPP presents details regarding quality assurance, quality control, standard procedures, and a variety of specific requirements. Both documents are needed to complete the investigation.

2.0 Problem Definition and Objectives

A goal of the RI is to determine the nature and extent of mining impacts on water quality within the BPMD site. The investigation described in this FSP will document the water quality and quantity emanating from seeps, springs, and other features (i.e. discharging mine adits) within a portion of the BPMD site. The primary goal of this investigation is to quantify metal loads to surface waters from seeps, springs, and discharging adits within the headwaters of all drainages within the BPMD site. The initial investigation area is generally in the vicinity of the Sunnyside Mine pool and will begin in the area of the Red and Bonita and Gold King mine sites (Map 5), and extend east and north over Bonita Peak towards the Mogul mine (Maps 3 and 4) and the Lake Emma basin at the head waters of Eureka Gulch to the east and north (Map 7). Additional sampling will occur in Prospect Gulch, a tributary to Cement Creek, which contains other BPMD sites under investigation. The investigation described in this FSP is expected to cover the same areal extent as the Spring 2017 seep and spring investigation completed during June and July of 2017 (MSI 2017). Sampling in this area will provide information to help address the main question:

- What is the water quality and discharge rates from seeps, springs, and draining adits in the area around the Sunnyside Mine Pool and across the Cement Creek and Animas River drainages within the BPMD?

The seeps and springs investigation will continue across all three drainages within the investigation area with the spatial extent expected to be the same or similar to the

area investigated in 2016 and 2017. In addition to areas investigated during previous years, opportunistic samples will be collected at additional seeps and springs encountered during the field campaign.

3.0 Schedule for Field Work

Reconnaissance and sampling of seeps and springs during low flow conditions will generally coincide with EPA's high flow sampling events scheduled between June 4 and June 29, 2018. The seeps and springs sampling will take 3-4 weeks to complete and sampling is scheduled to occur on 16-20 individual days within this time window, with an anticipated work schedule of Monday through Thursday each week. The exact sampling dates will be weather dependent and may shift within this time period to accommodate spring snow melt and road access to the alpine basins. Due to variable mountain weather conditions, access to sampling sites will be evaluated each day to meet safety requirements. It is expected that between 5-10 samples will be collected each day depending on travel time and difficulty of access between sites with the goal of approximately 150 samples collected during the sampling event. Spring 2018 high flow sampling is scheduled to be complete by June 29, 2018.

4.0 Data Quality Objectives

The Data Quality Objective (DQO) process specifies project decisions, the data quality required to support those decisions, specific data types needed, data collection requirements, and analytical techniques necessary to generate the specified data quality. The process also ensures that the resources required to generate the data are justified. Some of the collected data will be critical to achieve the established DQOs and project objectives, while others will be collected primarily for informational purposes or to supplement critical data.

4.1 State the Problem

Step 1 of the DQO process is to define or describe the environmental problem to be studied. Data generated will undergo a validation/usability determination prior to use in EPA's decision-making processes.

4.1.1 Describing the Problem

Various agencies and mining companies have collected surface water, spring and seep, an adit discharge samples at the site over the last two decades. These disparate investigations had a range of purposes, methods, scopes, geographical areas, and data quality. EPA is preparing an RI which will include seep, spring, and draining mine data. This investigation will provide data collected in a consistent and defined manner at locations previously identified and/or sampled by earlier investigators.

The 2018 activities will supplement data collection completed in the same areas during 2016 and 2017 and continue a process of sampling and measuring flow at all known seeps, springs and draining adits in the BPMD site and will focus on the area near the Sunnyside Mine pool (investigation area). The data will be used to support risk assessments, an FS, and the eventual remedy selection and design of remedial measures.

4.1.2 Planning Team

The planning team is comprised of individuals who are key to the development of the plan and the performance of the field activities. Those individuals are listed below:

- Rebecca Thomas, EPA, Remedial Project Manager (RPM) – Primary decision maker
- Jamie Miller, EPA, Remedial Project Manager (RPM) – Primary decision maker
- David Berry, EPA, QA Approving Official
- Ian Bowen, EPA, Hydrogeologist
- Thomas Cook, CDM Smith, Project Manager – Primary data user and CDM Smith resource manager
- Neil Smith, CDM Smith - Primary data user and RI coordinator
- Curt Coover, CDM Smith, Geologist
- Rory Cowie, PhD, Program Director, Hydrologist, MSI – Principal investigator for Seeps and Springs investigation
- Nate Rock, Silverton Field Manager, MSI – Field staff lead for Seeps and Springs investigation
- Scott Roberts, Program Director, MSI - QA Coordinator for MSI

Water samples will be submitted to EPA's Environmental Services Assistance Team (ESAT) laboratory. Samples for stable isotope analysis will be sent to the Stable Isotope Laboratory at the University of Arizona. A sub set of samples will be sent to the R.S. Kerr Environmental Research Center (EPA/Groundwater, Watershed, and Ecosystem Restoration Division) located in Ada, Oklahoma. These samples will be analyzed for Rare Earth Elements and Pb isotopes using Standard Operating Procedures NRMRL-GWERD-13-0 and NRMRL-GWERD-16-0.

4.1.3 Conceptual Model of the Potential Hazard

Site contamination is the result of mining, milling, and smelting activities at various locations. Mine wastes contain elevated concentrations of arsenic and heavy metals and are found in piles, on residential properties, in roads, and in and along streams. Contaminants have the potential to leach into soils and groundwater, and may also be carried into local streams through runoff of soils, surface water, or groundwater discharge. This contamination has impacted local fisheries and restricts water being used for its designated use. This contamination also presents a potentially unacceptable risk to human health and environment.

4.1.4 Available Resources, Constraints, and Deadlines

MSI has identified the project team and determined resources, budget, personnel, and schedule based on previous planning calls with EPA and CDM Smith. The field work is expected to be completed in June 2018, weather permitting. Time constraints for collecting data are limited to daylight hours and weather.

4.2 Goals of the Study

The RI activities are intended to contribute to ongoing efforts to characterize site contamination. This FSP is limited to sampling and discharge measurement at seeps, springs, and draining mines in the investigation area, associated field documentation, and analysis of samples.

The goal is:

- Seeps and Adit Discharges. Samples will be collected of discharging seeps and draining adits at locations known to have active discharge at least part of the year. The goal of the sampling is to provide data collected in a consistent and defined manner to supplement existing data. These data will be used to characterize loading sources to surface water emanating from seeps and springs.

4.2.1 Principal Study Questions

The principal study question is:

- What is the spatial distribution, flow rates, and magnitude and of mining related contaminants from discharges of known seeps, springs and draining adits? Results of this investigation will allow characterization of potential risks, primarily to ecological receptors. Of particular concern are seeps and springs that may be reaching surface water.

4.3 Information Inputs

- Type of Information. The following types of data are being collected to supplement existing data.
 - Groundwater (monitoring wells, seeps, adit discharges, and residential wells).
 - ESAT laboratory analytical for TAL metals and metalloids, sulfate, chloride, total alkalinity, and total dissolved solids (TDS).
 - EPA R.S. Kerr Environmental Research Center laboratory analytical for Rare Earth Elements and Pb isotopic ratios.
 - ESAT contract laboratory for water stable isotope analysis.
 - Field measurements of pH, specific conductivity (SC), and temperature.
 - Field measurements of flow rate (where possible from seeps and springs discharges).
 - Geospatial data will be collected for all samples, as will descriptive data about the locations of the seeps and springs.
- Sources of Information. Data will be obtained from sampling as described in the QAPP and this FSP. The data will be used with previously collected data to characterize the nature and extent of contamination at the site in the RI.
- Appropriate Sampling and Analysis Methods. The media to be sampled, sampling procedures, analytical parameters, expected contaminants of potential concern (COPCs) concentrations, and laboratory methods planned for this investigation are consistent with samples collected by MSI or CDM Smith for EPA at similar mining district sites. Standard procedures will be employed during the investigation so that analytical results can be comparable to historically collected data/information. This includes using a consistent sample labeling protocol used by MSI to facilitate study and management of this site during the remedial investigation.

4.4 Boundaries of the Study

4.4.1 Target Population of Interest

The population of interest is chemical and physical data for seeps, springs, and draining adits in the investigation area.

4.4.2 Spatial Boundaries

The sampling will be performed as follows:

- Seep, spring, and draining adit sampling. Seep, spring, and draining adit discharge samples will be collected from all known seep and springs and select draining adits in the investigation area. Additional samples may be collected from previously undocumented seeps and springs, if any, within the investigation area on an opportunistic basis.

4.4.3 Temporal Boundaries

Field activities will occur in June 2018, weather permitting. Travel to and from the site, as well as all sampling activities, will be conducted during daylight hours only. Sampling and data collection may be conducted at any time during daylight periods. Sample analysis will be conducted in June to July 2018. Data validation and management will be conducted consistent with the QAPP and Data Management Plan.

4.4.4 Practical Constraints on Collecting Data

Potential constraints that could delay performing field work include adverse weather conditions, fires, closed roads, inaccessible locations, and inability to obtain property access for sampling. If samples cannot be collected due to any of these constraints, this information shall be reported ASAP to the RPM and recorded in the field logs.

4.4.5 Scale of Decision Making

The scale of decision making refers to the way the planning team delineates decision units and identifies the smallest unit of subpopulation, area, volume, or time where data will be collected, aggregated, or interpreted to make a decision and control decision error. This is critical to most environmental investigations because it can influence the ability of the decision makers to reduce site risks and can affect the cost of future response actions.

In the context of this investigation, EPA will use the environmental media data to determine the presence or absence of mining-related contamination within the specified areas and determine if additional studies are needed to completely characterize the nature and extent of contamination and ultimately contribute to evaluation of risks at his site to help inform risk management decisions.

4.5 Analytic Approach

4.5.1 Parameter Selection

The key parameter important to making decisions about the target populations is the individual result. The individual result for each sample will be used in comparison with historically collected data/information to answer the principal study questions.

For seeps, springs, and draining adits, the water is considered to be both surface water and ground water, so samples are both filtered for analysis of dissolved metals and unfiltered for analysis of total recoverable metals. Samples are collected for stable isotope analysis. Samples will be analyzed in the field for time-sensitive parameters such as pH and temperature.

Water samples from selected locations will also be sampled for analysis of Rare Earth Elements and Pb Isotopic Ratios. Sample analysis will be conducted at the R.S. Kerr Environmental Research Center (EPA/Groundwater, Watershed, and Ecosystem Restoration Division, Ada, Oklahoma) using Standard Operating Procedures NRMRL-GWERD-13-0 and NRMRL-GWERD-16-0. The Rare Earth Elements, REEs or lanthanide elements, are a group of 14 elements from Lanthanum (atomic number 57) to Lutetium (atomic number 71). Promethium (atomic number 61) is excluded from the REE list because this element does not occur naturally, having no isotope with a half-life of greater than about 20 days. The REEs are useful tracers of water-rock interactions, water mixing, and redox processes and they are becoming widely utilized in studies of groundwater processes. Lead isotopes are also useful tools for solving a range of problems in environmental geochemistry due to the highly varied natural abundances and half-lives of the radionuclides that decay to different Pb isotopes. We plan to collect initial data to evaluate whether or not these tools could be useful to delineate sources of groundwater.

The analytical methods specified in QAPP Worksheet #23 for use by the analytical laboratory are capable of performing over the expected range of COPC values at the site. The usability of all analytical data will be determined based on the data validation and evaluation process specified in the work plan. If the data are determined to be unusable, then samples will be reanalyzed either from laboratory-held samples, archived samples, or from samples collected during a subsequent sampling phase.

4.5.2 Estimator

The estimator for this sampling event is that the planning team concluded that characterization of the spatial and temporal distribution of contamination of a variety of mine wastes was needed. The information will establish a more complete picture of contaminant distribution in previously uncharacterized or inadequately characterized locations. The information will be used to identify potentially significant fate and transport mechanisms and potentially complete exposure pathways for human and ecological receptors.

4.6 Performance or Acceptance Criteria

Tolerable limits on decision errors, which are used to establish performance goals for the data collection design, are described specified in this step and are listed in Worksheet #12 of the QAPP. Decision makers are interested in knowing the true value of the constituent concentrations. Since analytical data are only estimates of the true

values, decisions that are based on measurement data could be in error, which is referred to as decision error. There are two reasons why the decision maker may not know the true value of the constituent concentration:

- Sampling design error occurs when the sampling design is unable to capture the complete extent of variability that exists in the true state of the environment. Concentrations may vary over time and space. Limited sampling may miss some features of this inherent variation because it is usually impossible or impractical to measure every point of a population.
- Measurement error refers to a combination of random and systematic errors that inevitably arise during the various steps to the measurement process. Analytical methods and instruments are never absolutely perfect; hence a measurement can only estimate the true value of an environmental sample.

The combination of sampling design and measurement error is the total study error. Since it is impossible to completely eliminate total study error, basing decisions on sample concentrations may lead to a decision error. These errors may lead to either over-estimating or under-estimating the concentration of environmental contaminants. Over-estimating could result in removal of soil that is not a risk. Under-estimating may result in leaving contamination, which could continue to expose targets to unacceptable levels of contaminants.

Specific data validation processes ensure that analytical results are within acceptable limits. All the information and data gathered during this evaluation will be checked to ensure they are usable for their intended purposes. An evaluation of analytical control limits and of the precision, accuracy, representativeness, completeness, comparability and sensitivity (PARCCS) parameters will be performed. If significant issues with the data are found, data results will be discussed with. The EPA will then decide if the total study error could cause them to make an incorrect decision. Using this approach, the probability of making an incorrect decision (i.e., either a false negative or positive) based on the information collected is considered small.

The project-specific action limits and quantification limits for each sampled media are presented in the QAPP on Worksheet #15 for all analytical parameters with the exception of rare earth elements and Pb isotope ratios, which are included in Appendix 8. Measurement performance criteria are provided on Worksheet #12a, c. The measurement performance criteria for in-field measurements of real-time water quality parameters can be found in QAPP worksheet #12g. The analytical method and standard operating procedures (SOP) for the field meter will come from the manufacturer's instruction manuals.

4.7 Plan for Obtaining Data

This step identifies a resource-effective data collection design for generating data expected to satisfy the DQOs. The data collection design (sampling program) is described in detail in Section 6.

4.7.1 Quality Control Procedures

Analytical quality control procedures, assessment steps, and acceptance criteria are described in the QAPP. Pertinent information for this FSP includes the number of QC samples to collect. As specified in QAPP worksheet #28, field duplicates will be collected and analyzed at a rate of one per 10 samples, equipment rinsate blanks will be collected using any sampling equipment that is reused (for individual samples, not aliquots of a sample) and analyzed at a rate of one per day, and extra volume for a MS/MSD will be collected at a rate of one per 20 samples. These requirements are summarized in Table 1.

Table 1 QC Sample Requirements

Type of QC Sample	Matrix	Frequency	Analysis
Duplicate Sample	Water	1 per 10 natural samples	Same as natural sample
Rinsate Blanks	Water	1 per day that includes a decontamination event	Same as natural sample
Temperature Blank	Water	1 per cooler shipped or delivered to laboratory	Temperature
Matrix Spike (MS)	Water	1 MS and 1 MS duplicate per 20 natural samples	Same as natural sample

5.0 Personnel Responsibilities and Contact Information

The project manager and lead field technician will be Dr. Rory Cowie, hydrologist and research director at MSI. The field technician will be Nate Rock, Research Assistant at MSI. Both field technicians have extensive backcountry work experience and Dr. Cowie is certified in Wilderness Advanced First Aid and Mr. Rock is certified in Wilderness First Aid. Dr. Cowie has 40-hr OSHA HAZWOPER training and Mr. Rock is certified with 24-hr OSHA HAZWOPER training. All other MSI field technicians working on this project have the minimum requirement of 24-hr OSHA HAZWOPER training. The project will be overseen by Scott Roberts, Water Program Director at Mountain Studies Institute. Additional project management support will be provided by Neil Smith and Thomas Cook of CDM Smith. Technical oversight will be provided by EPA Region 8 hydrogeologist Ian Bowen and field operations support will be provided by Jamie Miller from EPA Region 8.

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6.0 Media, Sampling Locations, and Sample Quantities

The locations of seeps, springs, draining mines, and other hydrologic features have been established by several agencies and organizations over the past decades, including EPA, Bureau of Land Management (BLM), United States Forest Service (USFS), Colorado Department of Mining, Reclamation, and Safety (DRMS), and Sunnyside Gold Corporation. Water samples will be collected at all known seep and spring locations (see Figure 1 and Appendix 9). Additionally, draining or abandoned mine locations will be added to the list as directed by the BPMD decision team, and Kirsten Brown, project manager for DRMS (Table 5). MSI will coordinate with DRMS to determine which draining mines have been sampled and which remain in need of sampling at the time of the low flow sampling event.

Water samples will be collected from approximately 150 locations within the investigation area. Seeps, springs, and draining adits were not identified in QAPP Worksheet #18; however, the media is considered to be both surface water and ground water. Worksheet #18 requirements as applicable to seep, spring, and draining adit samples is presented in Table 2.

Seep, spring, and draining adit samples will be collected following the procedures contained in the Springs, Seeps, and Adit Discharge SOP attached in Appendix 3. Samples are to be analyzed for the same analytical groups as surface water and ground water as specified in QAPP Worksheet #18 (CDM Smith 2018).

Table 2 Sample Analytical Requirements Summary

Sampling Location/ID Number	Matrix	Depth	Type	Analytical Group	Sampling SOP	Comments
Seep and Spring Sampling						
Seep, Spring, Adit Locations/Approx. 150	Surface Water/Ground Water	To be Determined in Field	Discrete	TAL Metals (total/dissolved) Mercury (total/dissolved) Wet Chemistry – Anions Rare Earth Elements Pb Isotopes Stable Water Isotopes In-field Measurements	Springs, Seeps, and Adit Discharge – See Appendix 4,5	

Sample container and preservation requirements are specified in QAPP Worksheet #19 and 30 (CDM Smith 2018). A summary of applicable portions of that worksheet is presented in Table 3. All water samples will be collected as 1-liter grab samples which will then be separated into four individual sample containers. One 250 mL unfiltered sample will be collected for wet chemistry group analysis. One 250 mL unfiltered sample will be collected for total metals and one 250 mL filtered sample will be collected for dissolved metals analysis. One 20mL unfiltered sample will be collected for isotope analysis. One 125 ml filtered sample will be collected for Rare Earth Elemental analysis. The information to be collected and the analysis to be performed at each sample location is summarized below in Table 4.

Table 3 Sample Container and Preservation Requirements

Analyte/Analyte Group	Containers	Filtration	Preservation Requirements	Holding Time
Total Recoverable TAL Metals	(1) 250 mL HDPE	Unfiltered	HNO ₃ to pH<2; cool to 4°C	6 months
Dissolved TAL Metals	(1) 250 mL HDPE	Filtered through 0.45 µm membrane	HNO ₃ to pH<2; cool to 4°C	6 months
Wet Chemistry	(1) 250 mL HDPE	Unfiltered	Cool to 4°C	7 days to 28 days
Stable Isotope	(1) 20mL glass with polyseal cap	Unfiltered	None	1 year
Rare Earth Elements and Pb Isotopes	(1) 125 ml HDPE	Filtered through 0.45 µm membrane	HNO ₃ to pH<2;	6 months

Table 4 Number and type of samples and analytical parameters

Sample area	Anticipated number of samples	Description	Lat	Long	Flow	Field WQP	Metals	Cations, Anions	Stable isotopes
Bonita Peak (Cement & Upper Animas)	120-150	X	X	X	X	X	X	X	x

Surface water contaminants of potential concern, detection limits, and analysis methods are provided in Table A.7-3 of the Bonita Peak 2017 QAPP (EPA, 2017).

Table 5: Draining or abandoned mine sites to be monitored

NAME	TYPE (DRY_DRAINING)	LAT	LONG
Unnamed, N. Fork Cement	DM	37.89742532	-107.62727106
SFA05 unnamed # 16 USGS	DM	37.88252961	-107.59820485
SFA01 Mine #17 (USGS)	DM	37.87671863	-107.60242284
Prospect; no USGS name.	DM	37.89032021	-107.68913100
Natalie Occidental	DM	37.87676369	-107.64398990
Red and Bonita	DM	37.89723101	-107.64370253
Gold King #7 @ Gladstone	DM	37.89160400	-107.64892100
Queen Anne	DM	37.91447400	-107.63047600
American Tunnel	DM	37.89098100	-107.64844000
Mogul South	DM	37.90833000	-107.63842400
Grand Mogul	DM	37.90983100	-107.63088700
Mogul	DM	37.90999000	-107.63832400
Mogul South Adit 2	DM	37.90833000	-107.63842400
American Tunnel	DM	37.89098100	-107.64844000
Ben Franklin	DM	37.89448500	-107.60795000
Big Colorado	DM	37.87680200	-107.64664200
Terry Tunnel	DM	37.89286400	-107.60424700
Black Hawk	DM	37.88223100	-107.63560700
Red and Bonita	DM	37.87676369	-107.64398990
Senator	DM	37.88189000	-107.56798700
Bavarian Mine	DM	37.53300000	-107.36220000
Hercules	DRY	37.89243740	-107.68863263
Galena Queen	DRY	37.89187819	-107.68950439
Prospect Adit 01	DRY	37.88915913	-107.69178294
Henrietta #7	DRY	37.89096205	-107.68281740
Henrietta #8	DRY	37.89173755	-107.68247827
Lark	DRY	37.89341098	-107.68113110
Joe and Johns	DRY	37.89150400	-107.67907900
Adams	DRY	37.90021839	-107.64234601
Pride of Bonita	DRY	37.90363586	-107.64119560
Pride of Bonita Adit 01	DRY	37.90304900	-107.64192700
Solomon Group	DRY	37.89635248	-107.63961355
Gold King Unnamed Adit 01	DRY	37.89687397	-107.63706936
Gold King Unnamed Adit 02	DRY	37.89608000	-107.63664800
Gold King Sampson Level	DRY	37.89365410	-107.63431173
Gold King Upper Sampson	DRY	37.89757546	-107.63343548
Gold King Paul Level	DRY	37.89742113	-107.63239676
Gold King #1	DRY	37.89660712	-107.63202116

7.0 Field Activity Methods and Procedures

This section describes sampling methods that will be used, as well as applicable SOPs. In order to allow direct comparison of seeps, springs, and draining adit data to water quality data collected for surface waters in the investigation area, the methods outlined in the Bonita Peak 2017 QAPP (EPA, 2017; CDM Smith 2018) will be followed.

7.1 Site characterization

All previously identified seep, spring, and draining adit locations will be visited during this task and if water is flowing a sample will be collected. The following information will be collected and recorded at each sampling site: Georeference points, photo points, presence of wetland plant species, geology, and localized geomorphology. The complete site characterization parameters and descriptive terminology can be found in Appendices 1 and 2.

7.2 Water quality field parameters

For field sampling purposes, water quality meters are calibrated on site before use to account for barometric pressure. The main parameters for surface water quality are pH, specific conductance, and temperature. An Oakton waterproof PC 450 field probe will be used to collect the measurements. Calibration will follow the manufacture manual and will occur daily to account for variable barometric pressure conditions associated with changing weather conditions and changes in altitude between sampling sites. Because the SOP for collecting field parameters contained in Attachment C of the QAPP is for an instrument that will not be used during this investigation, instruments will be operated according to manufacturer's instructions for the Oakton instrument. Measured parameters will be recorded according to SOP 4-1.

7.2.1 Standards and Reagents

Certified standards and reagents will be used for calibration of the Oakton PC 450 water quality meter. pH calibration will be completed using three buffer solutions at pH 4, 7, and 10. Specific conductance will be calibrated with one point at 1000 us/cm. The Sampling Equipment Decontamination SOP FLD 02.00 (EPA, 2012) will be followed.

7.2.2 Pre-Deployment Activities

Batteries will be charged at least 24 hours prior to use. The water quality sensor will be stored, calibrated, and maintained in accordance with the operations manual.

Sufficient time for thermal stabilization of standards to ambient conditions will be considered before calibration.

7.2.3 Calibration

Due to the variability in barometric pressure between sampling sites, the re-calibration of water quality sensors will occur at greater frequency than manufacturer recommendations. Instruments will be calibrated at the beginning of each day with a calibration check conducted at least once per day. Instruments will also be recalibrated following a significant change in elevation or barometric pressure since the instrument was last calibrated. If the pH values are completely unknown at a sampling site, then a 3-point calibration will be used. If historical data indicate that the seep/spring water is anticipated to have a low pH, a two-point calibration may be used. Calibration for all parameters will follow manufacture operations manual and maintenance will be performed as needed. If field personnel feel uncertain about the quality of measurement data in the field, performance of the instrument will be checked using a known calibration standard. Corrective action will be determined on a case-by-case basis with all circumstances being considered. Data will be flagged as needed in the final data package.

7.3 Water quality sample collections

Seep, spring, and draining adit sampling will follow the project-specific SOP for Springs, Seeps, and Adits Discharge Water Sampling contained in Appendix 3. Sampling will progress in a manner that will eliminate the potential for sediment disturbance around the seep or spring that could result in cross-contamination of subsequent samples. Water quality samples will be collected prior to discharge measurements to minimize disturbance and potential contamination of the water quality samples.

7.4 Water quantity, discharge measurements

Systematic hydrological measurements are needed for classifying, understanding, and monitoring spring ecosystems. Discharge of seep and springs will be measured using SOP 722 attached in Appendix 4. Additional detail is provided in Appendix 5.

8.0 Sample Labeling and Shipping

Sample labeling will consist of a series of letters and numbers to indicate the location following procedure detailed in QAPP Worksheet #26 and 27 (CDM Smith 2018). For

this investigation, the first identifier group will be 0618BPMD to reflect June 2018 and the BPMD site. The second identifier group will, to the extent practicable, match previously collected samples from sites that have been previously sampled and named. Sample labels will match information provided by the different data sets included in the EPA geographic information system (GIS) viewer. The EPA viewer includes a listing of existing sample locations from multiple agencies which do not have EPA-generated identifiers including Sunnyside Mine, Bureau of Land Management (BLM), Colorado Department of Reclamation, Mining, and Safety (DRMS) and others. Therefore, a unique identifier number will be provided for every sample collected until the EPA decides on a uniform labeling procedure for all seeps and springs. For new sample sites that have not been previously named the location will be named based on reference to the nearest named surface water feature (i.e. stream or tributary) as previously described in section 2.0. The third identifier will be SW- for surface water, and the fourth identifier will be 00 for a natural sample, 30 for a duplicate sample, and 90 for a rinsate sample. Examples include:

0618BPMD-S4-SW-00 – This sample would be collected in June 2018 at the BPMD site at historic spring location S4 and is natural surface water sample; and

0618BPMD-S21-SW-90 – This is a rinsate sample collected following collection of a surface water sample at location S21 in June 2018.

All water samples will be kept on ice, in coolers, and shipped to the EPA Region 8 laboratory according to SOP 2-1 following chain-of-custody protocols in SOP FLD-11.00. MSI will use its existing FedEx account for shipping and will follow all EPA shipping protocols found in the 2017 EPA SAP/QAPP. Stable water isotope samples will be bubble-wrapped and packaged in hard-sided coolers for shipping.

At the laboratory, the sample custodian will inspect the coolers upon arrival to make sure that the proper temperature was maintained, that the sample containers are intact and sealed, and that the number of samples in the coolers match the information provided in the chain-of-custody forms. All the samples will be stored in an access-controlled sample cooler at the laboratory. An analytical chemist will log the samples in Laboratory Information Management System (LIMS) upon receipt and will enter all analytical data into the U.S. EPA SCRIBE environmental database management system for permanent storage and archiving.

All field measurements and observations will be recorded in a bound notebook or on appropriate data sheets by field personnel at the time they are performed, in accordance with the *Contract Laboratory Program Guidance for Field Samplers* (EPA, 2014). The personnel doing the recording will initial and date all measurements, observations, and any other notations made. Corrections will be performed by drawing a single line through the error accompanied by the date and the initials of the person performing the correction, followed by the proper entry. Chain-of-custody

forms will be filled out during the time of collection and will follow protocol provided in *Sample Custody and Labeling*, SOP FLD- 11.00 (EPA, 2012).

9.0 Sample Analysis

As specified in Table 2, samples will be analyzed for TAL Metals (total/dissolved), Rare Earth Elements, Pb isotopes, Wet Chemistry (anions), and stable water isotopes in the laboratory.

Samples will be analyzed in the field for time-sensitive parameters including water temperature, pH, conductivity, and dissolved oxygen. Field parameters will be measured as described in Section 7.2.

10. Data Information Processing, Storage, and Use

Field measurements will be recorded on field sheets (Appendix 1) that will be collected using an iPad and associated high precision blue-tooth GPS collector at the time of data collection. The field sheets will be developed and managed using Survey 123 for ArcGIS as outlined in the SOP appendix within the QAPP (EPA, 2017). All field measurement data sheets will be uploaded daily from the iPad to the EPA server. A brief description of the stream flow measurements will also be recorded in the field sheets. A full description of the terms and abbreviations used to complete individual sections of the field sheet are included in Appendix 2. Field notebooks, chain-of-custody forms, and other forms used for the Site investigation will be stored at the Region 8 EPA Laboratory Suite A127.

When and where applicable, the Survey 123 field sheets will have the following entries for each sampling site:

- Date
- Time
- Sample location
- Sampler/Scribe
- Team members
- Weather conditions, daily safety issues
- Water quality measurements
- Measurement/sample collection identification
- Measurement/sample collection method
- Equipment that was used to collect samples/measurements
- Camera and photo details to be used in the photo log

- Conditions that may adversely impact the quality of measurements/samples
- Maps/sketches if applicable
- Physical description of sample matrix

Deviations from Procedures

In accordance with QAPP Worksheet #14/16, all deviations from the guiding documents will be recorded in the field logbook(s). Any major deviations will be documented on a field change request (FCR) contained in Appendix 6, which will be approved by the PM and EPA RPM (if applicable). Any modifications to chain-of-custody forms will be made on all copies. As applicable, the EPA RPM will be notified and will approve of any major changes or deviations and the QAPP or FSP will be updated to reflect the change.

11.0 References

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MSI. 2017. 2017 Seeps and Springs Investigation Field Sampling Plan. June 2017.

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U.S Environmental Protection Agency. 2006. *Guidance on Systematic Planning Using the Data Quality Objectives Process*, EPA QA/G-4.

Standard Operating Procedures:

U.S. Environmental Protection Agency. 2014. *Data Management for Field Operations and Analytical Support*. SOP 16-DAT-01.00

U.S. Environmental Protection Agency. 2012. *Surface Water Sampling*. SOP FLD-01.00

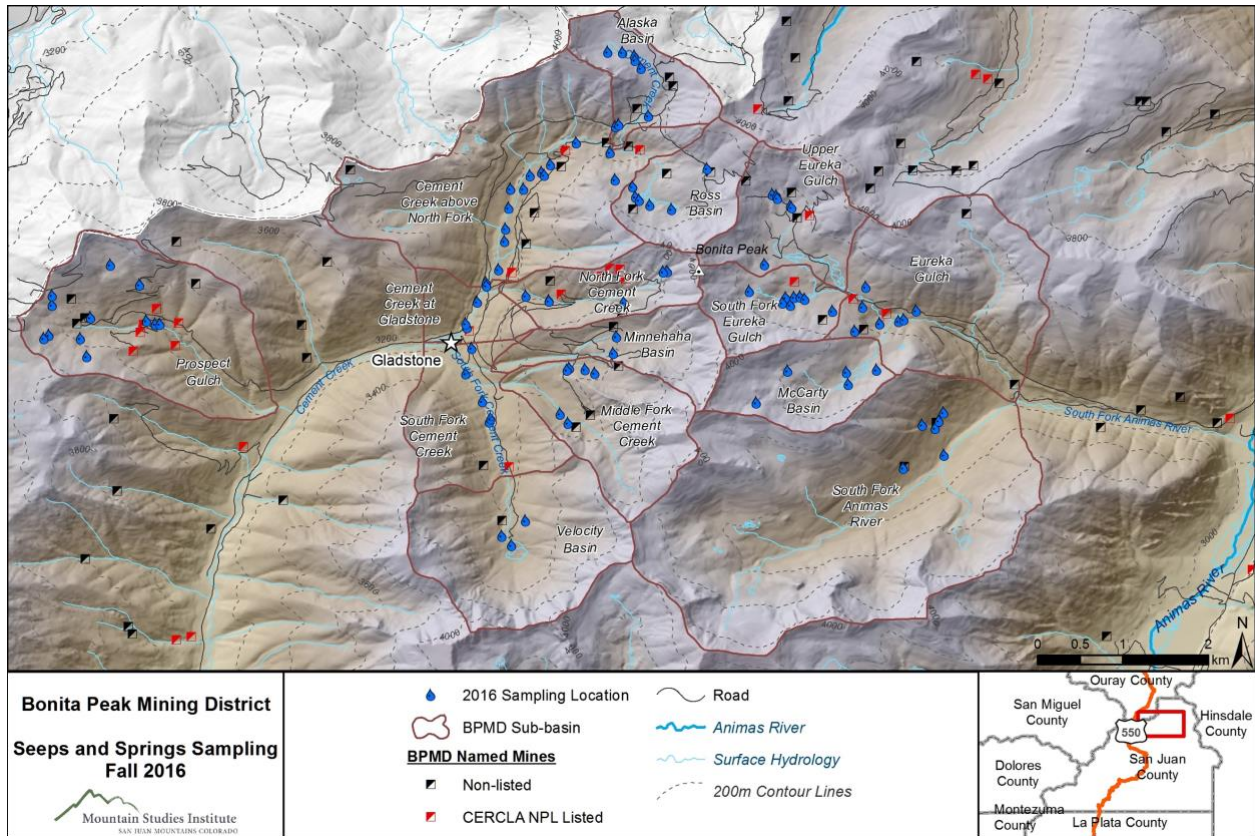
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U.S. Environmental Protection Agency. 2012. *General Field Sampling Protocols*. SOP FLD-12.00

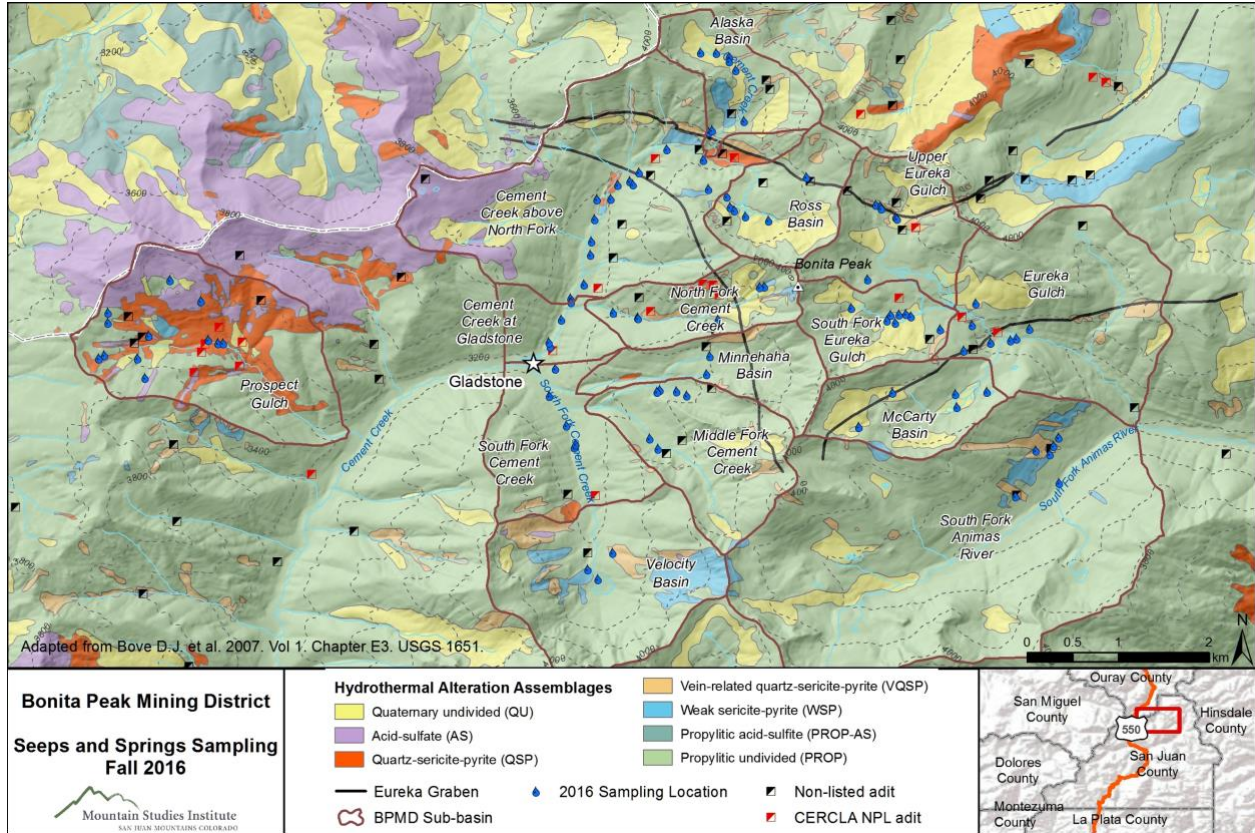
U.S. Environmental Protection Agency. 2012. *Sampling Equipment Decontamination*. SOP FLD-02.00

12.0 Site Maps

Map 1: Overview of sampling sites in 2018. Sub-basin delineation provided in red outline.



Map 2: Sampling sites overlain on Hydrothermal Alteration Assemblages



Appendix 1

Field Sheets: Modified xml format document from ArcGIS Survey 123 listing all parameters collected as listed in section 10.0.

type	name	label
select_one	SampleStatus	collection_type
		Sample Location Status (Process)
select_one	area	Area_Name
		Sample Area
geopoint	GPS_New_Location	New GPS Location
text	New_Sample_ID	New GPS Location ID
decimal	Latitude	Latitude
decimal	Longitude	Longitude
decimal	HorAccMeters	Accuracy (Meters)
select_one	id	Location
		Location ID
select_one	site	Site_type
		Sample Site Type
select_one	subbasin	BPMD_SS_subbasin
		BPMD Seeps and Springs Subbasin
select_one	collection_type	Sample_Collection
		Sample Collection Type
select_multiple	matrix	Matrix
		Sample Matrix
select_multiple	analysis	Analysis
		Analysis
date	Sample_Date	Date
time	Sample_Time	Time
text	Environmental_Conditions	Environmental Conditions
text	Form_Author	Form Author's Name
text	Sampler	Field Sampler's Name
begin group	barcodes	Field Equipment Barcodes
text	WQP_type	Water Quality Probe Type
text	Flow equip	Flow Measurement Equipment
barcode	TRMBottle_Barcode	TRM Bottle Lot Number
barcode	DMBottle_Barcode	DM Bottle Lot Number
barcode	AlkBottle_Barcode	Alk/Anion Bottle Lot Number
barcode	StblBottle_Barcode	Stable Isotope Bottle Lot Number
end group		
begin repeat	extra	Extra Field Equipment
text	Equipment_Name	Name of Equipment

type	name	label
select_one	SampleStatus	Sample Location Status (Process)
barcode	Code	Equipment Barcode
end repeat		
decimal	pH	pH
decimal	Temp_air	Air Temperature
decimal	Temp_water	Water Temperature
decimal	Conductivity	Conductivity
decimal	Diss_O2	Dissolved Oxygen
decimal	ORP	ORP
select_one	flow_type	Flow Method
decimal	Flow_Measurement	Flow Measurement
select_one	flow_unit	Flow Units
text	Flow_notes	Flow Notes/Comments
text	Remarks	Remarks
select_one	wetland	Obligate Wetland Species
text	Wetland_spec	Observed Obligate Wetland Flora or Fauna
begin group	pictures	Pictures
note	loc	Location ID =
image	Picture_North	Take Picture North
image	Picture_East	Take Picture East
image	Picture_South	Take Picture South
image	Picture_West	Take Picture West
begin repeat	Xtra_Pictures	Extra Pictures
note	loc2	Location ID =
image	Xtra_Pictures2	Supplemental Picture
end repeat		
end group		
image	Signature	Author's Signature

Appendix 2

Reference Terms and abbreviations for field sheets

1. Georeference Source

GPS, map, other

2. Land Unit

BLM, USFS, Private, State, other

3. Surface Type

AU: Adjacent Uplands

BW: Backwall

C: Cave

CH: Channel

CS: Colluvial slope

Org: Organic Ooze

P: Pool

PP: Plunge Pool

SB: Sloping bedrock

SM: Spring mound

TE: Terrace

TU: Tunnel

Oth: Other

4. Surface Subtype

NA

5. Slope Relief

Low, Medium, High

6. Soil Moisture

Dry Saturated

Dry-Moist Inundated

Moist-Dry

Wet-Dry

Moist

Saturated-Dry

Wet

Saturated-Moist

Wet-Saturated

7. Substrate

1 Clay 5 coarse gravel

2 Silt 6 cobble

3 sand 7 boulder

4 fine gravel 8 bedrock
9 organic matter

8. Emergence environment Detail

Cave
Subaerial
Subglacial
Subtalus
Subaqueous-lentic freshwater (lake/still)
Subaqueous-lotic freshwater (flowing)

9. Source Geomorphology

Contact Spring
Fracture Spring
Seepage or filtration
Tubular Spring

10. Flow Force Mechanism

Anthropogenic/mining
Artesian
Geothermal
Gravity
Other

11. Parent Rock Type

Igneous
Andesite, basalt, dacite, diorite, gabbro, grandodiorite, granite, peridotite, rhyolite
Metamorphic
Gneiss, marble, quartzite, slate, schist
Sedimentary
Conglomerate, limestone, mudstone, sandstone, shale, siltstone, unconsolidated

12. Channel Dynamics

Mixed runoff/spring dominated
Runoff dominated
Spring dominated
Subaqueous

13. Discharge Sphere

Cave
Exposure
Fountain
Geyser
Gushet
Hanging Garden

Helocrene
Hillslope
Hypocrene
Limnocrene
Mound-form
Rheocrene

14. Flow Consistency

Dry Intermittent
Erratic Intermittent
Perennial
Regular Intermittent

15. Measurement Technique

Current Meter
Weir
Cutthroat flume
Timed volume fill

16. Cover Codes

GC ground cover
SC shrub cover
MC Midcanopy cover
TC tall canopy cover
AQ Aquatic cover

Appendix 3

Project Specific SOP - Seeps, Springs, and Adit Discharge Water Sampling

Project Specific SOP

Springs, Seeps, and Adit Discharge Water Sampling Revision: 1 Date: April 2012

1.0 Objective

The purpose of this technical standard operating procedure (SOP) is to define requirements for collection and containment of water samples from low flow seep, springs, or adit discharges. This SOP details procedures specific to sampling these water sources and should be used in conjunction with the procedures in TSOP 1-1 for Surface Water Sampling.

This SOP assumes sampling for inorganic parameters only, where utilizing plastic sample containers is appropriate.

2.0 Background

Seep and adit discharge samples are collected to determine the type(s) and level(s) of contamination (typically heavy metals at mine sites) in a particular water body. Seeps and springs are often representative of ground water discharging to surface water. Adit discharge is water discharging from a mine portal.

Mine adits are horizontal mine openings and often have very shallow water depths with very little slope, making it difficult to fill sample bottles without entraining sediments or otherwise disturbing the site to be sampled. This SOP provides specific techniques for obtaining representative samples at these locations.

Mine adits are frequently located in remote areas which must be hiked into. It is necessary to bring a variety of sampling devices and extra containers to allow flexibility in sampling, and spare filters (if filtered or dissolved samples are required). Flow rates can change drastically over a season, so a method that worked during one sampling event may not work during a subsequent visit.

2.1 Definitions Adit Discharge – water that flows through underground mine workings and discharges out of a mine portal. Mine adits are horizontal tunnels accessing underground mine workings.

Seeps or Springs – shallow groundwater emerging from the ground to the land surface. **Surface Water** - Water that flows over or rests on the land and is open to the atmosphere. This includes ditches, streams,

rivers, lakes, pools, ponds, and basins. **Grab Sample** - A discrete portion or aliquot taken from a specific location at a given point in time.

2.2 Associated Procedures

▪ SOP 1-1, Surface Water Sampling ▪ SOP 1-2, Sample Custody ▪ SOP 2-1, Packaging and Shipping Environmental Samples ▪ SOP 4-1, Field Logbook Content and Control ▪ SOP 4-2, Photographic Documentation of Field Activities ▪ SOP 4-5, Field Equipment Decontamination at

Nonradioactive Sites

3.0 General Responsibilities Site Manager - The site manager is responsible for ensuring that field personnel are trained in the use of this SOP, related SOPs, and the required equipment.

Field Team Leader - The field team leader (FTL) is responsible for ensuring that sampling efforts are conducted in accordance with this procedure and any other SOPs pertaining to specific media sampling. The FTL also must ensure that the quantity and location of surface water samples collected meet the requirements of the site-specific plans.

Note: Responsibilities may vary from site to site. Therefore, all field team member responsibilities shall be defined in the field plan or site/quality assurance project plan (QAPP).

4.0 Required Equipment

All or part of the equipment listed under the “as needed” category may be required at any specific site, depending on the plan(s) for that site.

- ·Site-specific plans
- ·Field logbook
- ·Indelible black-ink pens and markers
- ·Labels and appropriate forms/documentation for sample shipment
- ·Appropriate sample containers
- ·Insulated cooler and waterproof sealing tape
- ·Ice bags or “blue ice”
- ·Plastic zip-top bags
- ·Clear waterproof tape
- Personal protective clothing and equipment ▪ Latex or appropriate gloves ▪ Rubber boots and/or rubberized waders ▪ Life jacket
- Kimwipe or paper towels ▪ Clean plastic sheeting ▪ Tap and deionized water ▪ Appropriate photographic equipment and supplies ▪ Appropriate decontamination equipment and supplies

As needed:

- ·Pond sampler with 1-liter (L) beaker (preferably Teflon[®]), clamp, and heavy-duty telescoping pole if needed for safely obtaining the sample.
- ·Peristaltic pump or suitable replacement
- ·0.45 micron filters (plus spare filters) and vacuum pump or other equipment needed

for filtration

- ·Temperature, pH, and conductivity meter(s), dissolved oxygen meter, redox potential meter (as required by project plan)
- ·Global positioning system (GPS) unit
 - ·Tape measure
 - ·Any personal protective equipment specified in the site-specific health and safety plan
 - ·Spare parts for all equipment
 - ·Syringes and tubing for obtaining samples from very low flow seeps (suggest 50-100 milliliter volume)
 - ·Small portable trough for consolidating flows, estimating flow rates, and filling sample containers (a 3-4 foot section of plastic rain gutter works well)
 - ·Buckets or other containers of known volume for gaging flow rates using “bucket and stopwatch” method. Typically a 5 gallon bucket and a 1 liter sample bottle are sufficient.
 - ·Stopwatch or other timer
 - ·Small hand trowel

5.0 Procedures The following steps should be taken when sampling springs, seeps, or adit discharges:

1. Review site-specific health and safety plan and project plans before initiating sampling activity. Under no circumstances will samplers enter an abandoned mine adit, shaft, building, or other portal to obtain samples, due to unknown physical hazards (e.g., collapse, unseen voids, shafts, etc.) and due to unknown atmospheric hazards such as depleted oxygen or the presence of other hazardous gases.
2. Don the appropriate personal protective clothing as dictated by the site-specific health and safety plan.
3. Approach the adit or seep from downstream in order to not disturb or contaminate the water to be sampled. Many adits have collapsed entrances which may be unstable or conceal openings in the ground. Care should be taken around adits due to unknown footing, unknown depth of ponded water, broken timbers, rusted metal, etc.

Samples of seeps and adits should be collected as close to its origin as it emerges from the ground as is safely possible. Based on the conditions of the individual seep or adit, determine the most appropriate method for sample collection. Unlike sampling streams, for many adits and seeps, the water is not deep enough to submerge a sample bottle in the water to fill it; care is required to prevent disturbing sediments as the sample is collected. However, if there is

sufficient flow and depth to the discharge, sample bottles can be filled as if for surface water streams.

- For very low flows on flat surfaces, a disposable syringe with tubing may be required. Draw the water into the syringe without drawing up sediments, and fill the sample bottles, taking care to distribute the water from each syringe filling among the different sample bottles.

If there is some horizontal drop available in the discharge, a 4-5 foot length of plastic rain gutter may be appropriate to channel a portion of the discharge to an area where a bottle can be filled. In this case, position one end of the rain gutter directly into the discharge as close to its origin as possible. This will stir up sediment. Physically stabilize the rain gutter and allow the water to flow for a while and clear of sediments before collecting the sample. Fill the sample bottles once the water clears, taking care to distribute the water among the different sample bottles.

5. Filter samples if required by the site-specific plan.
6. Make field measurements as required by the project plans in physical, chemical, and biological characteristics of the water (e.g., discharge, temperature, dissolved oxygen, conductivity, pH). Always place the field meter downstream of where the sample will be collected. If this is not possible due to shallow water depths, place the field meter in a spare bottle that will not be utilized for sample collection.

Note: Use a separate container when field testing pH, conductivity, temperature, etc. Do not insert pH paper or probe directly into sample container.

7. Document the sampling events, recording all information in the designated field logbook and take photographs if required or if possible. Document any and all deviations from this SOP and include rationale for changes.
8. The collection points shall be located on a site map and described in the field logbook. Use GPS if required or if possible.
9. Add appropriate preservatives to the sample containers if required. Always preserve a filtered sample AFTER filtering.
10. Cap the sample containers and wipe the outer surfaces of the sample containers clean with a Kimwipe or clean paper towel. Affix a completed sample label and protect the label with waterproof clear tape.
11. Place sample container(s) in individual zip-top plastic bags, if possible, and seal the bags.
12. Decontaminate reusable sampling equipment after sample collection.

Appendix 4 SOP 722 Flow Measurements

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EPA Region 8 Laboratory

Standard Operating Procedure Field Flow Measurements

Prepared for:

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Date

EPA approval:

Laboratory QA Officer

Date

Director, Regional Laboratory

Date

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1.0 Scope and Application

This document describes three basic techniques for measuring streamflow during a water quality sampling event. The first technique, referred to as the velocity-area procedure, measures stream discharge using a current meter attached to a wading rod. The second procedure measures discharge using a cutthroat flume. The third technique, known as the timed filling procedure, utilizes a bucket and stopwatch for discharge measurements. It is important to note that flow procedures can be modified in the field due to characteristics of the sampling location and the data quality objectives for the sampling event. This document serves as a basic flow measurement standard operating procedure (SOP) for the EPA Region 8 Laboratory and does not describe all types of flow measurement procedures that a hydrologist can use in the field.

Mention of trade names or commercial products in this document does not constitute endorsement or recommendation for use. Because the EPA Region 8 Laboratory uses the Marsh-McBirney Flo-mate model 2000 flowmeter, specific instructions for the calibration and use of this instrument will be described in this document. Hydrographers should consult their instrument's instruction manual when using a flowmeter from a different manufacturer.

2.0 Summary of Method

- Choose a method to measure flow.
- Choose an area to measure flow.
- Setup the flow measuring device (flowmeter, flume, etc.).
- Record data.
- Calculate flow.

3.0 Definitions and Attachments

Cross section	a plane that extends perpendicular to flow, from one stream bank to the other, and is used for depth and velocity measurements (also called a reach)
Discharge	The amount of water flowing past a point over a given amount of time (also referred to as flow)
Eddies	Areas where water moves in the opposite direction to the main flow current, typically in a circular pattern and characterized by waves or whirlpools
EPA	Environmental Protection Agency
Flow increment	the interval at which depth and velocity readings will be taken across the stream (also referred to as a width increment)
Gauge	A device used for measurement
Hydrographer	the person who takes streamflow measurements in the field
Laminar flow	The regular, continuous, and smooth movement of water
Measurement verticals	points in the stream where depth and velocity measurements are taken
Tag line	a line or tape measure that marks the stream cross section and is used to position the wading rod for depth and velocity measurements
Timed filling procedure	a procedure that uses a bucket and stopwatch to measure streamflow
Velocity-area procedure	a procedure that uses a velocity sensor and depth gauge to measure streamflow (also referred to as the flowmeter procedure)

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Wading rod the device to which the flow sensor is attached, is used to measure water depth, and positions the sensor at two-tenths, six-tenths, and eight-tenths depth

4.0 Cautions

Always obtain permission when measuring flows on private property. Keep all equipment in good working order and perform maintenance procedures as necessary.

5.0 Interferences

Several parameters can affect the accuracy of flow measurements. Interferences will be discussed separately for each flow measurement technique below.

5.1 Velocity-area (Flowmeter) Procedure

Stream discharge is equal to the product of the mean current velocity and vertical cross sectional area of flowing water (EPA 2003). Because the velocity-area procedure uses a flow sensor attached to a wading rod, anything that is likely to interfere with the performance of the sensor will have an effect on final discharge calculations. Hydrographers should assure that all batteries are fully charged when operating the flowmeter. Care should be taken to keep the sensor clear of all types of stream debris. Sediment, algae, macrophytes, wood, or rocks immediately in front of the sensor may result in inaccurate velocity measurements. Because the flowmeter uses an electromagnetic sensor to measure velocity in a conductive liquid (water), interference with the electromagnetic signal will affect meter performance. The presence of airspace (bubbles, rapids, etc.) around the sensor will cause a "Con Lost" error message to display on the screen, indicating that the sensor is out of the water and preventing the meter from taking readings. Naturally occurring geologic features, such as magnetite in the streambed, will also disrupt the meter's electromagnetic signal and will interfere with its performance. The accuracy of streamflow measurements can be increased by choosing a stream cross section that is free of obstructions.

5.2 Flume Procedure

The accuracy of streamflow measurements using a flume is highly dependent upon where the hydrographer chooses to place the flume. Flumes should always be placed in areas where water is flowing and not pooled. Flumes must always be level before readings are taken. Failure to do so will prevent water from properly flowing through the device and will result in an inaccurate depth measurement and subsequent discharge calculation. Hydrographers should also remove rocks or level uneven substrate immediately upstream of the flume so water does not undulate in the vicinity of the depth gauge and produce an inaccurate depth reading. All water at the flow measurement location must flow through the flume. Water that is pooled and not flowing properly through the device will result in an inaccurate discharge measurement. Hydrographers must adequately dam the flume using all available materials and check to be sure that leaks are not present. Flumes used to measure flow must also be the proper size. Discharge measurements taken with flumes that are too large or small for the flowing volume of water are likely to be inaccurate.

5.3 Timed Filling Procedure

When using the timed filling procedure, stream discharge is determined directly by measuring the time it takes to fill a container of known volume. Any physical barrier (rocks, logs, roots, etc.) that prevents the consolidation of water into the container will interfere with the accuracy of the final discharge calculation. Hydrographers should always remove any barriers that exist before readings are taken. In the event that barriers can not be removed, a new location should be selected for the timed filling procedure.

6.0 Health and Safety

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Measuring streamflow often requires walking on uneven and slippery substrate in the presence of rapidly flowing water. Hydrographers should exercise extreme caution when attempting to measure flow and should make decisions not to do so when conditions are too dangerous. Personnel should always wear the appropriate level of personal protective equipment (PPE) that is suited for the job. Flow procedures should be halted immediately if lightning is observed in the immediate vicinity.

7.0 Personnel Qualifications

Personnel should thoroughly read and understand this standard operating procedure before attempting flow measurements in the field. Personnel who do not have considerable experience measuring flow should always work with more experienced hydrographers until they gain the experience necessary to perform these measurements on their own.

8.0 Equipment and Supplies

8.1 Velocity-area (flowmeter) procedure

- Tape measure
- Tape measure securing device (pipes, rebar, stakes, sticks, rocks, etc.)
- Flowmeter with charged batteries
- Wading rod
- Clipboard
- Write in the rain flow forms
- Pencils / Pens
- Calculator

8.2 Flume procedure

- Flume (of the appropriate size for the sampling location with water depth gages)
- Shovel
- Bubble level
- Material in the surrounding location to dam the flume (dirt, rocks, etc.)
- Clipboard
- Write in the rain flow forms
- Pencils / Pens
- Calculator

8.3 Timed filling procedure

- Device of the appropriate size to measure water volume (bucket, flask, etc.)
- Stopwatch
- Clipboard
- Write in the rain flow forms
- Pencils / Pens
- Calculator

9.0 Reagents and Standards

Reagents and standards are not used for flow measurements.

10.0 Sample Collection, Preservation, and Storage

This section is not applicable to flow measurement procedures.

11.0 Procedures

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11.1 Determine the Appropriate Flow Procedure

When arriving at a sampling location, a hydrographer will need to determine which flow technique is best to use. The velocity-area procedure can measure discharges of any size, from small to large. The portable flume and timed filling procedures typically measure smaller discharges that are easily consolidated. A hydrographer may be able to choose between all three flow methods when discharges are less than 2 cubic feet per second (cfs). Several variables will need to be considered in order to choose the best flow technique, including: discharge size, width, depth, velocity, obstructions, ease of flow consolidation, levelness of the measurement location, and bottom substrate. A hydrographer may perform the velocity-area procedure when the discharge is spread out over a wider area and is not easily consolidated into a flume. Likewise, he or she may use the timed filling procedure when flow arises from a pipe or culvert or when the ground is too sloped to level a flume. If site conditions still warrant the use of all three techniques, the hydrographer should always use the flume method because it is the most accurate for smaller discharges.

11.2 Determine the Appropriate Measurement Location

Choosing a great location to collect measurements is the most important step in obtaining high quality flow data. It can also save the hydrographer a considerable amount of time and effort in the field. Personnel must always be mindful of safety issues and should consider other locations if conditions are too dangerous. Below is summary of things to consider when choosing a location for each flow technique.

11.2.1 Site considerations for the velocity-area procedure

Because the velocity-area procedure involves the collection of depth and velocity measurements at several points across the stream, hydrographers should choose a measurement area that is easy to wade across. Areas containing surging water or riffles should be avoided because they limit the accuracy of the flow sensor. Hydrographers should setup a cross section where flow is as consistent as possible across the entire reach. Stay away from uneven substrate where water rapidly changes in depth and velocity. Make sure that flow moves in a positive direction across the entire reach. Avoid backwater areas where flow is likely to go upstream (negative), especially at the banks. Choose a cross section where water flows directly perpendicular to the cross section. The accuracy of velocity measurements is decreased when water intersects the sensor at an angle other than 90 degrees. Undercut banks should also be avoided because it is very difficult to take depth and velocity measurements in these areas. Stay far enough downstream from obstacles such as rocks, logs, tree limbs, sand bars, and bridge posts so flow measurements are not obstructed.

Once the flow location has been chosen, survey the area to be sure that all of the streamflow will be captured. It is often easy to overlook side channels when vegetation is thick at the banks. In cases where side channels can not be avoided, measure the flow at both the stream location and the side channel and add these two values together in the final discharge calculation. Remove any obstructions in the cross section or upstream before starting flow measurements.

11.2.2 Site considerations for the flume procedure

Similar to the flowmeter technique, choosing a good location to take measurements is very important when installing a flume. The hydrographer should look for areas where water is actively flowing and can easily be consolidated into the flume. Avoid places where water is pooled or widely dispersed. Because flumes must be level when taking measurements, steer away from slopes or steep gradients. Hydrographers can always modify the discharge channel with a shovel in order to make it suitable for installation of the flume. Choose a location where material is available to easily dam the flume. Materials of a small particle size, such as dirt or clay, typically work the best.

11.2.3 Site considerations for the timed filling procedure

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When searching for a location to take flow measurements with the timed filling procedure, look for areas where water can easily be collected into the bucket. Waterfalls or discharges from the end of a culverts are the best to measure with this procedure. Avoid areas where obstructions hinder the consolidation of all water into the bucket. The hydrographer can always modify the discharge channel with a shovel to facilitate this process.

11.3 Velocity-Area Procedure

Once the flow location has been determined for the velocity-area procedure, it is time to setup the cross section for collection of depth and velocity measurements. Stretch a tape measure across the stream, perpendicular to the flow, from one bank to the other. The tape, also known as a tag line, can be secured at water's edge using a pipe, stake, or piece of rebar so the stream wetted width can be accurately measured. Secure the other end in the same fashion. Use rocks, tree limbs, etc. to secure the tape in the event that stakes are not available. Make sure that the tag line is pulled taut so it doesn't droop into the stream water. Remove rocks and other obstructions to improve the cross-section before taking measurements. Because removing obstacles from one part of a cross-section affects adjacent water velocities, hydrographers should not modify the cross-section once readings commence. Be sure to check for eddies, negative flow, or other onerous flow patterns under the tag line before taking measurements. Modify the substrate as necessary.

Record the sampling station, facility/site description, sampling crew, date/time, stream width, meter type, and measurement units on the top of the stream discharge form. See Figure 1 for an example of a stream discharge form. Be sure to always use the same measurement units when taking flow. When measuring depth in feet, record the tag line position and width in feet and the flow velocity in feet per second so that discharge can easily be calculated into cubic feet per second (cfs). Use a tag line that measures distance in feet and tenths of feet rather than feet and inches to avoid having to convert inches into tenths of feet for the discharge calculation. If discharge needs to be reported in cubic meters per second, record depth, width, and tag line position in meters and velocity in meters per second. The EPA Region 8 Laboratory will always report streamflow in cubic feet per second unless otherwise requested.

Choose an appropriate flow increment, the interval at which depth and velocity readings will be taken across the stream (ie. 1 ft, 2 ft, etc.). Choose an increment that is small enough to obtain between 20 and 30 measurement verticals within the stream width; 25 is preferred for quality control (QC) purposes. The best way to do this is to divide the total stream wetted width by 25 and round down to a convenient number. A stream that is 53 feet wide, for example, would require a 2-foot flow increment ($53/25 = 2.12$, round down to 2). It is important to note that flow increments do not have to remain consistent across the stream and can be changed when discharge changes across the tag line. Hydrographers should remember to always take more depth and velocity readings in areas of greater discharge. For this reason, a hydrographer may start taking measurements using a two-foot flow increment but may decide to reduce the flow increment to one foot in an area where water becomes deep and fast. Likewise, he or she may decide to increase the flow increment to three or four feet when water becomes shallow and slow. Figure 2 illustrates this principle.

Attach the velocity sensor to the calibrated wading rod. Be sure to adequately tighten the mounting screw so that the sensor does not spin on the housing. Mount it so that the three electrodes are parallel to the base of the wading rod and the cable exits from the top. It is always a good idea to attach the sensor to the wading rod before entering the stream so the mounting screw can be easily retrieved if accidentally dropped.

Determine where to start taking flow measurements across the tag line. In the event that there is a significant amount of discharge along the edge of the stream, take the first depth and velocity reading in the water at the bank edge (zero feet on the tag line). If there is not a significant amount of flow at the bank edge or if bank conditions prevent the hydrographer from submersing the sensor or obtaining an accurate measurement, the first reading should be taken out of the water on top of the bank at zero feet on the tag line. In this case, the depth and velocity for the first flow increment would be zero. Figure 2 illustrates this point.

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When taking measurements, stand downstream of the tag line, place the wading rod in the water, and measure the depth using the increments on the rod. Each single mark represents 0.1 foot, each double mark represents 0.5 foot, and each triple mark represents 1 foot (see Figure 3). Measuring depth can become a difficult task in areas of high velocity because water will wave and climb up the wading rod. When this happens, stand at arm's length to the side and downstream of the rod, observe the water surface, and determine which line on the wading rod best represents the average depth at the measurement vertical. Be sure that body position does not affect the depth reading. Record the tag line position in the first column of the flow form, the distance to the opposite bank in the second column, and the depth in the fourth column.

After determining the depth, position the sensor. In cases where the water is 2.0 feet deep or less, the velocity reading will need to be taken at a position 60% of the way down from the surface and 40% up from the stream bottom. To set the sensor in this position, also known as six-tenths (0.6) depth, line up the foot scale on the sliding rod with the tenth scale at the top of the depth gauge rod (see Figure 3). If, for example, the total depth is 1.7 feet, align the "1" on the foot scale with the "7" on the tenth scale. The sensor is now at six-tenths depth and velocity measurements can be taken.

In cases where water depth is greater than 2.0 feet, USGS recommends that velocity readings be taken at two positions along the vertical profile at two-tenths depth (0.2) and eight-tenths depth (0.8) and averaged for the final discharge calculation (see Figure 2). (Rantz and others 1982) Because the sliding rod and depth gauge rods are both calibrated for taking measurements at six-tenths depth, a hydrographer will need to perform two simple calculations in order to properly position the sensor at these two positions. To set the sensor at two-tenths depth, multiply the total depth by two and use this new value to position the sensor using the foot scale and tenth scale. To set the sensor at eight-tenths depth, divide the total depth by two and use this number to position the sensor. Let's say, for example, that a hydrographer measures a depth of 2.6 feet at one vertical. Because this water depth is greater than 2.0 feet, he/she knows that velocity measurements will need to be taken at both two-tenths depth and eight-tenths depth and averaged for the discharge calculation. Because $2.6 * 2 = 5.2$ and $2.6 \div 2 = 1.3$, the hydrographer will use the values of 5.2 feet and 1.3 feet to position the sensor for the two velocity readings.

Once the sensor has been properly positioned, face it upstream directly into the streamflow. Grasp the sensor cable with the hand that is holding the wading rod to prevent it from dipping into the stream current and causing the probe to spin on the housing. Turn the meter on and allow it to equilibrate before recording velocity. Readings will tend to change rapidly at the start of the measurement cycle but should stabilize as individual velocity readings are averaged. Usually one 30 second cycle is sufficient to obtain a stable velocity reading. Depending on the data quality objectives for the sampling event, the measurement cycle can be increased or decreased by pushing the up or down arrow keys. In cases where flow is not laminar and eddies cause the velocity reading to change erratically at the end of the first cycle, it will be necessary to run the meter for one or two additional cycles before recording the velocity. Record the velocity measurement in the fifth column on the flow form. In the event that velocity measurements are taken at both two-tenths and eight-tenths depth, be sure to also calculate and record the average of the two values on form.

Move to the next flow vertical, measure the depth, reposition the sensor, and determine the velocity as described earlier. Be sure to always reset the meter by pushing the "on" button before measuring velocity at a new vertical. Repeat this process until depth and velocity measurements are obtained across the entire reach of the stream and are transcribed to the flow form. Figure 6 shows an example of a stream discharge form that has been filled out properly.

Measuring streamflow typically requires two people; one to collect depth and velocity measurements and another to record the data. For quality control purposes, data transcribers should always calculate the streamflow before taking down the tag line and leaving the sampling location. Streamflow is calculated by summing the discharges of all measurement verticals to obtain total discharge. Discharge at each vertical is determined by multiplying the vertical's cross sectional area with its observed velocity. Hence, vertical discharge = width * depth * velocity. Because depth and velocity were measured by the hydrographer in the previous steps, the data transcriber must now determine the width of each vertical in order to calculate

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discharge.

The width of the measurement vertical can be determined by using one of two different techniques. Using the first technique, known as the midsection method, width is determined by the distance extending halfway from the previous measurement vertical to halfway to the next vertical. Depth and velocity measurements at the vertical occur midsection or in the middle of the resulting subsection. (See Figure 4.) The second technique is called the endsection method. In this case, depth and velocity measurements at the measurement vertical occur at the far end of the rectangular subsection and width is determined by the distance from the previous observation interval to the observation vertical. See Figure 5 for a visual representation of the endsection method.

When comparing Figures 4 and 5, several differences can be noted between the midsection and endsection methods. Notice the first measurement vertical at the left bank edge. When using the midsection technique (Figure 4), width of this vertical extends to the right from the bank edge to midway to the next vertical. Width does not extend to the left because this area is out of the water and there is no flow. When using the endsection technique (Figure 5) as previously described, width of the bank vertical extends to the left from the bank to the previous vertical. Because this area is entirely out of water, width is considered to be zero and discharge is zero even though depth and velocity measurements at the bank edge are greater than zero. Notice also how width calculations vary between the two techniques when the increment used to take depth and velocity measurements suddenly changes in the stream cross section. Compare the widths of subsections 5 and 13 between Figures 4 and 5.

After determining the width of each measurement vertical and recording the width values in the third column of the stream discharge form, the data transcriber should next calculate the final streamflow. Multiply width of the measurement vertical (column 3 on the stream discharge form shown in Figure 1) by its depth (column 4) by its velocity (column 5) to obtain discharge at the vertical. Write this value in column 6. Sum up all of the values in column 6 to obtain total discharge and write this value in the space provided at the bottom of the form.

Because width calculations can vary between the midsection and endsection techniques, the final discharge calculations will also vary between the two methods. Differences will occur when the measurement interval changes in the stream cross section or when readings are taken at bank edge. Typically the difference in discharge calculations between the two techniques is minimal. For purposes of this document, the EPA Region 8 Laboratory will use the midsection technique when taking flow measurements with the velocity-area procedure. In the event that volunteers or other governmental personnel assist the Region 8 Laboratory with streamflow measurements and calculate discharge in the field using the endsection technique, EPA personnel will recalculate discharge using the midsection technique before reporting the data to project managers.

For quality control purposes, the calculated discharge at any one measurement vertical must not account for more than 10% of the total discharge. This QC measure, known as the 10% rule, assures that the hydrographer has taken enough depth and velocity measurements across the stream in order to accurately characterize its flow. After calculating total discharge, the data transcriber should next look for violations of the 10% rule. The easiest way to do this is to multiply total discharge by 0.1 and compare this value to those found in column 6 of the stream discharge form. Any value in column 6 that exceeds this calculated value is in violation of the 10% rule. When an exceedance is discovered, the hydrographer should return to the vertical where the exceedance occurs and take additional measurement verticals on either side. It is best to place the additional verticals at half the distance (midway) to the adjacent verticals. Record depth and velocity measurements of the new verticals on the discharge form and be sure to adjust the corresponding width calculations. Figure 6 shows an example of a stream discharge form where a violation in the 10% rule has occurred. When in the field, a hydrographer can take steps to prevent violation of the 10% rule. Always remember to decrease the flow increment and take more depth and velocity measurements in areas where water is deep and flowing rapidly.

Once an acceptable discharge value has been obtained without violations in the 10% rule, turn off the flowmeter, remove the flow sensor from the wading rod, and take down the tag line. Move on to the next

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sampling location.

11.3.1 Troubleshooting

When a hydrographer properly sets up a stream cross-section for measurements with a flow meter, few problems are likely to occur. In some cases, however, unusual flow patterns underneath the tag line can not always be observed prior to taking measurements. A hydrographer may discover that velocity suddenly turns negative at a measurement vertical, indicating that flow is moving upstream. When this occurs, look for obstacles upstream that are likely to be the source of the problem. Because circumstances will vary at each sampling location, several remedies can be considered. The best option is to move the tag line to a different location and retake the flow measurements, especially when the obstruction can not be removed. When time is a constraint and there is little negative flow, consider removing the obstruction, if possible. When doing so, be sure to observe how the flow pattern changes at the previously measured verticals and retake depth and velocity measurements at the affected verticals as necessary. In some cases, negative flow can not be avoided at a sampling location. When this occurs, rotate the flow sensor 180 degrees and face it directly into the negative flow so that an accurate velocity can be determined. Record the negative velocity on the discharge form and determine the negative discharge at the measurement vertical.

Problems can also occur when measuring flow on a stream with silty or mucky substrate. Soft substrate often causes the wading rod to sink while velocity measurements are taken. When this happens, the flow sensor is no longer positioned at the required depth and could result in an inaccurate velocity measurement. To avoid this problem, hold the wading rod on top of the substrate and sustain its weight to prevent it from sinking while taking measurements.

When using a Marsh-McBirney flowmeter, a "con lost" message will display on the screen when the sensor is taken out of the water. This error message may occur when attempting flow measurements in rapids where airspace is likely to disrupt the sensor's electromagnetic field. Velocity readings in white water are very inaccurate and should never be attempted. If possible, select a better cross-section with more laminar flow for measurements. A "con lost" message may also appear when the sensor is in the water, indicating that something is interfering with the velocity measurement. When this occurs, first check for obstructions. Remove any debris (algae, macrophytes, trash, etc.) that may have drifted in front of the sensor. If there are no obstructions, check for an oil or grease coating on the sensor. Clean if necessary with soap and water and do not use hydrocarbon solvents. If the problem still persists, clean the electrodes with a very fine grit (600) sandpaper. (Marsh-McBirney 1990)

Because flowmeters use an electromagnetic signal to determine water velocity, anything that is likely to interfere with this signal will disrupt measurements. Natural geologic features that produce their own electromagnetic field, such as magnetite for example, can hinder the performance of the flowmeter. Noisy readings, negative readings, and even "con lost" errors may result. To solve the problem, perform the measurements in a new location away from the electromagnetic interference.

11.4 Flume Procedure

Once a suitable flume location has been determined, select an appropriate sized flume for measurements. Choose a flume with a throat size that can handle the flowing volume of water but is not so large that flow decreases in velocity or pools as it passes through the throat. If flow is dispersed over a wide area, select a flume with wingwalls to assist with flow consolidation. Next, prepare the installation site. Remove any rocks, vegetation or other debris from the area that could obstruct flume installation or the flow measurement processes. Because flumes must remain level for an accurate discharge reading, remove any obstacles that tip the flume to one side or the other. Do not dig too much while removing substrate; a deep hole may disrupt the flow and could affect the quality of the measurement.

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Place a bubble level on top of the flume and install the device. Use a circular bubble level so it can be leveled in all directions. If a circular bubble level is unavailable, a bar-type level can also be used and rotated in all directions. Place the flume into the flow so water passes directly into the short end, through the throat, and out the longer back end. Position it so that flow is even and water does not bank against one side or the other. When using a flume with wingwalls, extend the wingwalls as much as possible so they do not interfere with the flow of water. Check the water depth gauge in the front to be sure that the flume is not upsidetown. Dam the flume by shoveling dirt and debris around it and the wingwalls. This process may require the assistance from a volunteer to hold the flume level while the surrounding area is disturbed. Be sure to seal the front edge so that water does not pass under the device. Check for leaks and fix as necessary. Remove any obstructions upstream that cause water to wave near the depth gauge.

Once the flume has been installed, measure the upstream water depth, H_a , using the gauge on the front and compare this value to the water depth at the downstream gauge, H_b . In order to assure an accurate flow measurement, water depth at H_a must be at least twice the depth at H_b . If H_a is not at least twice H_b , water is not flowing fast enough through the device. To correct this problem, install a flume with a smaller throat width or move it to a shallower location where water is flowing more rapidly. In cases where pooled slow-moving water is unavoidable, the hydrographer can narrow the flow channel and decrease water depth by shoveling material into the channel. Consolidating flow in this manner will cause water velocity to increase, making an acceptable flume measurement more likely. Figure 7 depicts a flume that has been setup in the appropriate manner.

Once acceptable flume readings have been obtained, fill out the header information on the top of a stream discharge form including the sampling station, facility/site description, sampling crew, and date/time. Record the water depths at H_a and H_b and the flume's throat width in the spaces provided on the form. Calculate the flow in gpm and cfs using the appropriate formulas for the flume's throat width and transcribe these values to the bottom of each column. Remove the flume from the stream and clean it as necessary. Use the shovel to restore the measurement location to pre-flume conditions.

11.4.1 Troubleshooting

The most difficult task when measuring flow with a flume is getting water to flow properly through the device so that H_a is at least twice H_b . As discussed in section 11.4, a hydrographer can choose a different location, use a smaller flume, or modify the stream channel in order to solve the problem. If these techniques do not work, consider using the two other methods to measure the flow.

11.5 Timed Filling Procedure

Once an appropriate location has been determined for the timed filling procedure, modify the location as needed to assure that all flow can be consolidated into the sampling device (bucket, flask, etc.) for the measurement period. Remove rocks or other obstacles that prevent flow from being captured. Fill out the header information on the top of a stream discharge form including the sampling station, facility/site description, sampling crew, and date/time. Place the sampling device into the flow and measure the time it takes to fill the device to a reasonable level using a stopwatch. Record the volume of water that is collected and the elapsed time in the timed filling section of the discharge form. Be sure to also mark the units of volume and units of time on the form. Perform at least five measurement trials. In the event that a significant difference in volume collected per unit time is noted between trials, more trials may be necessary to obtain an accurate measurement. Sum the total volume collected and total time observed across all trials and record in the appropriate spaces on the discharge form. Divide total volume by total time to obtain an average discharge reading and transcribe it to the form. Proceed to the next sampling location.

11.5.1 Troubleshooting

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Problems will arise with the timed filling procedure when the sampling device (bucket, flask, etc.) is not the appropriate size for the flowing volume of water. It would be very difficult, for example, to use a 5 gallon bucket to measure a 300 gpm discharge surging from the end of a culvert. Likewise, a 5 gallon bucket could be too large for a mere trickle of water. If the sampling device is not the appropriate size for the volume of water, choose a different size or consider using one of the two other methods to measure the flow.

12.0 Data Analysis and Calculations

Sections 11.3 thru 11.5 describe all data analysis and calculation procedures that need to be performed in the field. Formulas used to calculate discharge using a flume are shown on the stream discharge form in Figure 1. Report discharge in cubic feet per second (cfs) unless otherwise requested by project managers. In the event that discharge needs to be reported in gallons per minute (gpm), use the following formula to convert units from cfs to gpm:

$$\text{gpm} = \text{cfs} * 448.8$$

Recalculate discharge upon return to the office using a spreadsheet to fix any transcription or rounding errors that may have occurred in the field. Figure 8 displays how a spreadsheet can be designed for final discharge calculations for all three flow techniques.

13.0 Computer Hardware and Software

As discussed in section 12.0, use spreadsheet software to calculate final discharge measurements before presenting the data to project managers. Choose between a number of different programs offered by various manufacturers, including: Lotus 123, Microsoft Excel, or Corel Quattro Pro.

14.0 Quality Control

When measuring flow in the field, hydrographers may encounter a flow device that is permanently installed near their sampling location. Devices may include Parshall flumes, cutthroat flumes, weirs, USGS staff gages, or real-time USGS streamflow gages. Hydrographers may choose to compare the streamflow data they collect in the field to the streamflow data measured by these devices for quality control (qc) purposes. Always contact the owner of the flow device to be sure that it has been properly serviced, calibrated, and maintained for accurate measurements. Flow data from real-time USGS streamflow gages can be accessed on the internet at <http://waterdata.usgs.gov/nwis/rt/>. Simply select the state in which the gage is located and then select the gage from the corresponding state map. Because real-time flow data is only available for a limited time, be sure to visit the website shortly after returning from the field event.

When encountering a USGS staff gage, contact the USGS to determine the accuracy of the device (whether or not it has been properly maintained) and to obtain a flow-rating curve. Be sure to record the gage measurement in the space provided near the bottom of the discharge form. In the event that USGS has not properly maintained the device, the measurement can not be used for qc purposes. When encountering a flume, record the throat width, the upstream height (H_u), and the downstream height (H_d), if available, on the discharge form. Also note the type of flume on the discharge form and consult the owner for the appropriate discharge formula. If necessary, consult the Bureau of Reclamation Water Measurement Manual for additional assistance. (US Department of Interior Bureau of Reclamation 1974)

Because streamflow constantly changes, the EPA Region 8 Laboratory does not recommend that hydrographers take duplicate flow measurements for qc purposes, especially during periods of high runoff. When duplicate flow measurements are required for the sampling event, take the measurements at the exact same time and do so in a manner where they do not interfere with each other.

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Enter all flow data into a spreadsheet after the field event for final calculation of discharge. This step will fix any rounding or transcription errors that may have occurred in the field when using the calculator. The EPA Region 8 Laboratory will store flow data in the Laboratory Information Management System (LIMS) and will peer review it before presentation to project managers. Additional qc procedures for the three flow techniques are described below.

14.1 Velocity-Area Procedure

Hydrographers should consult their flowmeter's instruction manual for specific requirements regarding instrument calibration. Marsh-McBirney, the manufacturer of the EPA Region 8 flowmeters, recommends that hydrographers perform a zero adjust calibration procedure at least once per year. The zero adjust procedure calibrates the sensor to zero velocity. To perform this procedure, first clean the sensor with soap and water to remove any oil or grease coatings that may cause noisy readings or conductivity lost errors. After cleaning, place the sensor in a 5 gallon bucket of water at least three inches away from the sides and bottom of the bucket. To assure that the water is not moving, wait ten to fifteen minutes after positioning the sensor. Press the STO and RCL keys at the same time to initiate the zero adjust sequence. When the number "3" displays on the screen, decrement the value to zero by pressing the "1" key. The number "32" will display next and will automatically decrement itself to zero and the unit will turn off. The meter is now calibrated to zero velocity. Document performance of the zero adjust procedure in the meter's calibration logbook.

Marsh-McBirney flowmeters can also be calibrated by the manufacturer to a known velocity. If velocity readings appear unusual after performing the zero adjust procedure, return the unit to the following address for calibration:

Marsh-McBirney, Inc.
4539 Metropolitan Ct.
Frederick, MD 21704-8364
(800) 368-2723

Upon receipt of the unit, Marsh-McBirney will run a sensor performance check by placing the probe in water that is moving at a known velocity. If the sensor fails the performance check, Marsh-McBirney will perform a factory calibration for a certain fee. The instruction manual makes no recommendations as to how often a factory calibration should be performed. The EPA Region 8 Laboratory will return flowmeters to Marsh-McBirney for performance checks and factory calibration when problems are noted with the zero adjust procedure or when performance has been compromised.

As noted in section 11.3, hydrographers should always calculate streamflow prior to taking down the tag line and proceeding to the next sampling location. In the event that an exceedance in the 10% rule is discovered at a measurement vertical, the hydrographer should return to the vertical where the exceedance occurs and take additional measurement verticals on either side. Additional quality control procedures are noted in section 11.3.1.

14.2 Flume and Timed Filling Procedures

Quality control procedures for flumes are described in sections 11.4 and 11.4.1. Quality control for the timed filling method is described in sections 11.5 and 11.5.1. It is important to note that instrument calibration is not required when measuring flow using these two procedures.

15.0 Data and Records Management

A copy of the field form used for discharge measurements is stored on the EPA Region 8 Laboratory's G drive at G:\Forms\DischargeForm.wpd. Hardcopies of all discharge forms that are filled out in the field will be stored with their corresponding field data package at the Region 8 Laboratory. Final discharge measurements will be hand entered into the EPA Region 8 Laboratory Information Management System (LIMS) for storage and presentation

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to project managers.

16.0 Pollution Prevention

Because of recent outbreaks of invasive species, hydrographers must take adequate precautions to prevent the spread of these species to other watersheds. Before performing fieldwork, hydrographers should familiarize themselves with locations where invasive species have been documented. In the event that work is to be performed in these locations, hydrographers must take adequate care to clean and disinfect their waders before leaving a sampling location. It is also highly recommended that hydrographers perform these steps after sampling in areas not known to have invasive species. Commercial products such as bleach or Formula 409 can be used to clean and disinfect waders and boots. These products are known to be effective in preventing the spread of *Didymosphenia geminata*, the New Zealand Mudsnail, and whirling disease, among others.

17.0 Waste Management

All batteries used in flowmeters will be recycled to minimize waste. No other waste is produced while measuring streamflow.

18.0 References

Baski Water Instruments, Inc. Cutthroat Flumes. <http://www.baski.com/other.htm> 800-552-2754.

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Figure 1: Stream Discharge Form

Sampling Station: _____ Sampling Crew: _____
 Facility/Site: _____ Date/Time: _____

<input type="checkbox"/> Velocity-Area					
Distance Units <input type="checkbox"/> ft <input type="checkbox"/> m <input type="checkbox"/> cm		Depth Units <input type="checkbox"/> ft <input type="checkbox"/> m <input type="checkbox"/> cm		Velocity Units <input type="checkbox"/> ft/s <input type="checkbox"/> m/s	
Total Stream Width:			Meter Type:		
Tape Measure Reading	Distance to Opposite Bank	Width (A)	Depth (B)	Velocity (C)	Discharge (A*B*C)
Total Discharge:					

<input type="checkbox"/> Timed Filling			
Volume Units <input type="checkbox"/> l <input type="checkbox"/> qt <input type="checkbox"/> gal		Time Units <input type="checkbox"/> sec <input type="checkbox"/> min	
Trial	Volume	Time	Notes
1			
2			
3			
4			
5			
Total Volume:		Total Time:	Total Discharge (Vol/Time):

<input type="checkbox"/> Flumes		
Throat Width (Inches): <input type="checkbox"/> 1 <input type="checkbox"/> 2 <input type="checkbox"/> 4 <input type="checkbox"/> 8		
h _u = Upstream gauge height in feet = _____		
h _d = Downstream gauge height in feet = _____		
Throat Width	Flow Rate	
	CFS	GPM
1 Inch	0.50 h _u ²	225 h _u ²
2 Inch	1.02 h _u ²	458 h _u ²
4 Inch	2.08 h _u ²	932 h _u ²
8 Inch	4.22 h _u ²	1900 h _u ²
Total Flow (cfs & gpm) _____		

<input type="checkbox"/> USGS Staff Gauge
Staff Gauge Reading: _____

Notes/Comments

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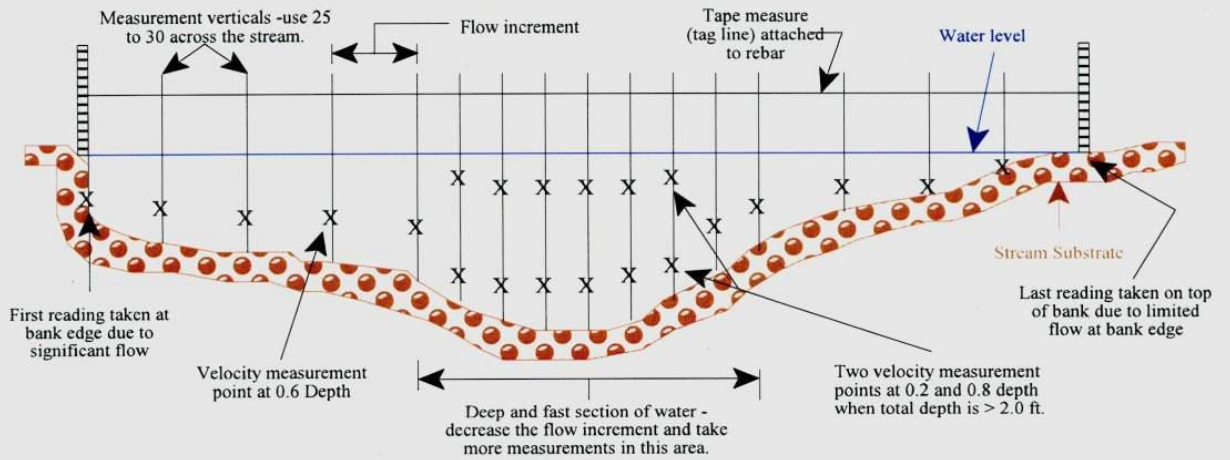


Figure 2: Stream cross section showing measurement verticals and velocity measurement points.

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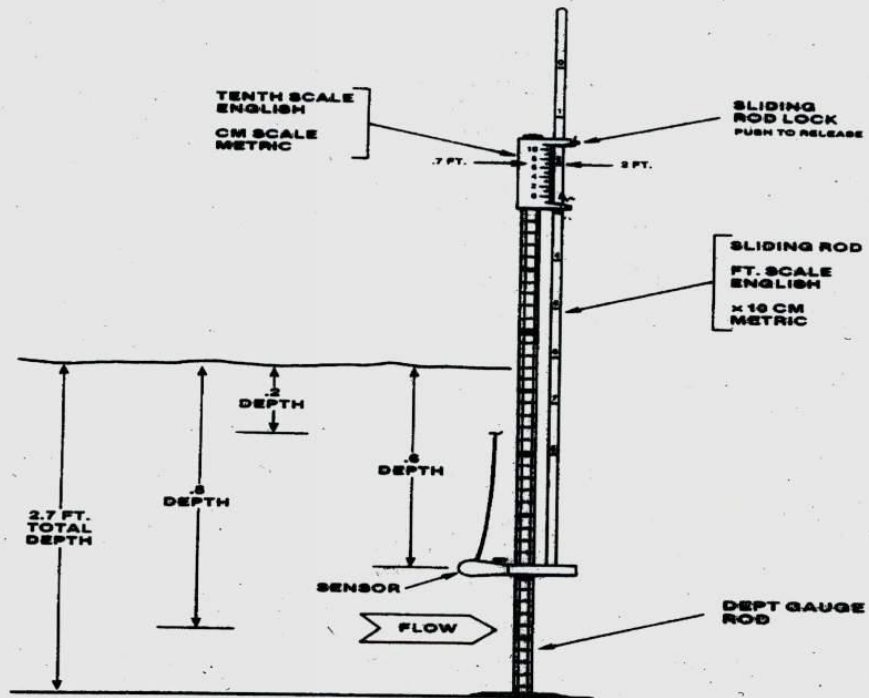


Figure 3: Top setting flow wading rod with a Marsh McBirney flow sensor.

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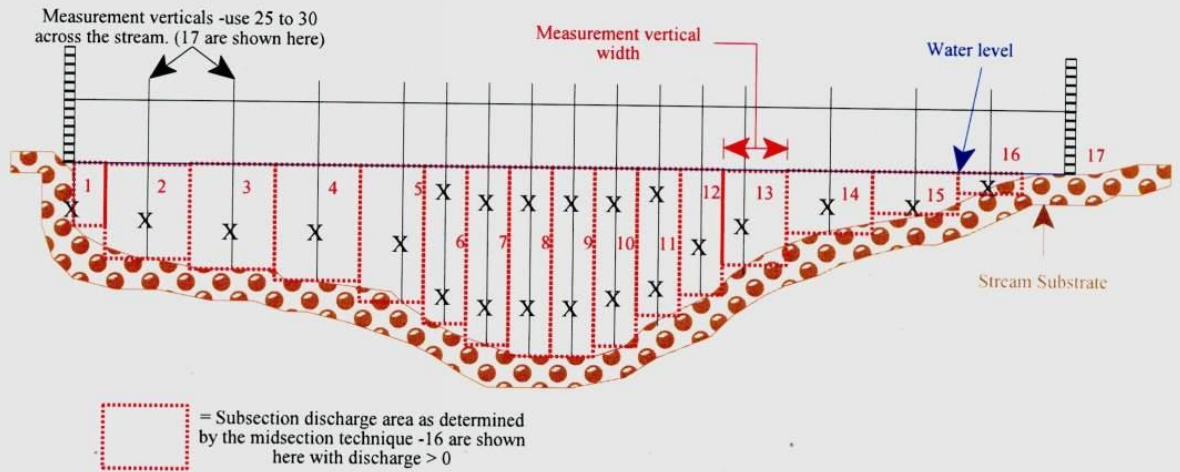


Figure 4: Streamflow measurements using the midsection technique

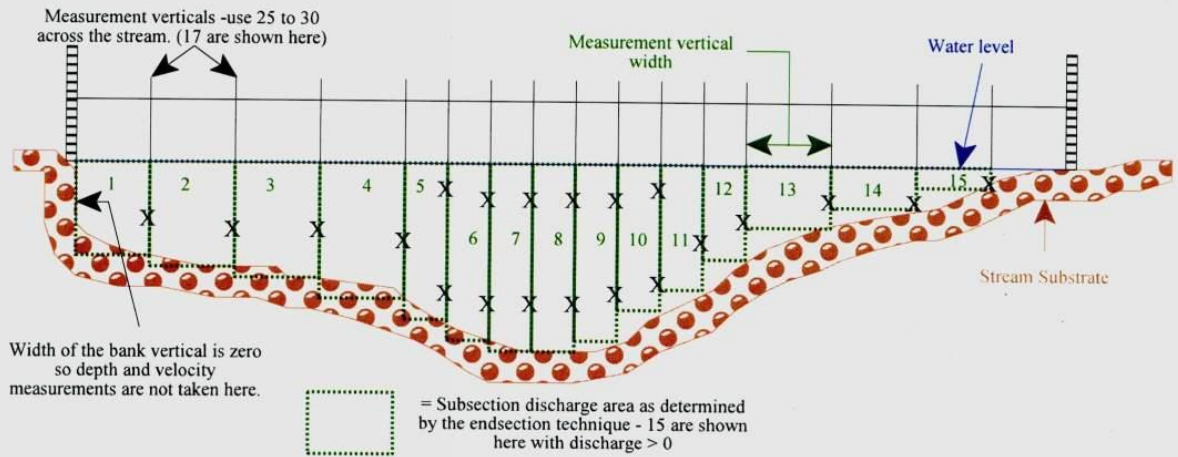


Figure 5: Streamflow measurements using the endsection technique.

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Figure 6: Example of a stream discharge form with a violation of the 10% rule

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Stream Discharge Form

Sampling Station: UR-XY Sampling Crew: WCS, SDS
 Facility/Site: Uncompahgre Divs Red Mtn. Date/Time: EXAMPLE ONLY

<input type="checkbox"/> Velocity Area					
Distance Units		Depth Units		Velocity Units	
<input checked="" type="checkbox"/> ft <input type="checkbox"/> m <input type="checkbox"/> cm		<input checked="" type="checkbox"/> ft <input type="checkbox"/> m <input type="checkbox"/> cm		<input checked="" type="checkbox"/> ft/s <input type="checkbox"/> m/s	
Total Stream Width: <u>30 FT</u>			Meter Type: <u>Marks Mc Birney</u>		
Tape Measure Reading	Distance To Opposite Bank	Width (A)	Depth (B)	Velocity (C)	Discharge (A*B*C)
<u>30</u>	<u>0</u>	<u>1</u>	<u>0</u>	<u>0</u>	<u>0</u>
<u>28</u>	<u>2</u>	<u>2</u>	<u>0.6</u>	<u>1.13</u>	<u>1.356</u>
<u>26</u>	<u>4</u>	<u>2</u>	<u>1.1</u>	<u>1.46</u>	<u>3.212</u>
<u>24</u>	<u>6</u>	<u>2</u>	<u>1.8</u>	<u>2.36</u>	<u>8.496</u>
<u>22</u>	<u>8</u>	<u>1.5</u>	<u>1.7</u>	<u>1.40</u>	<u>3.57</u>
<u>21</u>	<u>9</u>	<u>1</u>	<u>* 2.1</u>	<u>0.2: 1.39</u>	<u>3.024</u>
				<u>0.8: 1.49</u>	
				<u>AVG: 1.44</u>	
<u>20</u>	<u>10</u>	<u>1</u>	<u>1.9</u>	<u>1.32</u>	<u>2.508</u>
<u>19</u>	<u>11</u>	<u>1</u>	<u>1.8</u>	<u>1.23</u>	<u>2.214</u>
<u>18</u>	<u>12</u>	<u>1.5</u>	<u>1.6</u>	<u>1.48</u>	<u>3.552</u>
<u>16</u>	<u>14</u>	<u>2</u>	<u>1.7</u>	<u>1.19</u>	<u>4.046</u>
<u>14</u>	<u>16</u>	<u>2</u>	<u>1.8</u>	<u>1.20</u>	<u>4.32</u>
<u>12</u>	<u>18</u>	<u>2</u>	<u>0.7</u>	<u>2.56</u>	<u>3.584</u>
<u>10</u>	<u>20</u>	<u>2</u>	<u>1.1</u>	<u>1.86</u>	<u>4.092</u>
<u>8</u>	<u>22</u>	<u>2</u>	<u>0.8</u>	<u>2.32</u>	<u>3.712</u>
<u>6</u>	<u>24</u>	<u>2</u>	<u>0.9</u>	<u>1.65</u>	<u>2.97</u>
<u>4</u>	<u>26</u>	<u>2</u>	<u>1.1</u>	<u>2.03</u>	<u>4.466</u>
<u>2</u>	<u>28</u>	<u>2</u>	<u>0.6</u>	<u>0.47</u>	<u>0.564</u>
<u>0</u>	<u>30</u>	<u>1</u>	<u>0.4</u>	<u>0.12</u>	<u>0.048</u>
Total Discharge:					<u>55.7</u>

<input type="checkbox"/> Timed Filling			
Volume Units		Time Units	
<input type="checkbox"/> l <input type="checkbox"/> qt <input type="checkbox"/> gal		<input type="checkbox"/> sec <input type="checkbox"/> min	
Trial	Volume	Time	Notes
1			
2			
3			
4			
5			
6			
Total Volume:		Total Time:	Total Discharge (Vol/Time):

<input type="checkbox"/> Flumes		
Throat Width (Inches): <input type="checkbox"/> 1 <input type="checkbox"/> 2 <input type="checkbox"/> 4 <input type="checkbox"/> 8		
h_u = Upstream gauge height in feet =		
h_d = Downstream gauge height in feet =		
Throat Width	Flow Rate	
	CFS	GPM
1 Inch	$0.50 h_u^2$	$225 h_u^2$
2 Inch	$1.02 h_u^2$	$458 h_u^2$
4 Inch	$2.08 h_u^2$	$932 h_u^2$
8 Inch	$4.22 h_u^2$	$1900 h_u^2$
Total Flow (cfs & gpm)		

<input type="checkbox"/> USGS Staff Gauge
Staff Gauge Reading:

Notes/Comments
* NOTE: depth is greater than 2.0 Feet so velocity is measured AT 0.2 + 0.8 AND AVERAGED FOR THE FINAL DISCHARGE CALCULATION ✓ 10% OF 55.7 = 5.57. THE 10% RULE IS EXCEEDED AT 24 FEET ON THE TAPE MEASURE. TAKE DEPTH AND VELOCITY AT 25 + 23 FEET ON TAPE TO SOLVE THIS PROBLEM!

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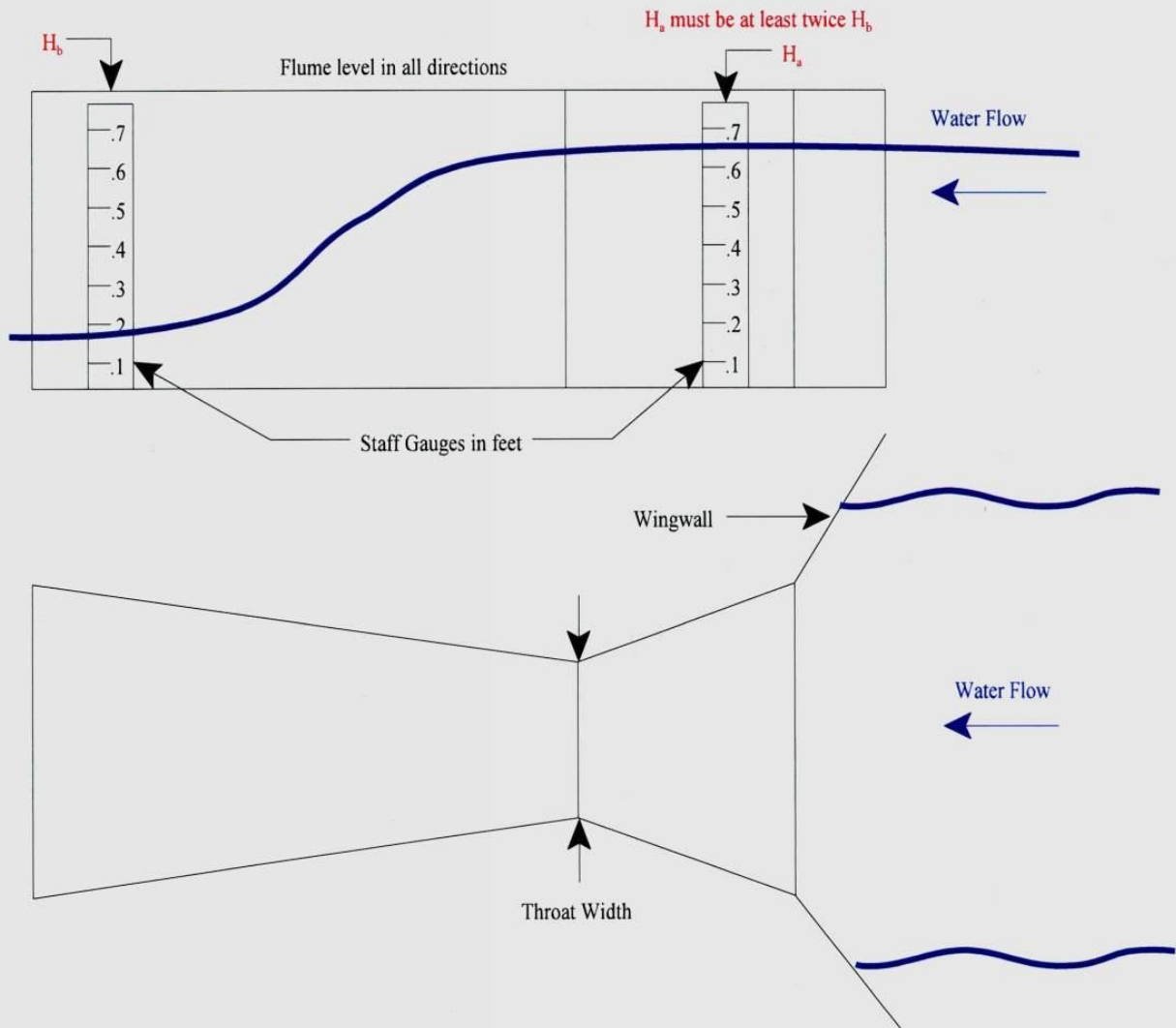


Figure 7: Diagram of proper flume installation

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Figure 8: Flow Calculation Spreadsheet

Velocity-area Procedure:															
Station ID:		^A Width (ft):	---	---	---	---	---	---	---	---	---	---	---	---	---
		^B Depth (ft):	---	---	---	---	---	---	---	---	---	---	---	---	---
		^C Velocity (ft/sec):	---	---	---	---	---	---	---	---	---	---	---	---	---
Date & Time:		^{A^{B^C} Discharge (cfs):}	0	0	0	0	0	0	0	0	0	0	0	0	0
Total Width (ft):	0	^A Width (ft):	---	---	---	---	---	---	---	---	---	---	---	---	---
		^B Depth (ft):	---	---	---	---	---	---	---	---	---	---	---	---	---
Total Flow (cfs):	0	^C Velocity (ft/sec):	---	---	---	---	---	---	---	---	---	---	---	---	---
		^{A^{B^C} Discharge (cfs):}	0	0	0	0	0	0	0	0	0	0	0	0	0

Timed filling Procedure:															
Station ID:		Volume (quarts):	---	---	---	---	---	---							
Date & Time:		Time (seconds):	---	---	---	---	---	---	Average =	0	qts/sec	=	0	gpm	
Total Flow (cfs):	0														
Total Flow (gpm):	0	quarts/second:	0	0	0	0	0	0	=	0	cfs				

Flume Procedure:						
Station ID:		Throat Width:	H _a	cfs	gpm	H _b
Date & Time:		1 Inch:	---	0	0	---
Total Flow (cfs):		2 Inch:	---	0	0	---
Total Flow (gpm):		4 Inch:	---	0	0	---
		8 Inch:	---	0	0	---

Appendix 5

Supplemental Procedures for Discharge Measurements at Seeps and Springs

Hydrological measurements for water quantity (discharge) will follow SOP 722 in Appendix 3. This appendix provides supplemental procedures in greater detail to be followed for various conditions encountered. Five potential methods to measure springs flow, ranging from standard streamflow cross-section velocity measurement, to the use of portable flumes or weirs, to simple capture, to the measurement of wetted patch area (when flow is unmeasurable). Table 1 lists the various instruments recommended for the range of discharges which occur in springs. Three additional methods are listed in the procedures (float velocity, static head change, and visual estimation), but these methods will generally be avoided, unless all other instruments are unable to measure discharge. Replicated flow measurements are needed to develop a trustworthy mean value and ascertain uncertainty around the measurement. It is recommend that at least three measurements be made and the average calculated.

Table 1: Measurement requirements for variable discharge ranges.

Discharge magnitude	Discharge (gpm)	Discharge (metric)	Instrument(s)
Unmeasurable	Not enough to measure	Not enough to measure	Depression
First	< 0.12	< 10 mL/s	Depression, Volumetric
Second	0.12 to 1.0	10 to 100 mL/s	Weir, Volumetric
Third	1.0 to 10	0.1 to 1 L/s	Weir, Flume
Fourth	10 to 100	1 to 10 L/s	Weir, Flume
Fifth	100 to 500	10 to 100 L/s	Flume
Sixth	> 500	> 0.1 m ³ /s	Current meter

Flow

Overview: Measure the quantity of water discharging from the spring. If the discharge of the spring is low (unmeasurable or first magnitude), the discharge measurement may take dozens of minutes and should be initiated early in the site visit. Second to fifth magnitude discharges are relatively quicker and easier to measure. The name,

serial number (if available), and accuracy of the instrument used to measure discharge should be recorded as well as any other important observations. Important observations may include the markers of any recent high discharges, such as high water marks, oriented vegetation or debris on or above the channel or floodplain. The following sections describe eight specific techniques to measure small discharges based on recommended techniques from the U. S. Geological Survey (Buchanan and Somers, 1984).

1. Volumetric measurements procedure

Volumetric measurements are typically used in first and second magnitude discharge springs (Table 1), where there is a pour off or other features that allow flow to be easily captured in a volumetric container. A temporary earthen dam is constructed using earth and non-permeable materials. Water is diverted through the temporary earthen dam with a temporary pipe or constructed channel. Flow is allowed to stabilize prior to measurement. A volumetric container is used to catch discharge from the pipe. The time to fill the container is recorded. Flow is recorded 3 to 5 times over a 3 to 5-minute interval, as appropriate. The mean value is calculated (mL/s) and recorded. Accuracy of the instrument is dependent upon the accuracy of the volumetric container. A suite of varying size of containers that are appropriate for first to second magnitude discharge springs should be taken to the field site. When not used for volumetric measurements, the containers can be used to help pack various other field gear used for the rapid assessment.

2. Portable weir plate procedure

Typically, weirs are used to measure discharge in spring channels which have low to moderate magnitude values of discharge. The weir pushed into a channel of loose material. The weir has a "V" notch, or other regular geometric shape through which all discharge in the channel must be focused. The weir should have a scale on the weir which directly reads discharge. The weir should have a solid plate below the notch which is driven into the loose material of the stream bed material. Weirs do not work in bedrock channels or channels with bed material coarser than fine gravel without a significant amount of channel modification. To use a weir in a bedrock channel or channel material coarser than gravel, the channel must be significantly modified for weir emplacement.

Once placed in the channel, the weir is leveled using a bubble level. The top of the weir plate is made horizontal and the plate must be plumb. Flow through the weir is allowed to stabilize prior to measurement. Gage height is recorded 3 to 5 times over a 3 to 5 minute interval, as appropriate. The mean is calculated from the three replicates and recorded. The volumetric discharge (m^3/s or l/s) is calculated using a standard equation specific to the weir plate being used. The accuracy of the weir is dependent on the size of the notch in the weir and the resolution of the scale of the weir.

3. Portable Parshall Cutthroat Flume procedure (Flume)

Typically, flumes are used in third to sixth magnitude discharge springs (Table 1). Flumes work best in low gradient channels with fine-grained bed material. The wing walls of the flume are pointed upstream in the channel in such a fashion as to focus as much flow as possible through the regular profile of the opening of the flume. The flume requires free fall of water out the downstream end of the flume. The flume is set in a channel of loose material. A bubble level is used to make sure the flume is level. The floor of the upstream section is leveled both longitudinally and transversely. Flow is allowed to stabilize prior to measurement. Gage height is recorded 3 - 5 times over a 3-minute interval. A standard rating curve for the flume is used to translate gage height to discharge. The mean value for discharge (m^3/s or l/s) is calculated and recorded. Accuracy of the instrument is dependent on the scale on the flume. On some occasions, it may not be possible to capture 100 % of the discharge in the flume. If less than 100 % of the discharge is captured by the flume, the percent of flow captured by the flume should be estimated by for each of the 3 to 5 measurements and recorded. A correction to the discharge measurement should be made to account for the percent of discharge not captured by the flume.

4. Current meter procedure

Current meters are used for measuring flow in wadable spring streams, wide channels, or high discharge channels where flow cannot be routed into a weir or a flume. Measurement locations are selected in a straight reach where the streambed is free of large rocks, weeds, and protruding obstructions that create turbulence, and with a flat streambed profile to eliminate vertical components of velocity. In the making of a discharge measurement, the cross section of the channel is divided into 20 to 30 partial sections, and the area and mean velocity of each section is measured separately. A partial section is a rectangle whose depth is equal to the measured depth at the location and whose width is equal to the sum of half the distances of the adjacent verticals. At each vertical, the following observations are recorded on the data sheet, (1) the distance to a reference point on the bank along the tag line, (2) the depth of flow, (3) the velocity as indicated by the current meter. The velocity should be measured at a depth which is 0.6 of the depth from the surface of water in the channel. The discharge of each partial section is calculated as the product of mean velocity times depth at the vertical times the sum of half the distances to adjacent verticals. The sum of the discharges of each partial section is the total discharge. Measurements are made by wading the stream with the current meter along the tag line. The person wading the channel should stand downstream of the velocity meter. Because of the safety involved in wading a channel, the person wading should not wade in too deep of water or should not use hip waders in swift water without the use of a safety rope or other appropriate safety gear. A life jacket will be worn during high flow conditions.

5. Float velocity procedure

Two cross sections are selected and marked with flagging along a reach of straight channel. The distance between the two sections is measured with the measuring tape. The width and depth of each channel cross section is measured with the tape measure and recorded. Cross section locations are separated to allow for a travel time of >20 seconds float time (if possible). A float, i.e., wooden disk(s), is placed in the stream channel and allowed to reach stream velocity before the upstream cross section is crossed. The position of the float relative to the channel sides is noted. The float is timed between the two cross sections. The position of the float is noted as it crossed the downstream cross section. This procedure is repeated 3 to 5 times, as the float is placed at different locations across the channel at the upstream cross-section. The velocity of the float is equal to the distance between the cross sections divided by the travel time. The mean value of surface horizontal velocity (m/s) is calculated. To convert mean surface velocity to mean vertical velocity a coefficient of 0.85 is multiplied by the mean surface velocity. Discharge (m^3/s) is calculated by multiplying the value of mean velocity by the average area of the section of the stream channel measured. This is a method of last choice compared to the more accurate velocity measurement techniques listed above.

6. The depression/sump procedure

This method is typically used for unmeasurable to first magnitude springs with little to no surface expression of flow. This method is used for relative comparison value of discharge. A depression is constructed in the seep area. The volume of depression is calculated using volumetric calibration or calculation. The volumetric containers used for the volumetric measurement may be used to estimate the volume of the depression. The depression is evacuated, and the time required to fill depression is recorded. This procedure is repeated 3 to 5 times and the mean value is recorded as the measurement.

7. The static head change procedure

This method may be used for a relative comparison value for change in elevation of standing pools. A metric staff gage is placed in the standing pool and relative gage elevation recorded, or efforts are made to locate and record an existing fixed point in or near standing pool and record vertical distance to pool surface. At a later date, the changes in the static head on the staff gage or fixed point are recorded. This measurement technique is of last choice compared to the more accurate methods listed in the protocol and should only be used if necessary.

8. Visual estimate procedure

Site conditions, such as dense vegetation cover, steep or flat slope, diffuse discharge into a marshy area, and dangerous access sometimes do not allow for a direct measurement of discharge by the techniques listed above. Although visual estimation is imprecise, it may be the only method possible for some springs. Photographs should be taken to record the surface area wetted or covered by water and

observations recorded on the datasheet. Also, it should be noted if another method could be recommended for future site visits to measure discharge.

Appendix 6

CDM Federal Programs Corporation Change Request Form

Contract/Project: _____ Date: _____

Requested by: _____

Description of requested change: _____

Reason for change: _____

Expected results or impact: _____

Submit this form to the project manager immediately.

Required before implementation of major changes:

Approved by: _____ (Project Manager) Date: _____

Approved by: _____ (Title: _____) Date: _____

Appendix 7



INTERNAL NRMRL PROCEDURE

Standard Operating Procedure for Measurement of Lead and Uranium Isotopic Ratios by High Resolution ICP-MS

NRMRL Standard Operating Procedure (SOP)

Title:	Standard Operating Procedure for Measurement of Lead and Uranium Isotopic Ratios by High Resolution ICP-MS		
Division/Staff:	GWERN/Technical Staff		
SOP Number:	NRMRL-GWERN-16-0		
Former SOP Number: (if applicable)	N/A		
Effective Date:	Date Management Approves		
SOP Author(s)			
Name: * Richard Wilkin	Name:		
Name:	Name:		
Name:	Name:		
Name:	Name:		
QA Approval			
Name: Steve Vandegrift	Signature/Date:		
SHEM Approval			
Name: Steve Musson	Signature/Date:		
Management Approval			
Name: Ann Keeley	Signature/Date:		
Name:	Signature/Date:		

* Primary Author

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1 INTRODUCTION

This document describes the procedure for lead (Pb) and uranium (U) analysis of aqueous samples and digestates for isotopic determination of Pb-204, Pb-206, Pb-207, Pb-208, U-234, U-235, and U-238 by High Resolution- ICP-MS (Inductively Coupled Plasma - Mass Spectrometry). ICP-MS methods are commonly used for the determination of Pb isotope ratios (Cuvier et al., 2016; Graney and Landis, 2013; Hosono et al., 2016). The traditional method for high precision isotopic analysis of U has been thermal ionization mass spectrometry (TIMS). The TIMS measurement precision is limited by time dependent mass fractionation and sample preparation using this method is time consuming. The magnetic sector HR-ICP-MS is capable of achieving nearly comparable precision and accuracy of TIMS, with less requirement in sample preparation (e.g., Krachler et al., 2004; Pappas et al., 2003; Marin et al., 2013). This method will be used in groundwater and sediment research to support the agency's regional and programmatic needs for understanding Pb and U behavior in the environment.

2 SCOPE

This standard operating procedure (SOP) applies to the Ground Water and Ecosystems Restoration Division (GWERD) staff that will perform isotopic analysis using the Thermo Scientific Element XR HR-ICP-MS. This SOP describes the analysis of Pb and U isotopic ratios in aqueous samples (typically groundwater or surface water) and digestates (typically microwave assisted digested solids). The digestion method for solids is described in a separate RSKSOP-180.

3 DEFINITIONS

<u>Term</u>	<u>Definition</u>
CRM	Certified Reference Material
DI	Deionized Water
HDPE	High Density Polyethylene
HR	High Resolution
ICP	Inductively Coupled Plasma
ICV	Initial Calibration Verification Standard
LDPE	Low Density Polyethylene
MS	Mass Spectrometry
PI	Principal Investigator
RO	Reverse-Osmosis (Water)
RPD	Relative Percent Difference
SOP	Standard Operating Procedure
SRM	Standard Reference Material

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4 ROLES AND RESPONSIBILITIES

This SOP applies to all GWERD staff with duties related to the use of the Thermo Scientific Element XR HR -ICP-MS. Prior to analyzing samples, staff should be trained and familiar with operation of this instrument and must demonstrate competency in implementation of this procedure. In addition, all staff must have completed required safety training before operating the instrument or carrying out related laboratory procedures.

Primary Analyst

The primary analyst responsibilities include the maintenance of the HR-ICP-MS; proper operation of the ICP and other equipment needed for the analysis; and maintaining supplies needed for conducting analyses covered by this SOP. The primary analyst is also responsible for performing the initial data verification of the data collected, ensuring that complete and accurate records are kept and maintained, and ensuring that the proper collection of these records is achieved. The primary analyst is also responsible for contacting the Principal Investigator (PI) about analytical issues that may arise. Finally, the primary analyst is responsible for implementing any corrective actions needed.

Data Validator

The data validator is responsible for providing a secondary independent data verification to confirm that all data meet the QA requirements of the analysis. The data validator will either pass the data on to the appropriate PI or will work with the primary analyst to rectify any QA problems noted, if possible, and ensure that all needed QA comments are documented in the analytical report.

7. Principal Investigator

The PI is responsible for ensuring that all required information is supplied to the primary analyst prior to sample analysis and for addressing any analytical issues that the primary analyst may have concerning the samples submitted for analysis (Failure to do so may result in delays in sample analysis or samples not being analyzed.). The PI is also responsible for ensuring that the data received meet the QAPP requirements. The GWERD metals lab is not responsible for additional QA requirements outside of the SOP requirements, for example field data collection QA requirements. Finally, the PI is responsible for maintaining data records for their project as required by the PI's QAPP and per the Agency File Code and Retention cited in Section 6.

5 PROCEDURES

12. Method Summary

Prior to analysis, samples must be solubilized or digested using appropriate preparation methods. When analyzing groundwater or surface water samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis. The Thermo Scientific Element XR is a double-focusing magnetic sector mass spectrometer capable of simultaneous analysis of most elements with a concentration range spanning up to 12 orders of

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magnitude. Aqueous samples and digestates are nebulized into a spray chamber, and a stream of argon carries the sample aerosol into the plasma with a very high temperature (~6000 K), where sample particles are atomized, ionized, and excited. Sample particles are swept through a sample cone into a vacuum chamber where the elemental mass of atoms and ions are quantified with a channel electron multiplier (counting mode detection).

The instrument has three resolution settings low, medium, and high that allow for increased separation of isotopes. In the Pb isotope method, analysis is conducted in low resolution where flat top peaks are obtained. The concentration of Pb is diluted to about 1.5 ppb to remain within counting mode detection and prevent tripping into analog mode detection. The method monitors the Pb-204, Pb-206, Pb-207, and Pb-208 masses. NIST Standard Reference Material (SRM) 981 Common Lead Isotopic Standard is used to determine and correct for mass bias (Yuan et al., 2016). In the U isotope method, analysis is also conducted in low resolution. The concentration of U is diluted to about 1 ppb to remain within counting mode detection and prevent tripping into analog mode. The method monitors the U-234, U-235, and U-238 masses. New Brunswick Lab (US DOE) Certified Reference Material (CRM) 145 Uranyl (Normal) Nitrate Assay and Isotopic Solution is used to determine and correct for mass bias.

5.2 Sample Preservation, Containers, Handling, and Storage

For the determination of isotopic ratios of Pb and U in aqueous and total recoverable samples, samples are acidified with HNO₃ to pH<2 in plastic (HDPE, LDPE) sample bottles. The concentration of Pb and/or U must be known from previous analyses by ICP-MS, using NRMRL-GWERD 11-0, for example. A single analysis for isotopic ratios requires a maximum of about 8 mL of sample with either 1 ppb U or 1.5 ppb Pb. These are nominal concentrations that depend on conditions of the skimmer and sampler cones, sample introduction settings, and the condition and efficiency of the detector. Prior to preparing samples for analysis, tests should be performed with standard U or Pb solutions to determine optimal concentrations that return approximately 3×10^6 cps of the most abundant isotopes (U-234 or Pb-208). This approach of determining optimal concentrations for instrument conditions prior to analyzing samples will provide for the best counting statistics on all determined isotopes, particularly the low mass abundance isotopes U-234, U-235, and Pb-204, and insure that instrumental detection remains within range of the pulse counting detector and prevent tripping into analog mode detection which introduces a source of uncertainty into isotope ratio measurements. Ideally, all samples and QC checks are run at the same concentration level for total U and/or Pb, but this is not mandatory since detector dead time is corrected for (see Section 5.7.5). Samples that are run at concentrations below the optimal determined values for any run will be noted in the analytical reports. Any required sample dilutions are prepared with 2% HNO₃. Generally, 50 mL of diluted sample is required to fulfill all QC checks and the possibility of re-analysis. In some cases, sample volumes less than 50 mL will be accepted for analysis, but it will be acknowledged in the analytical report if certain QC samples were not completed due to inadequate sample volume. For the determination of dissolved samples, a sample must be filtered through a 0.45 μm filter and acidified with HNO₃ to pH<2 prior to receipt by the laboratory. The holding time for analysis using this SOP is 6 months. Refrigeration is not required, but samples will generally be kept in a refrigerator.

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Aqueous samples that have been prefiltered and acidified will not need acid digestion. Digestion procedures for total recoverable metals in aqueous samples and in other matrices can be found in individual SOPs (RSKSOP-179; RSKSOP-180).

Samples that are to be analyzed using this procedure must be free of solids. Solids will plug the sample introduction probe and the nebulizer. Samples that are particle-free may be analyzed directly for Pb and U isotopic ratios. Digested samples that have settled overnight and that have no re-suspended particles may be analyzed by careful control of the sampling procedure. Solids that become re-suspended must be filtered out by using a 0.45 µm filter prior to analysis.

5.3 Health and Safety Precautions

The ICP has a safety interlock system designed to protect the user and other personnel working in the laboratory from radio frequency (RF) radiation and ultraviolet radiation, and to prevent access to high voltage areas. The following safety interlocks must be satisfied in order to ignite and maintain the plasma:

- 1) The torch compartment must be closed before the plasma can ignite;
- 2) Argon pressures for the torch must be correct; and
- 3) Cooling water must be flowing to the plasma induction plates and oscillator.

The ICP generates high levels of Radio Frequency (RF) energy. RF energy is potentially hazardous if permitted to escape. The ICP is designed to confine the RF energy inside the shielded area of the torch compartment and the RF power supply. Do not defeat or modify the safety interlocks that protect you from the RF energy and do not allow the operation of the ICP without all covers, doors, and shields in place.

The ICP generates a plasma that produces high intensity ultraviolet radiation. Directly viewing the plasma (without protection) can cause permanent damage to the eyes and impairment of eyesight. The safety interlock will automatically shut off the plasma if the sample compartment door is opened or the torch is removed. Do not attempt to defeat or modify the safety interlock. There is a specially designed viewing window for safely viewing the plasma. Do not alter this viewing window and if damaged replace the viewing window immediately before operating the ICP.

The exhaust fumes from the ICP are toxic and hot. The exhaust fumes must be properly vented by connection to a laboratory snorkel exhaust while operating the ICP. Ensure that the ventilation system is working properly prior to operating the ICP.

Do not operate the ICP unless the drain system is installed and functioning properly. The waste from the ICP is corrosive and potentially toxic. Plastic waste containers are recommended as a glass waste container may break and cause a spill of toxic or corrosive liquids. The following safety measures will be used for the drain system and waste containers:

- 1) Place the waste container in a place that is observable so that the level of collected waste can be viewed and the waste inside the waste container can be disposed of properly when full.
- 2) Monitor condition of the drain tubing regularly to check for deterioration of the draining tubing and replace the drain tubing when needed.

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The waste from the ICP system is acidic, with a pH generally < 1. Waste shall be turned over to the RSKERC SHEM Manager for disposal as hazardous waste.

Liquid argon is used to operate the ICP-MS. The major hazards associated with this gas are pressure, cold temperatures, and suffocation. Follow all gas cylinder and cryogenic liquid handling safety measures as described in the EPA RSKERC Chemical Hygiene Plan. When the ICP is turned off, ensure that argon gas valves are tightly closed at the cylinder. Contact the RSKERC SHEM Manager if there are questions concerning the hazards, storage and use of the argon gas cylinder. All staff should read, understand and sign the project specific HASP for necessary safety information prior to performing any work.

2) Interferences

Isobaric elemental interferences are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio. The heavy isotopes of Uranium and Lead are generally free from this type of interference. Polyatomic interferences are plasma-sourced interferences that are generated when the sample matrix ions combine to form a mass/charge (m/z) similar to that of the analyte. Common examples include oxides, hydrides, and chlorides of argon, rare-earth element oxides, and double-charged ions of barium. Polyatomic interferences for Pb include oxides of Os, Ir, and Pt and argon dimers with Er and Yb; none of these elements are expected to be present at significant levels within natural samples. The ^{204}Pb isotope has an isobaric interference from ^{204}Hg . In this method, ^{202}Hg is used to monitor Hg levels and to correct for the isobaric interference on ^{204}Pb according to the natural abundance ratio [correction = $(0.068/0.296) \times ^{202}\text{Hg}$]. Uranium is largely free from polyatomic interferences; however, the $^{198}\text{Hg}^{40}\text{Ar}^+$ dimer is possible in mercury-rich samples as an interference for ^{238}U , but the natural abundance of the ^{198}Hg isotope is <10% and ^{238}U is the most abundant U isotope. Double-charged Pb oxide species have been noted as possible interferences in the U isotope mass range, but these species are not problematic as long as Pb concentrations remain below 10 $\mu\text{g/L}$ (Plastino et al., 2013).

5.4 Reagents and Supplies

5.5 Concentrated HNO_3

Optima grade concentrated HNO_3 (67 - 70%, Fisher Scientific; catalog# A467-1) or high-purity HNO_3 prepared from Trace Metal Grade HNO_3 using a Savillex DST-4000 acid purification system (Eden Prairie, MN).

5.5.1 Rinsing 2% Nitric Acid (v/v)

Add 20 mL of concentrated HNO_3 to 800 mL deionized water and dilute to 1 L.

5.5.2 Deionized (DI) water

In house 18 $\text{M}\Omega/\text{cm}$ Millipore Synergy UV DI water. Distilled water is used to fill the fluid chamber in the water chiller.

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5.5.3 Tuning solution: 1 µg/L Ba, B, Co, Ga, In, Fe, Li, Lu, K, Rh, Sc, Na, Tl, U, and Y. High-Purity Standards Cat. # ICP-MS-TS-18

5.5.4 Uranium Isotopic Solution: CRM 145

Prepare by adding 500 mL of DI water to a 1000 mL volumetric flask. Add 20 mL of concentrated HNO₃, 100 µL of the primary CRM 145 uranyl nitrate solution (New Brunswick Lab, US DOE), and dilute to volume. The nominal concentration of this working solution is 1 mg/L. From this working solution a 1 µg U/L solution is prepared by adding 50 µL to 50 mL of 2% HNO₃.

5.5.4 Uranium Isotopic Solution: CRM U005-A

Dissolve 1.2 mg of CRM U005-A (U₃O₈ powder; New Brunswick Lab, US DOE) into 20 mL of HNO₃. Prepare a 1 mg/L working solution by adding 500 mL of DI water to a 1000 mL volumetric flask, add the 20 mL of concentrated HNO₃ with dissolved U₃O₈, and dilute to volume. The nominal concentration of this working solution is 1 mg/L. From this working solution a 1 µg U/L solution is prepared by adding 50 µL to 50 mL of 2% HNO₃.

5.5.5 Lead Isotopic Solution: NIST 981

Dissolve 1.0 mg of NIST 981 (high purity lead metal) into 20 mL of HNO₃. Prepare a 1 mg/L working solution by adding 500 mL of DI water to a 1000 mL volumetric flask, add the 20 mL of concentrated HNO₃ with dissolved lead, and dilute to volume. The nominal concentration of this working solution is 1 mg/L. From this working solution a 1.5 µg Pb/L solution is prepared by adding 75 µL to 50 mL of 2% HNO₃.

5.5.6 Lead Reference Solution: High-Purity Standards ICP-200.8-1

Prepare by adding 50 mL of DI water to a 100 mL volumetric flask. Add 2 mL of concentrated HNO₃, 15 µL of the High-Purity Standards cat. #ICP-200.8-1 (Lot # 1502715; 10 mg/L Pb), and dilute to volume. The nominal concentration of this solution is 1.5 µg Pb/L.

5.5.7 Argon

Bulk liquid for plasma, auxillary and nebulizer flows.

5.5.10 RO water

Lab supplied reverse osmosis water for rinsing glassware before acid soak.

5.5.11 3% nitric acid

Prepare by adding 5820 mL of DI water to a 11.3 L plastic tub. Add 180 mL of concentrated HNO₃. Used for the acid soaking of metals glassware.

5.5.8 Equipment/Apparatus

5.5.9 High Resolution Inductively Coupled Plasma Mass Spectrometer

Thermo Scientific Element XR system.

5.5.11 Refrigerated recirculator

Thermo Scientific Neslab ThermoFlex2500 set at 20 °C.

5.6 Controlling Computer

A Dell Optiplex 9020 computer with Windows 7 and Element ICP-MS/GD-MS Software for data acquisition and processing. The controlling computer is attached to the LABLAN network.

5.6.1 Printer

Dell B2360dn printer.

5.6.2 Analytical Balance

Mettler Toledo MS6035 analytical balance capable of weighing to 0.0000 g.

5.6.3 Pipettes

Either fixed volume (50 μ L, 100 μ L, 500 μ L, or 1 mL) or adjustable volume Eppendorf pipettes will be used. The pipette tips made for Eppendorf pipettes of the appropriate volume range will be used.

5.6.4 Nalgene plastic volumetric flasks

Volumetric flasks will be used to make all solutions in this SOP. Sizes range from 100 to 1000 mL.

5.6.5 Autosampler

Elemental Scientific, Inc (ESI) model SC-E2DXS autosampler.

5.6.6 Autosampler tubes

Autosampler tubes used in this SOP will be constructed of plastic and may be either 15 mL or 50 mL volumes (Thermo Scientific Nunc Part #339650 15 mL conical centrifuge tubes, blue cap; Serstedt No. 62.547.004 50 mL tubes, red cap).

5.6.10 Pump tubing and nebulizer

In this method sample introduction relies on direct aspiration rather than a peristaltic pump in order to maximize signal stability (Graney and Landis, 2013). The autosampler probe is connected to a self-aspiration capillary. The capillary tube is Teflon and provides a nominal flow

rate of 200 $\mu\text{L}/\text{min}$. The tubing extends to the nebulizer (Ezylok Micromist; Part # 1161870) which fits into the cyclonic spray chamber.

5.6.7 Semi demountable torch with 1.5 mm injector (quartz)

5.6.8 Nickel sampler and skimmer cones

5.6.8 Procedures

5.6.9 Glassware and Plasticware Cleaning

The following procedure is to be used to clean all glassware and plasticware used in this SOP.

Prepare cleaning solution by adding approximately 10 mL/L H_2O of 1% Liquinox detergent to a tub (8 L) of warm tap water. Remove all markings and residue from glassware using a lab brush or methanol if necessary. Submerge glassware in the solution and allow it to soak for a few minutes. Clean the glassware with a lab brush. Rinse four times with reverse osmosis (RO) water, place the rinsed glassware in a tub containing 3 % (v/v) HNO_3 ; and allow it to soak for 4 to 16 hours. Remove glassware, rinse four times with RO water and allow it to dry (open end down) on a clean surface.

5.6.11 Sample Preparation

Aqueous samples will be stored in polyethylene containers. Aqueous samples that have been prefiltered and acidified will not need acid digestion. Digestion procedures for total recoverable metals in aqueous samples and solid matrices can be found in individual SOPs (RSKSOP-179; RSKSOP-180).

Samples that are to be analyzed using this procedure must be free of solids. Solids will plug the sample introduction system. Samples that are particle-free may be analyzed directly. In most cases, sample dilutions will need to be conducted prior to analysis to reach the optimal concentrations of U or Pb as described in Section 5.2.

5.7 Instrument Startup Procedure

5.7.1 Argon Supply Check

Check and ensure that the Argon gas supply is sufficient to run the instrument. This can be accomplished by looking at the gas gauges on top of the liquid argon tank. If the tank is empty replace and then open the valve on the liquid argon. Adjust the pressure regulators attached to the liquid argon. The optimal pressure for argon is 115 psi; however, the pressure should be no lower than 100 psi and no higher than 120 psi.

5.7.2 Starting the Autosampler

Verify that the controlling computer is booted up and that power to the HR- ICP-MS and autosampler is on. Also verify that the refrigerated circulator is running and maintaining the set temperature (19°C). This value is displayed on the LED on the front of the chiller. From the

computer desktop double click on the ESI Autosampler icon. The autosampler program will load. Click on the Initialize button. Once the initialization sequence is complete, minimize the ESI Autosampler software.

Supply the autosampler rinse carboy with fresh 2% HNO₃ and verify the waste carboy has sufficient capacity.

5.7.3.3 Starting the Plasma

On the controlling computer's desktop, open the Thermo Element folder. Double click on the Network Processor icon. The Executive window will open. For isotope ratio measurements the instrument should set to Speed Mode with 3 pre-scans to eliminate hysteresis. See Section 5.7.5 for setting the instrument to Speed Mode and entering the dead time correction. Next, double click on the Instrument icon. Make sure that the sufficient carrier solution is available and verify that the waste carboy has sufficient capacity. In the Instrument program, click the HV icon and Peri icon; the indicators will switch from red to green. Note in this method the peristaltic pump is used to drain the spray chamber and not for sample introduction.

In the Instrument program, start the plasma by clicking **ON**. An automatic sequence will be initiated. When the plasma start procedure is successfully completed, the message "Plasma Successfully Started" is displayed. Move the autosampler probe to a 50 mL tube containing 2% HNO₃ (typically position 1 or position 9). Allow for a plasma warm up time of at least 30 minutes before proceeding to the instrument tune.

The nominal instrument settings should read as follows:

Cool Gas [L/min] = ~16
Auxiliary Gas [L/min] = 0.8-1.0
Sample Gas [L/min] = 0.8-1.0
Fore Vacuum [mbar] = 2.3e-4 (prior to torch)
High Vacuum [mbar] = 6.5e-8 (prior to torch)
Argon Max [bar] = 6.3
Argon Middle [bar] = 3.5
High Voltage [V] = -7878

5.7.3 Tuning the Thermo Element XR

Instrument tuning should be conducted prior to running an analytical sequence. On a day-to-day basis, the tune parameters will not substantially change, but this needs to be verified in order to establish optimal run conditions. To tune the HR-ICP-MS first allow the instrument to warm up for at least 30 minutes. Verify the spray chamber assembly is draining properly. Inspect the tubing for flow and for leaks.

Move the autosampler probe to a vial containing 1 µg/L tuning solution (Section 5.5.4).

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Low Resolution tuning: Open the Tune window of the software by double clicking on the Tune icon. The most recent tune file will open (.tpf). Go to Create Scan List, Load Thermo_HP_Tune_Li_In_U_UO.scl, open file, ok. Lithium, Indium, and Uranium should be in Pulse Counting mode. Hit Start Scan. If necessary, adjust the torch parameters (X- and Y-Positions; do not adjust Z-Position) and plasma group parameters (Sample Gas). Maximize for cps ^{238}U . Track the peak height in the upper right panel to obtain 2.5×10^6 cps at ^{238}U . If needed, adjust the lens settings to obtain a stable signal (Extraction stays at -2000 V; adjust Focus, X-Deflection, Y-Deflection, and Shape). Also track the stability of the ^{238}U count rate in the lower right panel. Adjust tune parameters to achieve a %RSD value of less than 2.5%. Stop scan and Save Current Parameters to the current tune file. On an approximate monthly basis, a new tune file will be named and saved (Thermo_Tune_MMDDYY.tpf); thus, minor day-to-day changes in the tune parameters will not result in a new tune file. Medium and High Resolution tuning are not necessary for this method because only Low Resolution is used. Note: if the 1 ppb tune solution returns pulse counting rates $>4 \times 10^6$, then the detector will trip from counting mode into analog mode. In this case, the tune solution and samples may need to be diluted to lower concentrations so that detection in the counting mode is insured.

5.7.3.1 Detector Dead Time

The detector dead time is the time after the impact of an ion for which the ion counting system is “blind” to further incoming ions (Nelms et al., 2001). The dead time is corrected for by the instrument if the proper dead time is supplied to the instrument settings. To determine the detector dead time, first open the Executive program and select Customize, Instrument Settings. Remove the tick mark in the Dead Time Correction box (upper right), i.e., the automatic dead time correction has to be turned off in order to properly determine the correction. Also select the Speed Mode in the Instrument Settings. Select Ok to save the new instrument setting. In the Sequence editor, open the file U Deadtime 021017 v1.seq and Save As with the current date. Prepare four solutions with U concentrations of 0.5, 0.3, 0.2, and 0.1 ppb. It is not necessary to use a certified standard, the Tune solution or any ICP-MS standard diluted to the appropriate concentrations is suitable. The U concentrations selected can vary; however, the maximum concentration solution should not exceed 4 million counts using the pulse counting detector. The lowest concentration solution should return less than 1 million counts. With the four solutions placed in their proper autosampler positions, run the sequence file. From the desktop open the MS Excel file Deadtime calculations.xls (appended with most recent run date). In the spreadsheet, manually enter values for the U concentrations and measured count rates for ^{235}U and ^{238}U . Because the concentration data were determined with no dead time correction, a positive trend on a U concentration versus $^{235}\text{U}/^{238}\text{U}$ plot is observed (automatically plotted in the Excel spreadsheet). To determine the dead time, manually adjust the yellow-colored cell (F28) until the plot of U concentration versus $^{235}\text{U}/^{238}\text{U}$ is a flat line (slope near 0). This reflects the dead time for which the isotope ratio is independent of concentration. Start with values between 10 and 40 ns; change the entry in smaller steps to determine the optimum dead time value. On February 9, 2017, the dead time value determined was 27 ns. Save the Excel spreadsheet with the new date appended to the file name on the desktop. Open the Executive program, enter the dead time correction, click the active box, and click Ok to save and close the Instrument Setting window (when running isotope ratio measurements keep the instrument in Speed Mode with 3 pre-scans; for concentration work switch to Mass Accuracy, 0 pre-scans). The dead time is detector specific, not isotope-specific. Thus, one dead time value is valid for the whole mass

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range. The dead time should be re-evaluated on a biannual basis or whenever a large set of isotope analyses will be run. The method described here for determining dead time is the same as Method 2 from Nelms et al. (2001). Also, this procedure should be repeated whenever a new detector is installed.

5.7.3.2 Isotope Ratio Methods

The Method file designates the isotopes to be monitored, resolution mode, mass windows, scan type, integration time, and detector mode. Currently there are two isotope ratio methods developed and tested. The method titled Pb Ratio 1.met is set up to monitor ^{202}Hg , ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb . Data are reported for the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios. A run of 10 samples plus QC samples takes approximately 1.5 hours to complete. The method titled U Ratio 1.met is set up to monitor ^{234}U , ^{235}U , and ^{238}U . Data are reported for $^{238}\text{U}/^{235}\text{U}$ and $^{238}\text{U}/^{234}\text{U}$ and a run of 10 samples plus QC samples takes about 6.5 hours to complete. A longer analysis time for U is needed in order to obtain sufficient counting statistics on the low abundance ^{234}U isotope (natural abundance = 0.005%).

5.7.4 Setting up a Sample Analysis Sequence

Data acquisition on the Thermo Element XR consists of a sequence file with a list of samples. The sample information includes the name, method used, tune file, autosampler position, autosampler uptake time (120 seconds), and autosampler wash time (80 seconds).

Two template sequence files have been developed for Pb and U isotope runs, respectively. The template to be used for Pb isotope runs is Pb Isotope Ratio Sample Setx MMDDYY.seq. The template to be used for U isotope runs is U Isotope Ratio Sample Setx MMDDYY.seq. To access these templates, open the Sequence Editor program and load the applicable sequence template. These sequence templates are developed for 10-sample queues and include all of the necessary QC samples. Table 1 shows the sequence of unknown samples and QC samples.

5.7.5 Mass Bias

The ICP-MS system suffers from a mass bias due to space charge effects in the interface and ion optics region (Al-Ammar and Barnes, 2001). Ions of high kinetic energy are transmitted more efficiently and heavier ions have a higher initial kinetic energy. Thus, heavier ions are favored and lighter ions are discriminated against. An external correction can be applied by bracketing the samples with an isotope reference material. The correction equation is:

$$K = \frac{R_{true}}{R_{obs}}, \text{ Equation 1}$$

Where K = the correction factor (K -factor) for mass discrimination, R_{true} is the certified isotope ratio of the reference material, and R_{obs} is the measured isotope ratio. An average K -factor is determined for reference materials based on measurements taken before and after sample measurements. Correction factors are calculated and applied to sample data using an automated Excel spreadsheet created for data reporting as described in Section 5.7.11.3. The CRM 145 reference sample is used for mass bias corrections for U isotope measurements and NIST SRM 981 is used for mass bias corrections for Pb isotope measurements. The certified standard is

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analyzed at the beginning of the sample analysis, after every three samples, and at the end of sample analysis (Table 1). The standard is used to monitor the Pb or U isotope ratios and any effect drift or mass bias may have had on the sample isotope ratios. Isotopic ratio data for reference materials used in this SOP are provided in Table 2. Isotope reference samples CRM 145, CRM U005-A, and NIST SRM 981 are certified materials. Lead isotope data for the High Purity Standards ICP-MS calibration standard are based on the average of 10 replicate analyses. The CRM U005-A and High-Purity Standards reference materials are used as second source isotope standards.

5.7.6 Analyze Samples

Once the entire sequence file is created, then it can be used to acquire data. For data acquisition, the sequence is started from the Sequence Editor. When the sequence is started, the software checks each item in the sequence to check file names, directory destinations, etc. Detailed error descriptions, if any, are displayed in the acquisition window at the bottom of the Sequence Editor.

To initiate a sample run sequence:

- 5.7.7 Open and modify the desired sequence in the Sequence Editor.
- 5.7.8 Load all samples in the correct Auto Sampler positions. Refer to Table 1 for the correct sequence of unknown samples and QC samples.
- 5.7.9 Click on the Start icon in the tool bar to start the sequence. The Acquisition window will open at the bottom of the sequence window.
- 5.7.10 Make sure that the following boxes are checked: Acquire, Evaluate, Sample: Print Report, Sample: ASCII Report, Sequence: Print Report, and Sequence: ASCII Report. The Print Report boxes can be left unchecked if hard copy print outs are not required. Make sure that Isotope Ratio is selected as the sequence report type. This will automatically create an ASCII file that is used to generate data reports (see Section 5.7.11.3).
- 5.7.11 Click on Run to start the sequence. The program will check if all items have been correctly entered. If no errors are found, then the sequence will be started. In case of missing or incorrect data, an error report will be generated in the Acquisition window. If required, correct the identified parameters and click on Run again.

5.7.10 Instrument Shutdown

To shut down the instrument the following procedure is used.

- 5.7.8 While the plasma is still on, place the carrier line in a container containing 2% nitric acid. Allow this to aspirate for at least 5 min. Next place the carrier line in deionized water and allow for at least 5 min. of aspiration before extinguishing the plasma.
- 5.7.9 Send the sample probe to the Home position. Allow the pump to drain the tubing lines while the torch extinguishes and cools down.
- 5.7.10 Extinguish the plasma by opening the Instrument window and switching the plasma to the off position.
- 5.7.11 Once the plasma has turned off, turn off the High Voltage and Peri Pump. The icons will switch to red when off.

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- 1) Close the Instrument window. Close the Network window. Close the Executive window.
Close the Autosampler window.
- 2) Release the peristaltic pump tension.
- 3) Shut off the Argon gas at the tank by closing the valve.

5.7.11 Reporting of Results

The following section will describe how data reporting will be conducted. The data collected during each analytical run are automatically stored on the hard drive of the instrument computer, along with all methods, results, and meta-data using the ELEMENT2 software. At the end of each analytical run, an ASCII file is created that contains isotope ratio data collected during the run. This file is used to create data reports of sample results, correct for mass bias, and evaluate QC sample results.

5.7.11.1 Data Archiving

Data archiving procedure described here is for transferring the analytical data collected from the HR-ICP-MS onto the LABLAN. The procedure described follows from the long-term archiving described in RSKSOP-293v1.

On a monthly basis all analytical data collected using the ICP will be archived on the LABLAN. All files and folders from the HR-ICP-MS computer located at c:\Element\user\Element\ will be copied over to the LABLAN. This procedure will ensure that all data files, methods, and instrument files will be preserved and archived.

5.7.11.2 Exporting Data for Data Report Generation

5.7.9 At the end of each analytical run an ASCII data file (.asc) is created and stored within the folder c:\Element\user\Element\data within a separate folder created when a new sequence is created. The folder name is the same as the sequence name.

5.7.10 Open a copy of Microsoft Excel. Open the ASCII file, as a delimited file, start at row 1, click on next and make sure the tab delimited box is checked, and click on finish. The resulting file can be copied and pasted into the Data Report Template in the Raw Data tab as described in 5.7.11.3.

5.7.11.3 Data Reports

Data reports are generated by importing an ASCII file into a template Excel spreadsheet file. This spreadsheet file will automatically generate most of the final data report (Cover Page, Data, and QA) in different tabs of the spreadsheet. In addition, the template spreadsheet will automatically generate summary tables for the various types of QC samples and mass bias corrections in separate tabs. The following procedure will be used to generate the data reports.

- 1) Open the report template (e.g., file name 'Element XR U Isotope Ratio Report.xls' or 'Element XR Pb Isotope Ratio Report.xls') in Excel located on the controlling computer or the office computer of the analyst.
- 2) Then save the report template using the save as command.

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- 6) From the save file as dialog enter the file name that was used when the data were analyzed. If this is a reanalysis (i.e., data did not meet QA requirements) then at the end of the file add the version number as v#.
- 7) Next obtain the ASCII file for the data to be reported and open this file in Excel.
- 8) Once opened, copy all the data from the ASCII file into the Raw Data tab of the report Excel spreadsheet. This will automatically generate most of the report. Fill in the non-automatically filled in fields with the correct information.
- 9) Save the report file.
- 10) Verify the data in the report. Add any analytical or QA comments in the appropriate fields.
- 11) Send the report to the independent data validator as defined in the roles and responsibilities section of this SOP (Section 4.2).

Once the data are received by the data validator from the primary analyst, a second review of the data will be performed. The data validator will review the report to ensure that all fields are correctly filled in, that the QA meet QA criteria specified in this SOP, and all appropriate analytical and QA comments have been added. Once this review is complete the data report and review comments will be delivered to the appropriate PI via email. Prior to sending the final checked report to the data requestor, the information in the data and QA tabs will be copied and saved as values. This will remove any of the programming codes needed to generate the report so that the data report cannot be changed inadvertently. The data will be checked to ensure that no changes were made during this step. Both copies of the final report will be saved to the validator's computer and to a SharePoint Site.

5.7.12 Mass Calibration

Periodically a mass calibration procedure needs to be run in order to maintain good accuracy of data. This routine is done on an as-needed basis. A mass calibration is required when the Automass Correction exceeds ± 500 ppm. When this occurs, a warning comes up on the instrument during the execution of an analytical sequence file; the warning prompts the analyst to conduct a Mass Calibration. To perform the Mass Calibration, place the autosampler probe in a vial containing the 1 $\mu\text{g/L}$ Element Tune solution. Also place the internal standard uptake line into the 2% Nitric Acid Blank solution.

- 1) In the Sequence editor, open the file *Thermo_Automasscal_Service_MJO_lastdate*. Select Actions, and make sure that Auto Lock Mass is unchecked. Next save as *Thermo_Automasscal_Service_MJO_newdate*. Open the Method tab on the acquisition pane of the Instrument screen.
- 2) In the Instrument pane, select the icon Run Mass Calibration. Go to the Calibration pull down menu and select Reinitialize Calibration - high resolution (yes), medium resolution (yes); never delete low resolution. Reset the EDAC values.
- 3) Go to the spreadsheet view of the Sequence Editor. Click on the Tune file and select the most recent tune file. In the sequence view of the Sequence editor, hit the barrel icon (reset all). Next select the flag icon, run, and continue (sample sequence boxes should be unchecked). Go to Show and wait for the analysis to finish.
- 4) Select the Mass Calibration icon and open the file just created in the folder titled *Thermo_Automasscal_Service_MJO_newdate*, *Thermo_LR_wide*. Select the Manual

confirming version status against the electronic version in the document control system.

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Calibration icon (finger) and double click on the first isotope (${}^6\text{Li}$) and sequence through the range of calibration isotopes to ${}^{238}\text{U}$. Make sure that the indicator line is within the data for each peak. If not, select trash, double click in center of peak, highlight the selected isotope and select add. Save, if any changes are made.

- 1) Go back to the Sequence Editor, select continue and return to method acquisition window and repeat the procedure, Show, Mass Calibration and open the Thermo_LR_narrow file and sequence through the peaks. Repeat the process for the Medium Wide, Medium Narrow, High Wide, and High Narrow files.
- 2) After completing the Mass Calibration, go to the Sequence editor and cancel the acquisition. Open the file called Thermo_Determine_MassOffset_Checkmass_MR. In the spreadsheet view, check that the most recent tune file is present. Go to the Building Blocks icon, and open the file CheckMassDrift_MR. Change yes to no, save the file. Next open the file CheckMassDrift_HR. Change yes to no, save the file.
- 3) In the Sequence editor, highlight 1_DetermineMassOffset and reset all (barrel icon), Hit the flag, run, continue. Go to Show, note the Argon dimer peak at mass 37.925. Sequence, hit stop. Make sure 1) Determine mass Offset is selected, go to the View Results. Open file, select Update Calculated Mass Offsets, open, ok. Next highlight Sample 2) Check Mass Offset, run, and continue. Repeat process from above. If result is >0.003 then go to file and update mass offsets.
- 4) Next Repeat steps 6 and 7 after opening the file Thermo_Determine_MassOffset_Checkmass_HR in the Sequence editor.
- 5) In Actions make sure that AutoLock mass is checked.
- 6) In Building blocks (in HR), change no to yes, save. Open checkmass Drift MR, change no to yes, save.
- 7) Next the mass offsets need to be updated for each method. See the SOP NRMRL-GWERD-11-0 for determining method-specific mass offsets. Note because the isotope ratio methods described in this SOP utilize low resolution mode for analysis, determining mass offsets is not a requirement.

3) Calculations

This section describes the calculations performed by the Element ICP-MS/GD-MS software. Calculations include determination of standard deviations and relative standard deviations (RSD). See Section 5.9 for QA/QC calculations.

The standard deviation (SD) equation used by the Element software to calculate the variability between replicate analyses is given by Equation 2:

$$SD = \sqrt{\frac{\sum(c_i - c_{mean})^2}{n-1}}, \text{ Equation 2}$$

where c_i is the value in each replicate measurement, c_{mean} is the mean isotope ratio of the multiple replicates as determined by the specific method file used for Pb and U isotope analyses, and n is the number of measurements. The equation used to measure the relative standard deviation (RSD), a measurement of precision in replicate analysis is given by Equation 3:

$$RSD (\%) = \left(\frac{SD}{mean} \right) \times 100, \text{ Equation 3}$$

where SD is the standard deviation for the replicates and the mean is the mean of the replicates.

1) Quality Assurance/Quality Control

A summary of QC sample types, acceptance criteria, and analysis frequencies is given in Tables 1 and 3.

Depending on project-specific requirements, re-analysis of samples may be needed in the event that the acceptance criteria provided in Table 3 are not met. Otherwise the sample data will be qualified to show the cases in which QC criteria were not met.

3) Initial Verification Standard

The initial verification standard (ICV or second source standard) is prepared from a different source than the reference samples used to calculate mass bias. It is analyzed immediately after the first mass bias reference sample (Table 1). The acceptance criteria of the various isotope ratios is based on a percent agreement (Equation 4). The acceptance criteria are listed in Table 3. If these acceptance criteria are not met, then specific results will be qualified in the data report submitted to the PI. Re-analysis of the ICV may be required based on project-specific requirements.

$$RPD (\%) = \frac{(|R_{measure} - R_{true}|)}{\left(\frac{R_{true} + R_{measure}}{2}\right)} \times 100, \text{ Equation 4}$$

1) Mass Bias Reference Samples

Continuing mass bias reference samples must be analyzed at the beginning, after every 3 samples, and at the end of each analytical run (Table 1).

1) Duplicates

A duplicate sample is run to check precision at a frequency of 1 per 10 samples. Relative Percent Difference (*RPD*; Equation 5) is used for comparing the duplicate results.

$$RPD (\%) = \frac{(|R_{duplicate} - R_{sample}|)}{\left(\frac{R_{sample} + R_{duplicate}}{2}\right)} \times 100, \text{ Equation 5}$$

Acceptance criteria for duplicate samples is provided in Table 3. Depending on project-specific requirements, re-analysis of samples may be needed in the event that the acceptance criteria provided in Table 3 are not met. Otherwise the sample data will be qualified to show the cases in which QC criteria were not met.

1) Blanks

Continuing analysis of blank samples is not necessary for isotope ratio measurements. However, analytical error can be introduced in the event that the 2% HNO₃ solution used for sample dilution is contaminated with a source of Pb or U that is different in isotopic composition than the samples run in a batch sequence. Memory effects are prevented by running all samples in a sequence at the same concentration and by insuring sufficient wash out and sample uptake times. To test for traces of contamination in the acid, prior to running a set of samples, the 2% HNO₃ used for sample dilution is analyzed using the appropriate method. For Pb isotope determinations, the integrated count rates (cps) for Pb-204, Pb-206, Pb-207, and Pb-208 should be <50, <300, <300, and <500, respectively. These count rates will result in errors of less than

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0.05% (assuming 3×10^6 cps for Pb-208 and normal isotope ratios as in NIST 981). For U isotope determinations, the integrated count rates (cps) for U-234, U-235, and U-238 should be <0.5 , <4 , and <400 , respectively. These count rates will result in errors of less than 0.02% for $^{238}\text{U}/^{235}\text{U}$ and $<0.3\%$ for $^{238}\text{U}/^{234}\text{U}$ (assuming 3×10^6 cps for U-238 and normal isotope ratios as in CRM 145).

5.10 Maintenance

Routine maintenance is an important part of maintaining the optimal performance of the instrument. This section describes the routine maintenance that is recommended by the manufacturer to maintain optimal performance of the ICP-MS.

5.10.1 Daily Checks

Before operating the instrument each day the following should be checked.

- 1) Check the Argon pressure and ensure that the pressure is approximately 120 psi.
- 2) Check the chiller pressure and water level.
- 3) Check the exhaust system for the torch box, the filter should be dust and particle free.
- 4) Check and empty the waste container.
- 5) Log fore and high vacuum pressures while the plasma is on, with the skimmer valve open and while aspirating sample.

5.10.2 Weekly Checks

Every week, when the instrument is in use, the following should be checked. If the instrument has not been used for an extended period of time the following should be checked prior to running samples.

- 1) Check the oil levels in the rotary vane pump and the interface pump once the instrument has warmed up.
- 2) Check the oil color in the rotary vane and the interface pump. See figure below as a guide. Do not let the color of the oil exceed the color 5 to 6 below. If pump oil color ranges from 7 to 8, permanent damage to the pump will occur.



Figure is from Thermo Fisher Scientific

5.10.2 Monthly Checks

Once a month check and replace if necessary the pump strainer in the external chiller.

5.10.3 Quarterly

On a quarterly basis (3 months) replace the cooling water in the external chiller. Do not use DI water, only use distilled water.

5.10.4 Every 6 months

The following should be replaced every 6 months.

- 1) Replace the oil in the DUO 5 rotary vane pump. The replacement oil must be Pfeiffer P3 oil (Part No. 109 4301).
- 2) Replace the oil reservoirs in all the turbo pumps TMH 071 (Part No. 017 2350) and TMH 262 (Part No. 105 0160).

5.10.5 Annually

Annually replace the interface pump (UNO 30M) oil. The replacement oil must be Pfeiffer F4 oil (Part No. 113 6532) approximately 1.1 L of oil is needed. It is expected that the instrument will be placed on an annual service and maintenance agreement which would include an annual evaluation by an authorized service technician.

5.10.6 As needed

The following should be replaced as needed.

- 1) Replace skimmer valve o-rings and extraction lens (Kit Part No. 112 0650) when extraction lens becomes contaminated or if the skimmer valve opens too slowly.
- 2) Replace detector (SEM Part No. 115 2700) when the plateau voltage is greater than 2800 V.
- 3) Replace entrance slits (Part No. 104 7360) when LR peak is no longer trapezoidal or HR transmission is less than 0.8%.

5.10.7 Before Plasma Ignition

- 1) Visually inspect the interface and inlet system. Clean or replace contaminated parts. Replace worn or damaged parts.
- 2) Check torch and coil to ensure they are not burned or damaged. Replace torch and coil if either of these conditions has occurred.
- 3) Check guard electrode contact problems or damage. Replace as needed.
- 4) Check quartz insulator for burn marks or metal coatings. Replace if these have occurred.
- 5) Check cones and gaskets for damage or contamination. Clean or replace cones and replace gaskets if needed.
- 6) Check peristaltic tubing and all other tubing. Replace as needed.

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6 RECORDS GENERATED

File Type	Agency File Code	Closure	Retention	Custodian/location records
Environmental Programs and Projects – Historically significant environmental program and project records	108_1035a	Close when activity, project, or topic completed.	Permanent	Custodian – PI Location – see QAPP
Environmental Programs and Projects – Long-term environmental program and project records	108_1035b	Close when activity, project, or topic completed.	Destroy 20 years after file closure.	Custodian – PI Location – see QAPP
Environmental Programs and Projects – Site-Specific – Long – term site-specific records.	108_1036c	Close when activity, project, or topic completed.	Destroy 30 years after file closure.	Custodian – PI Location – see QAPP
Environmental Programs and Projects-Short-term environmental program and project records (logbooks)	108-1035d	Close when logbook is full or activity is completed.	Destroy 5 years after file closure.	Custodian-Laboratory PI Location-lab where instrument is located

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8 TABLES

Table 1. Run Sequences for 10 Samples.

U Isotope Sequence	Pb Isotope Sequence
CRM 145* 1	SRM 981* 1
CRM U005-A**	High-Purity Standards Pb Reference**
Sample 1	Sample 1
Sample 1 duplicate	Sample 1 duplicate
CRM 145* 2	SRM 981* 2
Sample 2	Sample 2
Sample 3	Sample 3
Sample 4	Sample 4
CRM 145* 3	SRM 981 3
Sample 5	Sample 5*
Sample 6	Sample 6
Sample 7	Sample 7
CRM 145* 4	SRM 981* 4
Sample 8	Sample 8
Sample 9	Sample 9
Sample 10	Sample 10
CRM 145* 5	SRM 981* 5

*Mass bias reference

**Second source

Table 2. List of Reference Samples and corresponding Pb and U Isotopic Ratios.

Reference Sample	Isotope Ratios
NIST SRM 981	$^{206}\text{Pb}/^{204}\text{Pb} = 16.9406 \pm 0.0003^*$
	$^{207}\text{Pb}/^{204}\text{Pb} = 15.4957 \pm 0.0002$
	$^{208}\text{Pb}/^{204}\text{Pb} = 36.7184 \pm 0.0007$
High-Purity Standards	$^{206}\text{Pb}/^{204}\text{Pb} = 17.92 \pm 0.05^{**}$
Method 200.8	$^{207}\text{Pb}/^{204}\text{Pb} = 15.57 \pm 0.05$
Standard	$^{208}\text{Pb}/^{204}\text{Pb} = 37.75 \pm 0.10$
CRM 145	$^{238}\text{U}/^{235}\text{U} = 137.85 \pm 0.08^{***}$
	$^{238}\text{U}/^{234}\text{U} = 18924.7 \pm 30$
CRM U005-A	$^{238}\text{U}/^{235}\text{U} = 196.46 \pm 0.12^{***}$
	$^{238}\text{U}/^{234}\text{U} = 29261.5 \pm 590$

* Ratios and error limits (2σ) from Yuan et al. (2016). ** Pb isotope ratios determined by GWERD metals lab (2/26/17); ratios and errors based on 10 sample measurements.

***Ratios and errors provided on the CRM certificates of analysis.

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Table 3. QC Sample Information and Acceptance Criteria.

Reference/Isotope	Acceptance Criteria	True Value	Acceptance Range
Ratio	(% RPD)		
CRM U005-A			
²³⁸ U/ ²³⁵ U	<0.2	196.46	196.07 – 196.86
²³⁸ U/ ²³⁴ U	<2	29261.5	28676 – 29847
Duplicate			
²³⁸ U/ ²³⁵ U	<0.2	--	--
²³⁸ U/ ²³⁴ U	<2	--	--
High Purity Std			
²⁰⁶ Pb/ ²⁰⁴ Pb	<1	17.92	17.74 – 18.10
²⁰⁷ Pb/ ²⁰⁴ Pb	<1	15.57	15.42 – 15.73
²⁰⁸ Pb/ ²⁰⁴ Pb	<0.5	37.75	37.56 – 37.94
Duplicate			
²⁰⁶ Pb/ ²⁰⁴ Pb	<1	--	--
²⁰⁷ Pb/ ²⁰⁴ Pb	<1	--	--
²⁰⁸ Pb/ ²⁰⁴ Pb	<0.5	--	--

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9 REVISION HISTORY

Revision #	Description	Effective Date
0	Initial Version	Date Management Approves

Appendix 8

INTERNAL NRMRL PROCEDURE

Standard Operating Procedure for the Determination of Rare Earth Elements using HR-ICP-MS

NRMRL Standard Operating Procedure (SOP)

Title:	Standard Operating Procedure for the Determination of Rare Earth Elements using HR-ICP-MS		
Division/Staff:	NRMRL/GWERD		
SOP Number:	NRMRL-GWERD-13-0		
Former SOP Number: (if applicable)	N/A		
Effective Date:	Management Approval		
SOP Author(s)			
Name: Richard Wilkin	Name:		
Name:	Name:		
Name:	Name:		
QA Approval			
Name: Steve Vandegrift	Signature/Date:	STEVE VANDEGRIFT	<small>Digitally signed by STEVE VANDEGRIFT DN: c=US, o=U.S. Government, ou=USEPA, ou=Staff, cn=STEVE VANDEGRIFT, dnQualifier=0000015365 Date: 2016.11.21 07:32:26 -0600</small>
SHEM Approval			
Name : Steve Musson	Musson, Steve	Signature/Date:	<small>Digitally signed by Musson, Steve DN: cn=Musson, Steve, email=Musson.Steve@epa.gov</small>
Management Approval			
DAVID KOZLOWSKI		<small>Digitally signed by DAVID KOZLOWSKI DN: c=US, o=U.S. Government, ou=USEPA, ou=Staff, cn=DAVID KOZLOWSKI, dnQualifier=0000045312</small>	
Name :	Signature/Date:		

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1 INTRODUCTION

This document describes the procedures used to determine the concentration of rare earth elements (REE) in aqueous samples and digestates by HR-ICP-MS (High Resolution Inductively Coupled Plasma Mass Spectrometry) using the Thermo Scientific Element XR. This SOP follows NRMRL-GWERD-11-0 (Standard Operating Procedure for Operation of the Thermo Scientific Element XR HR-ICP-MS) which is based on EPA Method 200.8 “Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry” (U.S. EPA, 1994). EPA Method 200.8 does not include the REEs; therefore, this SOP has been developed to include operation parameters and optimized Quality Control (QC) procedures for analyzing samples for REEs.

The REEs, or lanthanide elements, are a group of 14 elements from Lanthanum (atomic number 57) to Lutetium (atomic number 71). Promethium (atomic number 61) is excluded from the REE list because this element does not occur naturally, having no isotope with a half-life of greater than about 20 days. The REEs are useful tracers of water-rock interactions, water mixing, and redox processes and they are becoming widely utilized in studies of groundwater processes (e.g., Johannesson et al., 1999; 2011).

This SOP covers the analysis of the following elements: Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Samarium (Sm), Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb), and Lutetium (Lu). Determining the concentrations of these elements is challenging because they are typically present at very low concentrations (parts per trillion or ng/L) and because of notorious Barium (Ba) and light REE (LREE) oxide interferences on heavy REEs (HREE). This SOP uses High Resolution (HR) methods to resolve these spectral interferences and applies a series of Interference Check solutions that are tailored to the analytical challenges of the REEs.

2 SCOPE

This SOP applies to the Ground Water and Ecosystems Restoration Division (GWERD) staff that will perform REE analyses using the Thermo Scientific Element XR HR-ICP-MS. This SOP describes the analysis of REEs in aqueous samples (typically groundwater or surface water) and digestates (typically unfiltered groundwater or surface water after microwave assisted digestion). QC practices follow EPA Method 200.8 with specialized Interference Check solutions. Digestion methods are described in separate SOPs using either RSKSOP-179 or RSKSOP-180.

3 DEFINITIONS

<u>Term</u>	<u>Definition</u>
CCB	Continuing Calibration Blank
CCV	Continuing Calibration Verification Standard
DI	Deionized Water
HDPE	High Density Polyethylene
HR	High Resolution
HREE	Heavy rare earth element

ICB	Initial Calibration Blank
ICP	Inductively Coupled Plasma
ICS	Interference Check Solution
ICV	Initial Calibration Verification Standard
LCS	Laboratory Control Sample
LDPE	Low Density Polyethylene
LDR	Linear Dynamic Range
LLQLS	Low-Level Quantitation Limit Standard
LREE	Light rare earth element
MS	Mass Spectrometry
MDL	Method Detection Limit
PI	Principal Investigator
REE	Rare earth element
QC	Quality Control
QL	Quantitation Limit
RO	Reverse-Osmosis (Water)
RPD	Relative Percent Difference
SOP	Standard Operating Procedure

4 ROLES AND RESPONSIBILITIES

This SOP applies to all GWERD staff with duties related to the use of the Thermo Scientific Element XR HR-ICP-MS. Prior to analyzing samples, staff should be trained and familiar with operation of this instrument and must demonstrate competency in implementation of this procedure. In addition, all staff must have completed required safety training before operating the instrument or carrying out related laboratory procedures.

Primary Analyst

The primary analyst responsibilities include the maintenance of the HR-ICP-MS; proper operation of the ICP and other equipment needed for the analysis; and maintaining supplies needed for conducting analyses covered by this SOP. The primary analyst is also responsible for performing the initial data verification of the data collected, ensuring that complete and accurate records are kept and maintained, and ensuring that the proper collection of these records is achieved. The primary analyst is also responsible for contacting the Principal Investigator (PI) about analytical issues that may arise. Finally, the primary analyst is responsible for implementing any corrective actions needed.

Data Validator

The data validator is responsible for providing a secondary independent data verification to confirm that all data meet the QA requirements of the analysis. The data validator will either pass the data on to the appropriate PI or will work with the primary analyst to rectify any QA problems noted, if possible, and ensure that all needed QA comments are documented in the analytical report.

8. Principal Investigator

The PI is responsible for ensuring that all required information is supplied to the primary analyst prior to sample analysis and for addressing any analytical issues that the primary analyst may have concerning the samples submitted for analysis (Failure to do so may result in delays in sample analysis or samples not being analyzed.). The PI is also responsible for ensuring that the data received meet the QAPP requirements. The GWERD metals lab is not responsible for additional QA requirements outside of the SOP requirements, for example field data collection QA requirements. Finally the PI is responsible for maintaining data records for their project as required by the PI's QAPP.

5 PROCEDURES

13. Method Summary

Prior to analysis, samples must be solubilized or digested using appropriate preparation methods. When analyzing groundwater or surface water samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis. The Thermo Scientific Element XR is a double-focusing magnetic sector mass spectrometer capable of simultaneous analysis of most elements with a concentration range spanning up to 12 orders of magnitude. Liquid samples aspirated with a nebulizer are ionized in an argon plasma for introduction into the mass spectrometer where elemental isotope separation and detection occurs. Magnetic and electric field mass filters separate the sample ions by their mass to charge ratio at an analyzing vacuum of about 10^{-7} mbar. Only the positively charged ions are focused through the flight tube of the instrument to the detector array. Ions hitting the detector create a secondary voltage that is used to measure the analyte concentrations. The instrument has three resolution settings low, medium, and high that allow for increased separation of isotopes. Because of the difficulty in separating oxide interferences using the low resolution mode, analysis of the REEs with the Element XR utilizes the medium and high resolution modes. Thus, the use of correction equations is minimized or not needed for accurate quantitative analysis (see Section 5.4).

5.3 Sample Preservation, Containers, Handling, and Storage

For the determination of dissolved and total recoverable elements in aqueous samples, samples are acidified with HNO_3 to $\text{pH} < 2$ in 120 mL plastic (HDPE, LDPE) sample bottles. This is the minimum volume required to ensure that all required QC checks can be completed. In some cases sample volumes less than 120 mL will be accepted for analysis, but it will be acknowledged in the analytical report if certain QC samples were not completed due to inadequate sample volume. For the determination of dissolved elements, a sample must be filtered through a $0.45 \mu\text{m}$ filter and acidified with HNO_3 to $\text{pH} < 2$ prior to receipt by the laboratory. The holding time for analysis using this SOP is 6 months. Refrigeration is not required, but samples will generally be kept in a refrigerator.

Aqueous samples that have been prefiltered and acidified will not need acid digestion. Digestion procedures for total recoverable metals in aqueous samples and in other matrices can be found in individual SOPs (RSKSOP-179; RSKSOP-180).

Samples that are to be analyzed using this procedure must be free of solids. Solids will plug the sample introduction probe and the nebulizer. Samples that are solid-free may be analyzed directly for most elements. Digested samples that have settled overnight and that have no resuspended particles may be analyzed by careful control of the sampling procedure. Solids that become resuspended must be filtered out by using a 0.45 µm filter prior to analysis. In cases where solutions are filtered, a filter blank sample will also be analyzed. The filter blank will be prepared by filtering 10 mL of blank water, in the same way that samples are filtered.

5.4 Health and Safety Precautions

EPA employees and contractors performing laboratory work at EPA are required to complete initial laboratory safety training and maintain 4 hours of refresher training annually. In addition, demonstration of analyst proficiency is required prior to performing sample analysis.

The ICP has a safety interlock system designed to protect the user and other personnel working in the laboratory from radio frequency (RF) radiation and ultraviolet radiation, and to prevent access to high voltage areas. The following safety interlocks must be satisfied in order to ignite and maintain the plasma:

- 4) The torch compartment must be closed before the plasma can ignite;
- 5) Argon pressures for the torch must be correct; and
- 6) Cooling water must be flowing to the plasma induction plates and oscillator.

The ICP generates high levels of Radio Frequency (RF) energy. RF energy is potentially hazardous if permitted to escape. The ICP is designed to confine the RF energy inside the shielded area of the torch compartment and the RF power supply. Do not defeat or modify the safety interlocks that protect you from the RF energy and do not allow the operation of the ICP without all covers, doors, and shields in place.

The ICP generates a plasma that produces high intensity ultraviolet radiation. Directly viewing the plasma (without protection) can cause permanent damage to the eyes and impairment of eyesight. The safety interlock will automatically shut off the plasma if the sample compartment door is opened or the torch is removed. Do not attempt to defeat or modify the safety interlock. There is a specially designed viewing window for safely viewing the plasma. Do not alter this viewing window and if damaged replace the viewing window immediately before operating the ICP.

The exhaust fumes from the ICP are toxic and hot. The exhaust fumes must be properly vented by connection to a laboratory snorkel exhaust while operating the ICP. Ensure that the ventilation system is working properly prior to operating the ICP.

Do not operate the ICP unless the drain system is installed and functioning properly. The waste from the ICP is corrosive and potentially toxic. Plastic waste containers are recommended as a glass waste container may break and cause a spill of toxic or corrosive liquids. The following safety measures will be used for the drain system and waste containers:

- 3) Place the waste container in a place that is observable so that the level of collected waste can be viewed and the waste inside the waste container can be disposed of properly when full.

- 3) Monitor condition of the drain tubing regularly to check for deterioration of the draining tubing and replace the drain tubing when needed.

The waste from the ICP system is acidic, with a pH generally < 1. Waste shall be turned over to the RSKERC SHEM Manager for disposal as hazardous waste.

Liquid argon is used to operate the ICP-MS. The major hazards associated with this gas are pressure, cold temperatures, and suffocation. Follow all gas cylinder and cryogenic liquid handling safety measures as described in the EPA RSKERC Chemical Hygiene Plan. When the ICP is turned off, ensure that argon gas valves are tightly closed at the cylinder. Contact the RSKERC SHEM Manager if there are questions concerning the hazards, storage and use of the argon gas cylinder. All staff should read, understand and sign the project specific HASP for necessary safety information prior to performing any work.

5.5 Interferences

Isobaric elemental interferences are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio. Most elements have multiple isotopes and some elements have isotopes with a nominal mass shared by another element (e.g., $^{82}\text{Kr}=81.9134$ and $^{82}\text{Se}=81.9167$). In some cases, the instrument may not have the resolution required to separate these isotopes. Isotopes selected for this SOP are free from this type of interference.

Polyatomic interferences are plasma-sourced interferences that are generated when sample matrix ions combine to form a mass/charge (m/z) similar to that of the analyte. Common examples include oxides, hydrides, and chlorides of argon, rare-earth element oxides, and double-charged ions of barium. Refer to Table 1 for a list of the common polyatomic interferences for the elements covered in this SOP. The ^{16}O polyatomic species (bold and underlined in Table 1) are the abundant interfering species for which previous quadrupole ICP-MS methods have relied upon the use of mathematical corrections (e.g., Lichte et al., 1987; Vaughan and Horlick, 1990). Barium oxides, in particular, can be especially difficult interferences for europium analysis because barium can be present in groundwater at mg/L levels and the REEs are typically present at 10-100 ng/L levels. For example, assuming a Ba concentration of 1 mg/L, the amount of ^{151}Eu expected in the detector response without the ability to resolve the spectral interference is estimated as: $10^6 \text{ (ng/L)} \times 0.065$ (natural fractional abundance of ^{135}Ba) $\times 0.005$ (assumed 0.5% Ba-oxide formation) = 325 ng/L. The impact of LREE oxide formation on the HREE is less pronounced because of a smaller concentration differential, but it can still be significant in the absence of applied correction equations or the ability to spectrally resolve the polyatomic interferences.

Table 2 shows the results of calculations performed to determine the required instrument resolution necessary to resolve the polyatomic interferences. The resolving power (R) of a mass spectrometer is calculated as $R = m/(|m_1 - m_2|) = m/\Delta m$, where m_1 is the mass of one species or isotope and m_2 is the mass of the species or isotope it must be separated from; m is the nominal mass. Increasing instrumental resolution has the cost of reducing instrumental sensitivity. The results show that R values between 80 and 11,219 are needed to spectrally resolve the polyatomic interferences; thus, the medium (R=4000) and/or high resolution (R=10000) modes are capable of resolving all but the $^{150}\text{Nd}^{16}\text{O}^+$ interference on ^{166}Er . Note that the ^{150}Nd isotope

has a natural abundance of 5.6%, so it is unlikely to provide a significant signal at typical concentrations. Based on the information in Table 2 it was decided to use high resolution mode for analysis of the REE. Tests were performed to evaluate whether calibration curves could be developed for the 20 to 2000 ng/L concentration range and these tests showed that instrument sensitivity was sufficient to quantify REE concentrations at low levels. In this case, it was decided that the ability to resolve the interferences was more advantageous than obtaining extra instrument sensitivity. In order to test that the spectral interferences are indeed resolved a series of Interference Check Solutions (ICS) are used as QC samples (see Section 5.7.16.4). In addition, a second method that uses both medium resolution and high resolution was developed. This method improves sensitivity for several of the REEs that have multiple isotopes and therefore have lower mass spectral responses. This method utilizes the same calibration and QC samples, and includes the use of several correction equations, the validity of which is tested during each analytical sequence through the analysis of Interference Check Solutions (Table 1).

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. Total solid levels below 0.2% are recommended to minimize solid deposition on the nebulizer tip and cones. These interferences are minimized by the use of a mass flow controller to control the argon flow rate, the use of a peristaltic pump for sample delivery and the use of an internal standard to normalize sample viscosity and surface tension. The internal standard is added at a constant rate through the peristaltic pump to all standards and samples during the analytical run to monitor any change in signal sensitivity during the run. Corrections are made, by the software, by comparing the sensitivity for the internal standard in each run of a sample with the sensitivity of the internal standard of the calibration blank at the start of the run. When intolerable physical interferences are present in a sample, a significant suppression or enhancement of the internal standard signal (to less than 60% or more than 125% of the signal in the calibration blank) will be observed. Dilution of the sample fivefold will usually eliminate the problem. Memory interferences result when analytes in a previous sample contribute to the signals in a new sample. Memory effects are minimized by flushing the system with 2% HNO₃ between samples. For this method ¹⁰³Rh is selected as the internal standard. Note that ¹³⁹La and ¹⁴¹Pr have RhAr⁺ interferences (Table 1), however, the natural abundances of ³⁶Ar and ³⁸Ar are both below 0.35% and neither La nor Pr have appeared in blank samples.

5.6 Reagents and Supplies

5.5.2 Concentrated HNO₃

Optima grade concentrated HNO₃ (67 - 70%, Fisher Scientific; catalog# A467-1).

5.5.3 Rinsing 2% Nitric Acid (v/v)

Add 20 mL of concentrated HNO₃ to 800 mL deionized water and dilute to 1 L.

5.5.5 Deionized (DI) water

In house 18 MΩ/cm Millipore Synergy UV DI water. Distilled water is used to fill the fluid chamber in the water chiller.

5.5.5 Calibration standards

Calibration standard stock solutions must be certified to be free of other trace metals. Calibration standards are prepared by diluting multi-element standard solutions in 2% HNO₃. The shelf-life of calibration standards and QA standards is six months from the date they were made.

5.5.6 Blank

2% HNO₃ in DI Water (5.5.3).

5.5.7 Calibration Stock Solution

Multi-Element Solution, Inorganic Ventures Cat. # CMS-1. Contains 10 mg/L Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, and Yb. See Table 3 for summary of calibration solutions and Quality Control solutions.

5.5.8 Calibration Standard 1: 2 µg/L Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb

Prepare by adding 2 mL concentrated HNO₃ to 50 mL of DI water in a 100 mL volumetric flask. Pipette 1000 µL of Calibration Stock Solution (5.5.6), dilute to the mark and mix; this is a 100 µg/L solution. Prepare the 2 µg/L calibration solution by first adding 4 mL concentrated HNO₃ to 50 mL of DI water in a 200 mL volumetric flask; pipette 4000 µL of the 100 µg/L solution and dilute to the mark.

5.5.9 Calibration Standard 2: 0.50 µg/L Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb

Prepare by adding 2 mL concentrated HNO₃ to 50 mL of DI water in a 100 mL volumetric flask. Add 25 mL of Calibration Standard 1 (5.5.7) and dilute to the mark.

5.5.10 Calibration Standard 3: 0.10 µg/L Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb

Prepare by adding 2 mL concentrated HNO₃ to 50 mL of DI water in a 100 mL volumetric flask. Add 5 mL of Calibration Standard 1 (5.5.7) and dilute to the mark.

5.5.10 Calibration Standard 4: 0.02 µg/L Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb

Prepare by adding 2 mL concentrated HNO₃ to 50 mL of DI water in a 100 mL volumetric flask. Add 1.0 mL of Calibration Standard 1 (5.5.7) and dilute to the mark.

5.5.12 Tuning solution: 1 µg/mL Ba, B, Co, Ga, In, Fe, Li, Lu, K, Rh, Sc, Na, Tl, U, and Y.
High-Purity Standards Cat. # ICP-MS-TS-18

Prepare by adding 2 mL concentrated HNO₃ to 50 mL of DI water in a 100 mL volumetric flask. Add 100 µL of tuning solution (1 µg/mL) and dilute to the mark. The final concentration is 1 µg/L.

5.5.12 Internal Standard Solution: 1 µg/L Rh

Prepare by adding 500 mL of DI water to a 1000 mL volumetric flask. Add 20 mL of concentrated HNO₃, 100 µL of 10 mg/L Rh Standard Solution (Inorganic Ventures Cat. #MSRHN-10PPM 10 µg/mL), and 10 mL of 5% Triton-X 100. Dilute to volume.

5.5.13 Initial Calibration Verification (ICV, second source standard): 2 µg/L Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb

Prepare by adding 2 mL concentrated HNO₃ to 50 mL of DI water in a 100 mL volumetric flask. Add 20 µL of the multi-element second source standard [High Purity Standards Cat. #ICP-MS-B 10 mg/L].

5.5.14 Continuing Calibration Verification (CCV): 2 µg/L Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb

Prepare the same as Calibration Standard 1 (5.5.7).

5.5.15 Low-Level Quantitation Limit Check Solution 1 (LLQL): 0.02 µg/L Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb

Prepare the same as Calibration Standard 4 (5.5.10).

5.5.16 Interference Check Solution 1: 500 µg/L Ba

Prepare by adding 50 mL of DI water to a 100 mL volumetric flask. Add 2.0 mL of concentrated HNO₃ and 50 µL of 1000 mg/L Ba single element standard (Inorganic Ventures, CGBA1, 1000 mg/L). Dilute to volume.

5.5.17 Interference Check Solution 2: 2 µg/L Pr, Nd, and Eu

Prepare by first adding 50 mL of DI water to a 100 mL volumetric flask. Add 2.0 mL of concentrated HNO₃, 100 µL of Pr single element standard (Inorganic Ventures, CGPR1, 1000 mg/L), 100 µL of Nd single element standard (Inorganic Ventures, CGND1, 1000 mg/L), and 100 µL of Eu single element standard (Inorganic Ventures, CGEU1, 1000 mg/L). Dilute to volume and mix. To prepare the 2 µg/L Pr, Nd, and Eu Interference Check Solution, add 50 mL of DI water to a 100 mL volumetric flask. Add 2.0 mL of concentrated HNO₃ and 200 µL of the prepared solution. Dilute to volume.

5.5.18 Interference Check Solution 3: 2 µg/L Sm, Gd, and Tb

Prepare by adding 50 mL of DI water to a 100 mL volumetric flask. Add 2.0 mL of concentrated HNO₃, 100 µL of Sm single element standard (Inorganic Ventures, CGSM1, 1000 mg/L), 100 µL of Gd single element standard (Inorganic Ventures, CGGD1, 1000 mg/L), and 10 mL of Tb single element standard (Inorganic Ventures, MSTB-10PPM, 10 mg/L). Dilute to volume and mix. To prepare the 2 µg/L Sm, Gd, and Tb Interference Check Solution, add 50 mL of DI water to a 100 mL volumetric flask. Add 2.0 mL of concentrated HNO₃ and 200 µL of the prepared solution. Dilute to volume.

5.5.19 Matrix Spike Solution for Undigested Samples and Post- and Pre-digestion Matrix Spikes

Prepare by adding 2 mL concentrated HNO₃ to 50 mL of DI water in a 100 mL volumetric flask. Pipette 1000 µL of Calibration Stock Solution (5.5.6), dilute to the mark and mix; this is a 100 µg/L solution.

Matrix spike solution is added to each sample that is scheduled to be used for either matrix spikes. Using the 15 mL autosampler tube: add 10 mL of the sample and spike with 100 µL of the matrix spike solution; the expected increase in concentration is 1 µg/L.

5.5.20 Argon

Bulk liquid for plasma, auxillary and nebulizer flows.

5.5.21 Contrad 70 liquid detergent

5 L, Fisher Scientific Cat #04-355-1.

5.5.22 RO water

Lab supplied reverse osmosis water for rinsing glassware before acid soak.

5.5.23 3% nitric acid

Prepare by adding 5820 mL of DI water to a 11.3 L plastic tub. Add 180 mL of concentrated HNO₃. Used for the acid soaking of metals glassware.

5.7 Equipment/Apparatus

5.6.2 High Resolution Inductively Coupled Plasma Mass Spectrometer

Thermo Scientific Element XR system.

5.6.3 Refrigerated recirculator

Thermo Scientific Neslab ThermoFlex2500 set at 20 °C.

5.6.4 Controlling Computer

A Dell Optiplex 9020 computer with Windows 7 and Element ICP-MS/GD-MS Software for data acquisition and processing. The controlling computer is attached to the LABLAN network.

5.6.5 Printer

Dell B2360dn printer.

5.6.6 Analytical Balance

Mettler Toledo MS6035 analytical balance capable of weighing to 0.000 g.

5.6.7 Pipettes

Either fixed volume (50 μ L, 100 μ L, 500 μ L, or 1 mL) or adjustable volume Eppendorf pipettes will be used. The pipette tips made for Eppendorf pipettes of the appropriate volume range will be used.

5.6.9 Nalgene plastic volumetric flasks

Flasks will be used to make all solutions in this SOP. Sizes range from 100 to 1000 mL.

5.6.9 Autosampler

Elemental Scientific, Inc (ESI) model SC-E2DXS autosampler.

5.6.10 Autosampler tubes

Autosampler tubes used in this SOP will be constructed of plastic with a 15 mL volume (Thermo Scientific Nunc Part #339650 15 mL conical centrifuge tubes, blue cap).

5.6.10 Pump tubing

The pump tubing used for the ICP is made of polyvinyl chloride (PVC) and is suitable for aqueous and acidic solutions. Other materials such as viton could be substituted if the matrix to be analyzed is not compatible with PVC. The ICP peristaltic pump uses two different sizes of pump tubing which are color coded; purple-black (2.286 mm; Thermo Fisher 50001202160) and yellow-orange (0.508 mm; Thermo Fisher 50002403160).

5.6.12 Cyclonic spray chamber (quartz) with ESI Peltier cooled sample introduction (PC³)

5.6.13 Semi demountable torch with 1.5 mm injector (quartz)

5.6.14 Nickel sampler and skimmer cones

5.6.15 Peristaltic pump

5.8 Procedures

5.7.2 Glassware and Plasticware Cleaning

The following procedure is to be used to clean all glassware and plasticware used in this SOP.

Prepare cleaning solution by adding approximately 10 mL/L H₂O of 1% Contrad detergent to a tub (8 L) of warm tap water. Remove all markings and residue from glassware using a lab brush or acetone if necessary. Submerge glassware in the solution and allow it to soak for a few minutes. Clean the glassware with a lab brush. Rinse four times with reverse osmosis (RO) water, place the rinsed glassware in a tub containing 3 % (v/v) HNO₃; and allow it to soak for 4 to 16 hours. Remove glassware, rinse four times with RO water and allow it to dry (open end down) on a clean surface.

5.7.3 Sample Preparation

Aqueous samples will be stored in polyethylene containers. Aqueous samples that have been prefiltered and acidified will not need acid digestion. Digestion procedures for total recoverable metals in aqueous samples and other matrices can be found in individual SOPs (RSKSOP-179; RSKSOP-180).

Samples that are to be analyzed using this procedure must be free of solids. Solids will plug the sample introduction system. Samples that are solid-free may be analyzed directly for most elements. Samples that are to be analyzed for metals must be filtered using a 0.45 µm filter. If samples are not free from solids and do not settle out, then contact the originator of the samples to see if they wish to filter the samples or have the samples digested. Digested samples that have settled overnight and that do not have resuspended particles may be analyzed. Solids that become resuspended must be filtered out by a 0.45 µm filter prior to analysis.

In addition, it is important that all submitted field samples analyzed have field conductivity or total dissolved solids (TDS) data within 72 hrs of sample receipt. Without this information the samples will not be analyzed. This information is vital to allow the analyst to determine if dilution of the sample is needed. Samples that exceed a conductivity value of about 1.0 mS/cm or 620 mg/L TDS will need to be diluted prior to analysis. Refer to NRMRL-GWERD-11-0 for suggested dilution factors. Samples with conductivity values >5.6 mS/cm or TDS >3640 mg/L will need to be discussed with the originator prior to analysis. The dilution required will likely affect REE detections. Sample dilutions will need to be conducted prior to analysis. Lab generated samples are exempt from this requirement. Although the analyst will inquire about the nature, anticipated concentrations, and the matrix of lab generated samples.

Matrix spikes will be prepared using the following procedure. For 15 mL autosampler tubes, pipette 10 mL of sample for the matrix spike solution into a clean autosampler tube. Then pipette 100 µL of the matrix spiking solution into the same autosampler tubes. Place the cap on the autosampler tube and carefully invert the autosampler tube three times. Depending on the analytical run size, this procedure will need to be repeated until all matrix spikes have been made for the analytical sequence. See QA Section (Section 5.7.16) for matrix spike frequencies.

5.7.4 Instrument Startup Procedure

5.7.3.2 Argon Supply Check

Check and ensure that the Argon gas supply is sufficient to run the instrument. This can be accomplished by looking at the gas gauges on top of the liquid argon tank. If the tank is empty replace and then open the valve on the liquid argon. Adjust the pressure regulators attached to the liquid argon. The optimal pressure for argon is 115 psi, however the pressure should be no lower than 100 psi and no higher than 120 psi.

5.7.3.3 Starting the Autosampler

Verify that the controlling computer is booted up and that power to the HR-ICP-MS and autosampler is on. Also verify that the refrigerated circulator is running and maintaining the set temperature (20°C). This value is displayed on the LED on the front of the chiller. From the computer desktop double click on the ESI Autosampler icon. The autosampler program will load. Click on the Initialize button. Once the initialization sequence is complete, minimize the ESI Autosampler software.

Supply the autosampler rinse carboy with fresh 2% HNO₃ and verify the waste carboy has sufficient capacity.

5.7.3.3 Starting the Plasma

On the controlling computer's desktop, open the Thermo Element folder. Double click on the Network Processor icon. The Executive window will automatically open; minimize this window. Next, double click on the Instrument icon. Change the peristaltic pump tubing if any tube looks flat. From left to right, use purple-black (2.286 mm I.D.; waste), yellow-orange (0.508 mm I.D.; sample), and yellow-orange (0.508 mm I.D.; internal standard). Clamp the tubing in the middle of the track for each channel of the autosampler. Make sure that the carrier and internal standard containers are full. Verify that the waste carboy has sufficient capacity. In the Instrument program, click the HV and Peri Pump icons; the indicators will switch from red to green and the peristaltic pump will start rotating. Move the autosampler probe to a 50 mL tube containing 2% HNO₃ (typically position 1) and place the internal standard line into the vessel containing the internal standard solution. Turn on the Peltier cooled sample introduction unit by turning the switch to the up position (~2 °C).

In the Instrument program, start the plasma by clicking **ON**. An automatic sequence will be initiated. When the plasma start procedure is successfully completed, the message "Plasma Successfully Started" is displayed. Allow a plasma warm up time of at least 30 minutes before proceeding to the instrument tune.

The nominal instrument settings should read as follows:

Cool Gas [L/min] = ~16
Auxiliary Gas [L/min] = 0.8-1.0
Sample Gas [L/min] = 0.8-1.0
Fore Vacuum [mbar] = 2.3×10^{-4} (prior to torch)
High Vacuum [mbar] = 6.5×10^{-8} (prior to torch)
Argon Max [bar] = 6.3
Argon Middle [bar] = 3.5
High Voltage [V] = -7878

5.7.5 Tuning the Thermo Element XR

Instrument tuning should be conducted prior to running an analytical sequence. On a day-to-day basis, the tune parameters will not substantially change, but this needs to be verified in order to establish optimal run conditions. To tune the HR-ICP-MS first allow the instrument to warm up for at least 30 minutes. Verify the peristaltic pump is rotating and the spray chamber assembly is draining properly. Inspect the tubing for flow and for leaks.

Move the autosampler probe to a vial containing the 1 µg/L tuning solution (Section 5.5.11); place the internal standard intake tube in the 2% Nitric Acid Blank solution.

Low Resolution tuning: Open the Tune window of the software by double clicking on the Tune icon. The most recent tune file will open (.tpf). Go to Create Scan List, Load Thermo_HP_Tune_Li_In_U_UO.scl, open file, ok. Lithium, Indium, and Uranium should be in Pulse Counting mode. Hit Start Scan. If necessary, adjust the torch parameters (X- and Y-Positions; do not adjust Z-Position) and plasma group parameters (Sample Gas). Maximize for cps ${}^7\text{Li}$ and ${}^{115}\text{In}$ in the lower continuous read-out windows. Obtain a signal of at least 3×10^6 cps at ${}^7\text{Li}$ and 2.5×10^7 cps at ${}^{115}\text{In}$. Track the peak height in the upper right panel to obtain 2.5×10^6 cps at ${}^{238}\text{U}$. If needed, adjust the lens settings to obtain a stable signal (Extraction stays at -2000 V; adjust Focus, X-Deflection, Y-Deflection, and Shape). Also track the stability of the ${}^{238}\text{U}$ count rate in the lower right panel. Adjust tune parameters to achieve a %RSD value of less than 2.5%. Stop scan and Save Current Parameters to the current tune file. On a monthly basis, a new tune file will be named and saved (Thermo_Tune_MMDDYY.tpf); thus, minor day-to-day changes in the tune parameters will not result in a new tune file.

Medium Resolution Tuning: Go to Create Scan List, Load Thermo_MR_Tune_Fe_ArO_Resolution.scl and begin scanning in medium resolution to stabilize the High Resolution lenses (Focus, Rotation Quad 1, Rotation Quad 2, not Lens, Filter=0). The target resolution in MR is >4000, providing separation between Fe and ArO. Hold shift/left click to move peak (position clicked is centered) and remove the ArO component from the window in order to view the accurate resolution. Stop scan and Save Current Parameters to the tune file (Thermo_Tune_MMDDYY.tpf).

High Resolution Tuning: Go to Create Scan List, Load Thermo_HR_Tune_K_ArH_Resolution.scl and begin scanning in high resolution to stabilize the

High Resolution lenses (Focus, Rotation Quad 1, Rotation Quad 2, not Lens). The target resolution in HR is >9000, providing separation between K and ArH. Hold shift/left click to move peak and remove the ArH component in order to view the accurate resolution. Stop scan and Save Current Parameters to the tune file (Thermo_Tune_MMDDYY.tpf).

5.7.6 Perform a Method Scan

Perform a Method Scan to verify the mass calibration is valid and that the mass windows are sufficiently wide in the sequence method to acquire complete peaks in all resolutions. Use the Show window for visual inspection of the acquired data.

Open the Instrument application. The main pane in the Instrument application contains two tabbed pages: the Method tab and the Manual tab. In the Method tab, enter the Data File name to be used (i.e., Test_MM-DD-YY), enter the Method (i.e., REE HR v1.met or REE HR MR v1.met), and load the most recent Tune file. Click on the Scan button in the tool bar to start the scan. View results in Show. Verify the mass calibration is valid and that the mass windows are sufficiently wide in the sequence method to acquire complete peaks in all resolutions. If necessary, make adjustments to the method of interest or redo the mass calibration.

5.7.7 Setting up a Sample Analysis Sequence

Data acquisition on the Thermo Element XR consists of a sequence file with a list of samples. The sample information includes the name, method used, tune file, calibration, internal standard, dilution factor, autosampler position, autosampler uptake time (80 seconds), and autosampler wash time (20 seconds).

Two template sequence files have been developed for undigested and digested samples, respectively. The template to be used for undigested samples is 200_8 Sample Sequence Template Dis.seq. The template to be used for digested samples is 200_8 Sample Sequence Template Tot.seq. To access these templates, open the Sequence Editor program and load the applicable sequence template. These sequence templates are developed for 20-sample queues and include all of the necessary calibration and QC samples. Table 4 shows the sequence of samples and QC samples.

5.7.12 Calibration

Calibration must be performed on a daily basis prior to sample analysis. The calibration procedure is outlined in this section. In this method, 4-point calibration lines are created from standards prepared at 0.02, 0.10, 0.50, and 2 µg/L.

Make sure that the 50 mL vials in Auto Sampler locations 5-8 are filled with the correct calibration standards, prepared as described in Section 5.5. The calibration blank (2% nitric acid) is loaded into the 50 mL vial in Auto Sampler location 1.

Once a sample sequence has been initiated (see Section 5.7.8), the calibration blank is analyzed followed by the four calibration standards. To view the calibration results, open the Results Program. Click on the Open icon, select the file type *.cal, and load the most recent calibration file. When the calibration file is loaded in the Results Program, the tool bar icons can be used to

examine all of the isotopes specified in the method. The calibration line is shown by plotting the nominal concentration versus the normalized intensity (calibration standard intensity/internal standard intensity). In this method, all isotopes utilize a linear calibration model and a forced 0 y-intercept. This calibration was found to give the most consistent results over the entire calibration range and resulted in more consistent results for sample concentrations below the low calibration standard (0.02 µg/L).

5.7.12 Analyze Samples

Once the entire sequence file is created, then it can be used to acquire data. For data acquisition, the sequence is started from the Sequence Editor. When the sequence is started, the software checks each item in the sequence to check file names, directory destinations, etc. Detailed error descriptions, if any, are displayed in the acquisition window at the bottom of the Sequence Editor.

To initiate a sample run sequence:

- 4) Open and modify the desired sequence in the Sequence Editor.
- 5) Load all samples in the correct Auto Sampler positions. Refer to Table 4 for the correct sequence of unknown samples and QC samples.
- 6) Click on the Start icon in the tool bar to start the sequence. The Acquisition window will open at the bottom of the sequence window.
- 7) Make sure that the following boxes are checked: Acquire, Evaluate, Sample: Print Report, Sample: ASCII Report, Sequence: Print Report, and Sequence: ASCII Report.
- 8) Click on Run to start the sequence. The program will check if all items have been correctly entered. If no errors are found, then the sequence will be started. In case of missing or incorrect data, an error report will be generated in the Acquisition window. If required, correct the identified parameters and click on Run again.

5.7.11 Instrument Shutdown

To shut down the instrument the following procedure is used.

- 3) While the plasma is still on, place the carrier line and the internal standard line in a container containing 2% nitric acid. Allow this to pump for at least 5 min. before extinguishing the plasma.
- 4) Turn off the Peltier cooled (PC³) sample introduction unit by turning the switch to the middle position.
- 5) Send the sample probe to the Home position and remove the internal standard line from the internal standard solution. Allow the pump to drain the tubing lines while the torch extinguishes and cools down.
- 6) Extinguish the plasma by opening the Instrument window and switching the plasma to the off position.
- 7) Once the plasma has turned off, turn off the High Voltage and Peri Pump. The icons will switch to red when off.

- 12) Close the Instrument window. Close the Network window. Close the Executive window.
Close the Autosampler window.
- 13) Release the peristaltic pump tension.
- 14) Shut off the Argon gas at the tank by closing the valve.

5.7.10 Reporting of Results

The following section will describe how data reporting will be conducted. The data collected during each analytical run are automatically stored on the hard drive of the instrument computer, along with all methods, results, and meta-data using the ELEMENT2 software. At the end of each analytical run, an ASCII file is created that contains concentration data collected during the run. This file is used to create data reports of sample results and QC sample evaluations.

5.7.10.1 Data Archiving

Data archiving procedure described here is for transferring the analytical data collected from the HR-ICP-MS onto the LABLAN. The procedure described follows from the long-term archiving described in RSKSOP-293v1.

On a monthly basis all analytical data collected using the ICP will be archived on the LABLAN. All files and folders from the HR-ICP-MS computer located at c:\Element\user\Element\ will be copied over to the LABLAN. This procedure will ensure that all data files, methods, and instrument files will be preserved and archived.

5.7.10.2 Exporting Data for Data Report Generation

- 5) At the end of each analytical run an ASCII data file (.asc) is created and stored within the folder c:\Element\user\Element\data within a separate folder created when a new sequence is created. The folder name is the same as the sequence name.
- 6) Open a copy of Microsoft Excel. Open the ASCII file, as a delimited file, start at row 1, click on next and make sure the tab delimited box is checked, and click on finish. The resulting file can be copied and pasted into the Data Report Template in the Raw Data tab.

5.7.10.3 Data Reports

Data reports are generated by importing an ASCII file into a template Excel spreadsheet file. This spreadsheet file will automatically generate most of the final data report (Cover Page, Data, and QA) in different tabs of the spreadsheet. In addition, the template spreadsheet will automatically generate summary tables for the various types of QC samples in separate tabs and for each element will state if the element passed QA. The following procedure will be used to generate the data reports.

- 8) Open the report template in Excel; the report template file is named Element XR REE Template.xls. This template file is located on the office computer of the analyst.
- 9) Then save the report template using the save as command.

- 4) From the save file as dialog enter the file name that was used when the data were analyzed. If this is a reanalysis (dilutions, data did not meet QA requirements) then at the end of the file add the version number as v#.
- 5) Next obtain the ASCII file for the data to be reported and open this file in Excel.
- 6) Once opened copy all the data from the ASCII file into the Raw Data tab of the report Excel spreadsheet. This will automatically generate most of the report. Fill in the non-automatically filled in fields with the correct information. Much of this information (i.e., analysis date, sample date, received date, STAD number) is entered into the 2nd Tab of the report template called "Meta Data".
- 7) Save the report file.
- 8) Verify the data in the report. Add any analytical or QA comments in the appropriate fields.
- 9) Send the report to the independent data validator as defined in the roles and responsibilities section of this SOP (Section 4.2).

Once the data are received by the data validator from the primary analyst, a second review of the data will be performed. The data validator will review the report to ensure that all fields are correctly filled in, that the QA meet QA criteria specified in this SOP, and all appropriate analytical and QA comments have been added. Once this review is complete the data report and review comments will be delivered to the appropriate PI via email. Prior to sending the final checked report to the data requestor, the information in the data and QA tabs will be copied and saved as values. This will remove any of the programming codes needed to generate the report so that the data report cannot be changed inadvertently. The data will be checked to ensure that no changes were made during this step. Both copies of the final report will be saved to the validator's computer and to a SharePoint Site.

5.7.11 Mass Calibration

Periodically a mass calibration procedure needs to be run in order to maintain good accuracy of data. This routine is done on an as-needed basis. A mass calibration is required when the Automass Correction exceeds ± 500 ppm. When this occurs, a warning comes up on the instrument during the execution of an analytical sequence file; the warning prompts the analyst to conduct a Mass Calibration. Other situations that would prompt a Mass Calibration include loss of the vacuum system or the inability to observe resolved peaks when running a method scan. It is first advised to reset the method mass offsets (see section 5.7.12) prior to running a Mass Calibration. To perform the Mass Calibration, place the autosampler probe in a vial containing the 1 $\mu\text{g/L}$ Element Tune solution. Place the internal standard uptake line into the 2% Nitric Acid Blank solution.

- 2) In the Sequence editor, open the file *Thermo_Automasscal_Service_MJO_lastdate*. Select Actions, and make sure that Auto Lock Mass is unchecked. Next save as *Thermo_Automasscal_Service_MJO_newdate*. Open the Method tab on the acquisition pane of the Instrument screen.
- 3) In the Instrument pane, select the icon Run Mass Calibration. Go to the Calibration pull down menu and select Reinitialize Calibration - high resolution (yes), medium resolution (yes); never delete low resolution. Reset the EDAC values.

- 4) Go to the spreadsheet view of the Sequence Editor. Click on the Tune file and select the most recent tune file. In the sequence view of the Sequence editor, hit the barrel icon (reset all). Next select the flag icon, run, and continue (sample sequence boxes should be unchecked). Go to Show and wait for the analysis to finish.
- 5) Select the Mass Calibration icon and open the file just created file in the folder titled Thermo_Automasscal_Service_MJO_newdate, Thermo_LR_wide. Select the Manual Calibration icon (finger) and double click on the first isotope (${}^6\text{Li}$) and sequence through the range of calibration isotopes to ${}^{238}\text{U}$. Make sure that the indicator line is within the data for each peak. If not, select trash, double click in center of peak, highlight the selected isotope and select add. Save, if any changes are made.
- 6) Go back to the Sequence Editor, select continue and return to method acquisition window and repeat the procedure, Show, Mass Calibration and open the Thermo_LR_narrow file and sequence through the peaks. Repeat the process for the Medium Wide, Medium Narrow, High Wide, and High Narrow files.
- 7) After completing the Mass Calibration, go to the Sequence editor and cancel the acquisition. Open the file called Thermo_Determine_MassOffset_Checkmass_MR. In the spreadsheet view, check that the most recent tune file is present. Go to the Building Blocks icon, and open the file CheckMassDrift_MR. Change yes to no, save the file. Next open the file CheckMassDrift_HR. Change yes to no, save the file.
- 8) In the Sequence editor, highlight 1_DetermineMassOffset and reset all (barrel icon), Hit the flag, run, continue. Go to Show, note the Argon dimer peak at mass 37.925. Sequence, hit stop. Make sure 1) Determine mass Offset is selected, go to the View Results. Open file, select Update Calculated Mass Offsets, open, ok. Next highlight Sample 2) Check Mass Offset, run, and continue. Repeat process from above. If result is >0.003 then go to file and update mass offsets.
- 9) Next Repeat steps 6 and 7 after opening the file Thermo_Determine_MassOffset_Checkmass_HR in the Sequence editor.
- 10) In Actions make sure that AutoLock mass is checked.
- 11) In Building blocks (in HR), change no to yes, save. Open checkmass Drift MR, change no to yes, save.
- 12) Next the mass offsets need to be updated for each method.

5.7.12 Changing Mass Offsets for a Method

Place the autosampler probe in a vial containing the 2.0 $\mu\text{g/L}$ calibration solution (see 5.5.7). Also place the internal standard uptake line into the 1 $\mu\text{g/L}$ internal standard solution. In the building blocks/method editor, make sure that the specified offsets are all set to 0. In the Sequence editor, open the file Thermo_Determine_MassOffset_analytical.seq. In the spreadsheet view, make sure that the most recent tune file is loaded and load the method requiring the new mass off set change. In the sequence view, under Actions, make sure that Auto Lock Mass is unchecked. Highlight the first line, select reset all (barrel icon). Select flag icon, run, and continue. This process takes a while. You can observe the Argon dimer peak in the Show program, when finished hit stop. In the View Results program, highlight 1 and update. Next highlight the second line, run, continue, and Show. Go to View Results, update. Finally in

Actions, make sure the Auto Lock Mass is checked, and save. Now go to the sequence pane and cancel. Repeat for all methods in use.

5.7.13 Determining Method Detection Limits

The Method Detection Limits are 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 and is determined from analysis of a sample in a given matrix containing the analyte.” (RSKSOP-248v1). For each element the MDL is determined from analysis of a sample in a given matrix that contains the element(s). The MDL studies must be repeated on an annual basis or if the procedure changes or if there are changes to the instrument.

The MDLs will initially be estimated from previously determined MDLs and based on the QLs for each element. The following is the method that will be used to determine the MDLs.

- 2) Prepare a stock solution between two to five times the estimated MDL. Generally, a concentration set at ½ the QL will be used.
- 3) Calibrate the instrument.
- 4) Analyze the stock solution prepared in step 1 ten times.
- 5) Calculate the standard deviation, s , of the ten replicate measurements using a software package such as Excel.
- 6) Compute the MDL using: $MDL = t \cdot s$

Where t is the Student’s t -value at the 99% confidence level and s is the standard deviation of the replicates. The Student’s t value (1 sided) for ten replicates is 2.821.

The MDLs must be verified by analyzing an MDL Check standard. This check standard is spiked with all target analytes at 2x the calculated MDL and analyzed to verify that detection of each analyte is evident. The MDL check sample must show a response for each analyte. If a response is not detected the MDL study must be repeated at higher concentrations.

The QL and MDL for each element covered in this SOP is provided in Table 5.

5.7.14 Linear Dynamic Range

When using this SOP, sample concentrations must fall within the calibration range, i.e., within the linear dynamic range, or $<2 \mu\text{g/L}$. Sample concentrations that exceed the high calibration sample (after any dilution) will be rejected. The PI will be consulted to determine if sample dilution is required for specific analytes that fall outside of the calibration range.

5.7.15 Calculations

This section describes the calculations performed by the Element ICP-MS/GD-MS software. Calculations include determination of calibration lines using linear regression, regression coefficients, standard deviations, and relative standard deviations (RSD). See Section 5.7.16 for QA/QC calculations. Any dilution factors must be entered into the sample sequence file in order

for the software to calculate correct results. The average of 6 replicate readings for each sample and QC check is reported.

A linear regression is used for calculating the concentrations of all elements in this SOP and is calculated by the Element software. The linear regression equation is based on a linear relationship between the concentration and the normalized intensity relative to the internal standard with a forced intercept through 0, and the basic equation used is:

$$y=mx+0, \text{ Equation 1}$$

The standard deviation (SD) equation used by the Element software to calculate the variability between replicate analyses is given in Equation 2:

$$SD = \sqrt{\frac{\sum(c_i - c_{mean})^2}{n-1}}, \text{ Equation 2}$$

where c_i is the concentration in each replicate measurement, c_{mean} is the mean concentration of the 6 replicates, and n is the number of measurements. The equation used to measure the relative standard deviation (RSD), a measurement of precision in replicate analysis is given in Equation 3:

$$RSD (\%) = 100 \times \left(\frac{SD}{mean}\right), \text{ Equation 3}$$

where SD is the standard deviation for the replicates and the mean is the mean of the replicates.

5.7.16 Quality Assurance/Quality Control

A summary of QA Types, acceptance criteria, and analysis frequencies is given in Table 6.

5.7.16.1 Blanks

There are two types of blanks, the initial calibration blank or continuing calibration blank and the digestion or preparation blank. An initial calibration blank (ICB) is analyzed at the beginning of each analytical run, immediately after the calibration and the ICV (Table 4). Continuing calibration blanks (CCB) are analyzed after every 10 samples during the analytical queue and at the end of each analytical run. The acceptance criteria for the ICB and CCBs are that the concentrations are less than the QL for each element analyzed. If this criterion cannot be met, then the specific element for which the criterion was not met will be noted in the data report issued to the PI. Depending on project-specific requirements, re-calibration and reanalysis of samples may be needed, otherwise the samples will be qualified to show that the blank criteria were not met. Whether the samples prior to the failure of the blank should be re-analyzed or not, is decided by evaluation of the sample prior to the blank analysis to determine if the blank value is caused by sample carry-over. If the samples analyzed prior to the blank are less than the MDL or greater than 10 times the blank concentration the samples will not have to be reanalyzed.

A digestion blank (using DI water) should be carried out for each digestion batch of 20 or less samples for microwave digestion. The digestion or preparation blanks will be analyzed after the ICB or CCB (Table 4). The acceptance criteria for the digestion blanks or preparation blanks are

that the concentrations in the blanks are less than the QL. If this criterion cannot be met, re-analysis of the digestion blank or preparation blank may be required depending on project-specific requirements, otherwise the samples will be qualified to show that the blank criteria were not met.

5.7.16.2 Initial Calibration Verification Standard

The initial calibration verification standard (ICV) is prepared from a different source than the calibration standards. It is analyzed immediately after the calibration standards (Table 4). The acceptance criterion is based on a percent recovery (Equation 4). The acceptance criteria for the ICV are that the percent recoveries must fall within the range of 90 – 110% of their expected value. If this acceptance criterion is not met, then element specific results will be qualified in the data report submitted to the PI. Re-analysis of the ICV may be required based on project-specific requirements.

$$\text{Percent Recovery} = \left(\frac{C_{\text{result}}}{C_{\text{true concentration}}} \right) \times 100, \text{ Equation 4}$$

In addition, natural reference waters were obtained from P. Verplanck (U.S. Geological Survey). These REE-containing mine waters were used to verify the analytical method described here. Approximately 500 mL of each reference water (SCREE and PPREE) were received and analyzed using this method. Results are shown in Figure 1. Percent errors were typically less than 5% (93% of elements were <5%), with none above 10%. These reference waters will be analyzed periodically to verify the method response, however, the ICV will utilize commercial multi-element standards.

5.7.16.3 Continuing Calibration Standards

Continuing calibration verification (CCV) standards must be analyzed at the beginning, every 10 samples and at the end of each analytical run. The analysis of the CCV immediately following calibration should be after the ICV (Table 4). The acceptance criteria for the percent recoveries for all analytes must fall within the range of 90 – 110% of the expected value. If this acceptance criterion is not met, then element specific results will be qualified in the data report submitted to the PI. The percent recovery is calculated as shown in Equation 4.

5.7.16.4 Interference Check Solutions (ICS1, ICS2, and ICS3)

These check solutions verify the accuracy of results in the presence of Ba and interfering REEs (e.g., Pr, Nd, Eu, Sm, Gd, and Tb). In this method, the ICS1 (500 µg/L Ba), ICS2 (2 µg/L Pr, Nd, and Eu) and ICS3 (2 µg/L Sm, Gd, and Tb) check solutions are run at the end of each analytical sequence. The acceptance criterion for the ICS1 solution is that the concentration of Eu is below the QL. The acceptance criteria for the ICS2 solution are that the concentrations of Gd(Pr), Tb(Nd), Er(Nd), and Tm(Eu) are below the QL. The acceptance criteria for the ICS3 solution are that the concentrations of Dy(Sm), Ho(Sm), Er(Gd), and Lu(Tb) are below the QL. The recovery of the primary elements (Pr, Nd, Eu, Sm, Gd, and Tb) should be within the range of 80 - 120% of the expected value for all elements. If these criteria are not met, then element specific results will

be qualified in the data report submitted to the PI. The percent recoveries are calculated using Equation 4.

5.7.16.5 Low-Level Quantitation Limit Standard (LLQLS)

A low-level quantitation limit standard (LLQLS) should be prepared and analyzed at the beginning of the analytical sequence. The acceptance criterion for the LLQLS is a percent recovery (Equation 4) that ranges from 70 - 130% of its true value. After the calibration acceptance criteria are met, the LLQLS concentration is used to demonstrate the lower limit of quantitation. Sample results reported between the MDL and the quantitation limits are reported as estimated. Samples concentrations < MDL are not reported.

5.7.16.6 Laboratory Control Sample (LCS)

For each batch of 20 samples digested, a laboratory control sample (LCS) must be carried through the digestion procedure. The LCS will be spiked at the same concentrations as the matrix spike. The acceptance criterion for the LCS's percent recovery (Equation 5) is the analyzed concentration must be within the range of 85 – 115% of the expected value for each element. If the LCS acceptance criterion is not met, then the QA results will be reported to the PI. Re-analysis may be required based on project specific requirements. If enough sample remains, then the entire batch of samples may require redigestion. For undigested samples, the CCCs are prepared at the same range of concentrations as the matrix spikes and as there is no sample preparation involved they may serve as the undigested LCS.

5.7.16.7 Digested Samples: Matrix Spikes

For each batch of 20 or fewer samples requiring digestion, one sample that is representative of each sample matrix should be spiked prior to digestion at a concentration approximately near the mid-point of the calibration curve. The ideal sample for spiking would contain a low analyte concentration, but still have the same matrix as the remaining samples. The spiked sample is then digested and analyzed the same way as the other samples. The acceptance criterion for pre-digestion spikes is that the percent recoveries (Equation 5) must be within a range of 70 - 130%, otherwise, re-analysis of the spiked sample may be required based on project specific requirements. If matrix spike results still fail and the LCS for the affected analytes is in control, the recovery problem is most likely matrix related and the matrix spike results should be flagged. If the concentration of the spiked analyte is <30% of the native analyte concentration in the sample, then recovery limits are not evaluated.

$$\text{Percent Recovery} = \left((C_{\text{spiked sample}} - C_{\text{unspiked sample}}) / C_{\text{spike}} \right) \times 100, \text{ Equation 5}$$

For each predigestion matrix spike, a post-digestion spike is prepared, from the same sample that the matrix spike was analyzed on. The spike is added to the digestate just prior to analysis. Preferably, the spike amount will yield a concentration that is a minimum of 20 times the MDL and a maximum of 100 times the MDL. For each matrix, the acceptance criterion is the percent recovery of post-digestion spikes which must be in the range of 70 – 130%. If re-analysis for an individual spiked sample does not meet the latter criteria then matrix effects are confirmed.

Bonita Peak Mining District 2018 High Flow Seeps, Springs, and Draining Adits Investigation Field Sampling Plan
confirming version status against the electronic version in the document control system.

5.7.16.8 Serial Dilution

The serial dilution test is performed every 20 samples (for digested samples, every 20 samples digested). If the sample concentration is sufficiently high (minimally a factor of 50 above the MDL in the original sample but less than the highest calibration standard) an analysis of a 5x dilution should agree within 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

5.7.16.9 Undigested Samples: Matrix Spikes

For samples that can be analyzed without digestion, at least two samples should be spiked per 20 samples or less will be conducted for each sample matrix type to measure the signal suppression or enhancement caused by the sample matrix. Preferably, the spike amount will yield a concentration that is in the mid-range of the calibration curve. The acceptance criteria are that for each matrix, the spiked analytes percent recoveries (Equation 5) must fall with the range of 70 - 130%. If this criterion is not met then results will be qualified in the data report to the PI. If the concentration of the spiked analyte is less than 30% of the native analyte concentration in the sample, then recovery limits are not evaluated.

5.7.16.10 Duplicates

For digested samples a sample is digested as a duplicate to check precision at a minimum of every 20 or fewer samples. Relative Percent Difference (*RPD*; Equation 6) is used for comparing the duplicates.

$$RPD = \frac{(|C_{duplicate} - C_{sample}|)}{\left(\frac{C_{sample} + C_{duplicate}}{2}\right)} \times 100, \text{ Equation 6}$$

For concentrations $\geq 5x$ the QL, the acceptance criterion for the digested duplicate is $RPD \leq 20\%$ for aqueous samples and $RPD \leq 35\%$ for solid samples. If the acceptance criteria are not met then the results will be noted in the data report submitted to the PI. For results less than five times the QL, the difference between the sample and duplicate should be within \pm the QL. If the RPD is still outside the acceptance criteria, then the sample originator should be contacted to determine if the entire batch of samples will have to be re-digested and reanalyzed unless there is a reason to believe that the variation is caused by the sample itself rather than the digestion procedure. If they are not re-analyzed, the duplicate results will be qualified in the data report.

For undigested samples two samples will be analyzed with a duplicate per 20 samples. For concentrations $\geq 5x$ the QL, the acceptance criterion is $RPD \leq 15\%$. If the acceptance criteria are not met, results will be qualified in the data report submitted to the PI. If the concentrations of metals of interest are less than five times the quantitation limit then the difference between the sample and duplicate should be within \pm the QL.

5.7.17 Maintenance

Routine maintenance is an important part of maintaining the optimal performance of the instrument. This section describes the routine maintenance that is recommended by the manufacturer to maintain optimal performance of the ICP-MS.

5.7.17.1 Daily Checks

Before operating the instrument each day the following should be checked.

- 2) Check the Argon pressure and ensure that the pressure is approximately 120 psi.
- 3) Check the chiller pressure and water level.
- 4) Check the exhaust system for the torch box, the filter should be dust and particle free.
- 5) Check and empty the waste container.
- 6) Log fore and high vacuum pressures while the plasma is on, with the skimmer valve open and while aspirating sample.

5.7.17.2 Weekly Checks

Every week, when the instrument is in use, the following should be checked. If the instrument has not been used for an extended period of time the following should be checked prior to running samples.

- 2) Check the oil levels in the rotary vane pump and the interface pump once the instrument has warmed up.
- 3) Check the oil color in the rotary vane and the interface pump. See figure below as a guide. Do not let the color of the oil exceed the color 5 to 6 below. If pump oil color ranges from 7 to 8, permanent damage to the pump will occur.



Figure is from Thermo Fisher Scientific

5.7.17.3 Monthly Checks

Once a month check and replace if necessary the pump strainer in the external chiller.

5.7.17.4 Quarterly

On a quarterly basis (3 months) replace the cooling water in the external chiller. Do not use DI water, only use distilled water.

5.7.17.5 Every 6 months

The following should be replaced every 6 months.

- 6) Replace the oil in the DUO 5 rotary vane pump. The replacement oil must be Pfeiffer P3 oil (Part No. 109 4301).
- 7) Replace the oil reservoirs in all the turbo pumps TMH 071 (Part No. 017 2350) and TMH 262 (Part No. 105 0160).

5.7.17.6 Annually

Annually replace the interface pump (UNO 30M) oil. The replacement oil must be Pfeiffer F4 oil (Part No. 113 6532) approximately 1.1 L of oil is needed. It is expected that the instrument will be placed on an annual service and maintenance agreement which would include an annual evaluation by an authorized service technician.

5.7.17.7 As needed

The following should be replaced as needed.

- 3) Replace skimmer valve o-rings and extraction lens (Kit Part No. 112 0650) when extraction lens becomes contaminated or if the skimmer valve opens too slowly.
- 4) Replace detector (SEM Part No. 115 2700) when the plateau voltage is greater than 2800 V.
- 5) Replace entrance slits (Part No. 104 7360) when LR peak is no longer trapezoidal or HR transmission is less than 0.8%.

5.7.17.8 Before Plasma Ignition

- 3) Visually inspect the interface and inlet system. Clean or replace contaminated parts. Replace worn or damaged parts.
- 4) Check torch and coil to ensure they are not burned or damaged. Replace torch and coil if either of these conditions has occurred.
- 5) Check guard electrode contact problems or damage. Replace as needed.
- 6) Check quartz insulator for burn marks or metal coatings. Replace if these have occurred.
- 7) Check cones and gaskets for damage or contamination. Clean or replace cones and replace gaskets if needed.
- 8) Check peristaltic tubing and all other tubing. Replace as needed.

6 RECORDS GENERATED

File Type	Agency File Code	Closure	Retention	Custodian/location records
Environmental Programs and Projects – Historically significant environmental program and project records	108_1035a	Close when activity, project, or topic completed.	Permanent	Custodian – PI Location – see QAPP
Environmental Programs and Projects – Long-term environmental program and project records	108_1035b	Close when activity, project, or topic completed.	Destroy 20 years after file closure.	Custodian – PI Location – see QAPP
Environmental Programs and Projects – Site-Specific – Long – term site-specific records.	108_1036c	Close when activity, project, or topic completed.	Destroy 30 years after file closure.	Custodian – PI Location – see QAPP
Environmental Programs and Projects-Short-term environmental program and project records (logbooks)	108-1035d	Close when logbook is full or activity is completed.	Destroy 5 years after file closure.	Custodian-Laboratory PI Location-lab where instrument is located

7 REFERENCES

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8 TABLES & FIGURES

Table 1. Analytes covered in this SOP, resolution scanned, and potential interferences. Relative abundance of the isotope is provided in parentheses (%).

Analyte	Mass	Resolution ¹		Polyatomic Interferences
		HR	MR	
La	139 (99.9)	•		101Ru ³⁸ Ar ⁺ , 99Ru ⁴⁰ Ar ⁺ , 103Rh ³⁶ Ar ⁺ , 123Sb ¹⁶ O ⁺ , 123Te ¹⁶ O ⁺ , 121Sb ¹⁸ O ⁺
Ce	140 (88.5)	•		100Ru ⁴⁰ Ar ⁺ , 102Ru ³⁸ Ar ⁺ , 100Mo ⁴⁰ Ar ⁺ , 104Pd ³⁶ Ar ⁺ , 104Ru ³⁶ Ar ⁺ , 124Te ¹⁶ O ⁺ , 124Sn ¹⁶ O ⁺ , 124Xe ¹⁶ O ⁺ , 123Sb ¹⁷ O ⁺
Pr	141 (100)	•		101Ru ⁴⁰ Ar ⁺ , 103Rh ³⁸ Ar ⁺ , 105Pd ³⁶ Ar ⁺ , 125Te ¹⁶ O ⁺ , 123Sb ¹⁸ O ⁺
Nd	146 (17.2)	•	•	98Ru ¹⁶ O ³⁺ , 106Pd ⁴⁰ Ar ⁺ , 108Pd ³⁸ Ar ⁺ , 106Cd ⁴⁰ Ar ⁺ , 110Cd ³⁶ Ar ⁺ , 110Pd ³⁶ Ar ⁺ , 130Xe ¹⁶ O ⁺ , 130Te ¹⁶ O ⁺ , 130Ba ¹⁶ O ⁺ , 128Te ¹⁸ O ⁺ , 129Xe ¹⁷ O ⁺
Sm	147 (15.0)	•	•	107Ag ⁴⁰ Ar ⁺ , 111Cd ³⁶ Ar ⁺ , 131Xe ¹⁶ O ⁺ , 129Xe ¹⁸ O ⁺ , 130Te ¹⁷ O ⁺
Eu	151 (47.8)	•	•	111Cd ⁴⁰ Ar ⁺ , 113In ³⁸ Ar ⁺ , 113Cd ³⁸ Ar ⁺ , 115Sn ³⁶ Ar ⁺ , 115In ³⁶ Ar ⁺ , 135Ba ¹⁶ O ⁺ , 133Cs ¹⁸ O ⁺
Gd	157 (15.7)	•		117Sn ⁴⁰ Ar ⁺ , 119Sn ³⁸ Ar ⁺ , 121Sb ³⁶ Ar ⁺ , 141Pr ¹⁶ O ⁺ , _____ 140Ce ¹⁷ O ⁺ , 139La ¹⁸ O ⁺ , 138Ba ¹⁹ F ⁺
Tb	159 (100)	•		143Nd ¹⁶ O ⁺ , 119Sn ⁴⁰ Ar ⁺ , 121Sb ³⁸ Ar ⁺ , 123Sb ³⁶ Ar ⁺ , 123Te ³⁶ Ar ⁺ , 141Pr ¹⁸ O ⁺ , 142Nd ¹⁷ O ⁺
Dy	163 (24.9)	•	•	123Sb ⁴⁰ Ar ⁺ , 123Te ⁴⁰ Ar ⁺ , 125Te ³⁸ Ar ⁺ , 127I ³⁶ Ar ⁺ , 147Sm ¹⁶ O ⁺ , 145Nd ¹⁸ O ⁺
Ho	165 (100)	•	•	149Sm ¹⁶ O ⁺ , 125Te ⁴⁰ Ar ⁺ , 127I ³⁸ Ar ⁺ , 129Xe ³⁶ Ar ⁺ , 147Sm ¹⁸ O ⁺
Er	166 (33.6)	•		150Nd ¹⁶ O ⁺ , 150Sm ¹⁶ O ⁺ , 126Te ⁴⁰ Ar ⁺ , 128Xe ³⁸ Ar ⁺ , 126Xe ⁴⁰ Ar ⁺ , 128Te ³⁸ Ar ⁺ , 130Xe ³⁶ Ar ⁺ , 148Sm ¹⁸ O ⁺ , 148Nd ¹⁸ O ⁺
Tm	169 (100)	•		153Eu ¹⁶ O ⁺ , 129Xe ⁴⁰ Ar ⁺ , 131Xe ³⁸ Ar ⁺ , 133Cs ³⁶ Ar ⁺ , 152Sm ¹⁷ O ⁺ , 151Eu ¹⁸ O ⁺
Yb	172 (21.9)	•	•	132Xe ⁴⁰ Ar ⁺ , 134Ba ³⁸ Ar ⁺ , 132Ba ⁴⁰ Ar ⁺ , 134Xe ³⁸ Ar ⁺ , 136Ba ³⁶ Ar ⁺ , 136Xe ³⁶ Ar ⁺ , 156Gd ¹⁶ O ⁺ , 156Dy ¹⁶ O ⁺ , 154Sm ¹⁸ O ⁺
Lu	175 (97.4)	•		159Tb ¹⁶ O ⁺ , 135Ba ⁴⁰ Ar ⁺ , 137Ba ³⁸ Ar ⁺ , 139La ³⁶ Ar ⁺ , 157Gd ¹⁸ O ⁺

Notes: ¹Two method files are available for use. REE HR v1.met has all elements in high resolution and no correction equations are used. REE HR MR v1.met has Nd, Sm, Eu, Dy, Ho, and Yb in medium resolution and all other REEs in high resolution. Correction equations are utilized as follows:

$$\text{Eu}151 = -0.0015 * \text{Ba}135; \text{Dy}163 = -0.0069 * \text{Sm}147; \text{and } \text{Yb}172 = -0.0205 * \text{Gd}157.$$

The validity of these correction equations is checked during each analytical sequence through the analysis of Interference Check Solutions (ICS1, ICS2, and ICS3). The ¹⁴⁹Sm¹⁶O⁺

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interference on Ho165 does not produce a signal at 2 µg/L (ICS3) in medium resolution;
thus, no correction equation is used for Ho165.

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Table 2. Instrumental resolution required to separate polyatomic interferences.

Isotope	Mass	Polyatomic Interference	Interferent Mass	Abundance ¹ %	Resolution Required
Eu151	150.9196	¹³⁵ Ba ¹⁶ O ⁺	150.9005	6.6	7910
Gd157	156.9339	¹⁴¹ Pr ¹⁶ O ⁺	156.9023	100	4970
Tb159	159.9250	¹⁴³ Nd ¹⁶ O ⁺	158.9045	12.2	156
Dy163	162.9284	¹⁴⁷ Sm ¹⁶ O ⁺	162.9096	15.1	8675
Ho165	164.9303	¹⁴⁹ Sm ¹⁶ O ⁺	164.9118	13.9	8924
Er166	165.9304	¹⁵⁰ Nd ¹⁶ O ⁺	165.9156	5.6	11219
Er166	165.9304	¹⁵⁰ Sm ¹⁶ O ⁺	165.9119	7.4	8974
Tm169	168.9344	¹⁵³ Eu ¹⁶ O ⁺	168.9158	52.2	9086
Yb172	171.9366	¹⁵⁶ Gd ¹⁶ O ⁺	171.9170	20.6	8780
Lu175	174.9409	¹⁵⁹ Tb ¹⁶ O ⁺	176.9199	100	80

Notes: ¹The natural abundance (%) is provided for the interfering isotope.

Table 3. Summary of calibration solutions and Quality Control samples used with this SOP.

Description	Concentration
Calibration Solutions (4-point calibration)	0.02 µg/L, 0.10 µg/L, 0.50 µg/L and 2 µg/L of Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb
Initial Calibration Verification (ICV) (second source standard)	2 µg/L of Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb
Initial Calibration Blank (ICB)	2% HNO ₃
Low-Level Quantitation Limit Check (LLQL)	0.02 µg/L of Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb
Continuing Calibration Verification (CCV) (primary source standard)	2 µg/L of Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb
Interference Check Solution 1 (ICS1)	500 µg/L of Ba
Interference Check Solution 2 (ICS2)	2 µg/L of Pr, Nd, Eu
Interference Check Solution 3 (ICS3)	2 µg/L of Sm, Gd, Tb
Matrix Spike Solution (undigested/post-digestion matrix Spikes)	100 µg/L of Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb

Table 4. Example run sequences for 20 undigested and digested samples.

Undigested sample run sequence	Digested sample run sequence
Calibration Blank	Calibration Blank
Calibration Standards (4 point)	Calibration Standards (4 point)
ICV	ICV
ICB	ICB
LLQL	LLQL
CCV1	CCV1
CCB1	CCB1
Sample 1	Digestion Blank
Sample 1 Duplicate (D)	Lab Control Sample
Sample 1 Serial Dilution (L)	Sample 1
Sample 1 Matrix Spike (SP)	Sample 1 Duplicate (D)
Samples 2-7	Sample 1 Serial Dilution (L)
CCV2	Sample 1 Matrix Spike (SP)
CCB2	Sample 1 Post-Digestion Spike (PDS)
Samples 8-11	Samples 2-4
Sample 11 Duplicate (D)	CCV2
Sample 11 Matrix Spike (SP)	CCB2
Samples 12-16	Sample 5-10
CCV3	Sample 11
CCB3	Sample 11 Matrix Spike (SP)
Samples 17-20	CCV3
CCV4	CCB3
CCB4	Samples 12-20
ICS1	CCV4
ICS2	CCB4
ICS3	ICS1
	ICS2
	ICS3

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Table 5. Method Detection Limit (MDL) and Quantitation Limit (QL) for elements covered in this SOP.

Analyte	HR-ICP-MS		HR-ICP-MS	
	HR Method		MR HR Method	
	MDL ($\mu\text{g/L}$)	QL ($\mu\text{g/L}$)	MDL ($\mu\text{g/L}$)	QL ($\mu\text{g/L}$)
La	0.002	0.02	0.002	0.02
Ce	0.002	0.02	0.002	0.02
Pr	0.002	0.02	0.002	0.02
Nd	0.005	0.02	0.001	0.02
Sm	0.003	0.02	0.001	0.02
Eu	0.003	0.02	0.001	0.02
Gd	0.003	0.02	0.003	0.02
Tb	0.001	0.02	0.001	0.02
Dy	0.002	0.02	0.001	0.02
Ho	0.001	0.02	0.001	0.02
Er	0.002	0.02	0.001	0.02
Tm	0.001	0.02	0.001	0.02
Yb	0.003	0.02	0.001	0.02
Lu	0.001	0.02	0.001	0.02

Table 6. QC Sample Type, Acceptance Criteria, and Analytical Frequency for this SOP based on EPA Method 200.8.

QC Type	Acceptance Criteria	Frequency
Initial Calibration Verification (ICV)	90-110% Recovery	Immediately after calibration
Initial Calibration Blank (ICB)	≤QL	Analyzed at the beginning of the analytical run
Low-Level Quantification Limit Standard (LLQL)	70-130% Recovery	Analyzed after the ICB
Continuing Calibration Verification (CCV)	90-110% Recovery	At the beginning and end of run, and after every 10 samples
Continuing Calibration Blank (CCB)	≤QL	Analyzed immediately after every CCV; at beginning and end of run and every 10 samples
Duplicate Sample (undigested)	RPD<15% for sample values >5xQL; for sample values <5xQL, control limit = QL	Every 10 samples
Serial Dilution	If the analyte concentration is sufficiently high (minimally a factor of 10 above the MDL in the original sample but <the high calibration standard), the serial dilution (a five-fold dilution) shall then agree within 10% of the original determination after correction for dilution.	Every 20 samples
Matrix Spike (digested and undigested)	70-130% Recovery (Recovery calculations are not required if the spiked analyte is <30% of the native analyte concentration.)	Every 10 samples
Digestion Blank	≤QL	Every 20 samples
Laboratory Control Sample	85-115% Recovery	Every 20 samples
Post-Digestion Spike	70-130% Recovery	1 per batch of 20 samples
Duplicate Sample (digested)	RPD≤20% for aqueous sample (≤35 for solid samples) values ≥5x QL; for sample values <5xQL, control limit = QL	Every 20 samples
Interference Check Standard	For solution ICS1, Eu≤QL; for solution ICS2 Gd, Tb, Er, and Tm≤QL; for solution ICS3 Dy, Ho, Er, and Lu≤QL. For ICS2 and ICS3, the primary elements (Pr, Nd, Eu and Sm, Gd, Tb) should have 80-120% Recovery.	Run at the end of each sequence.

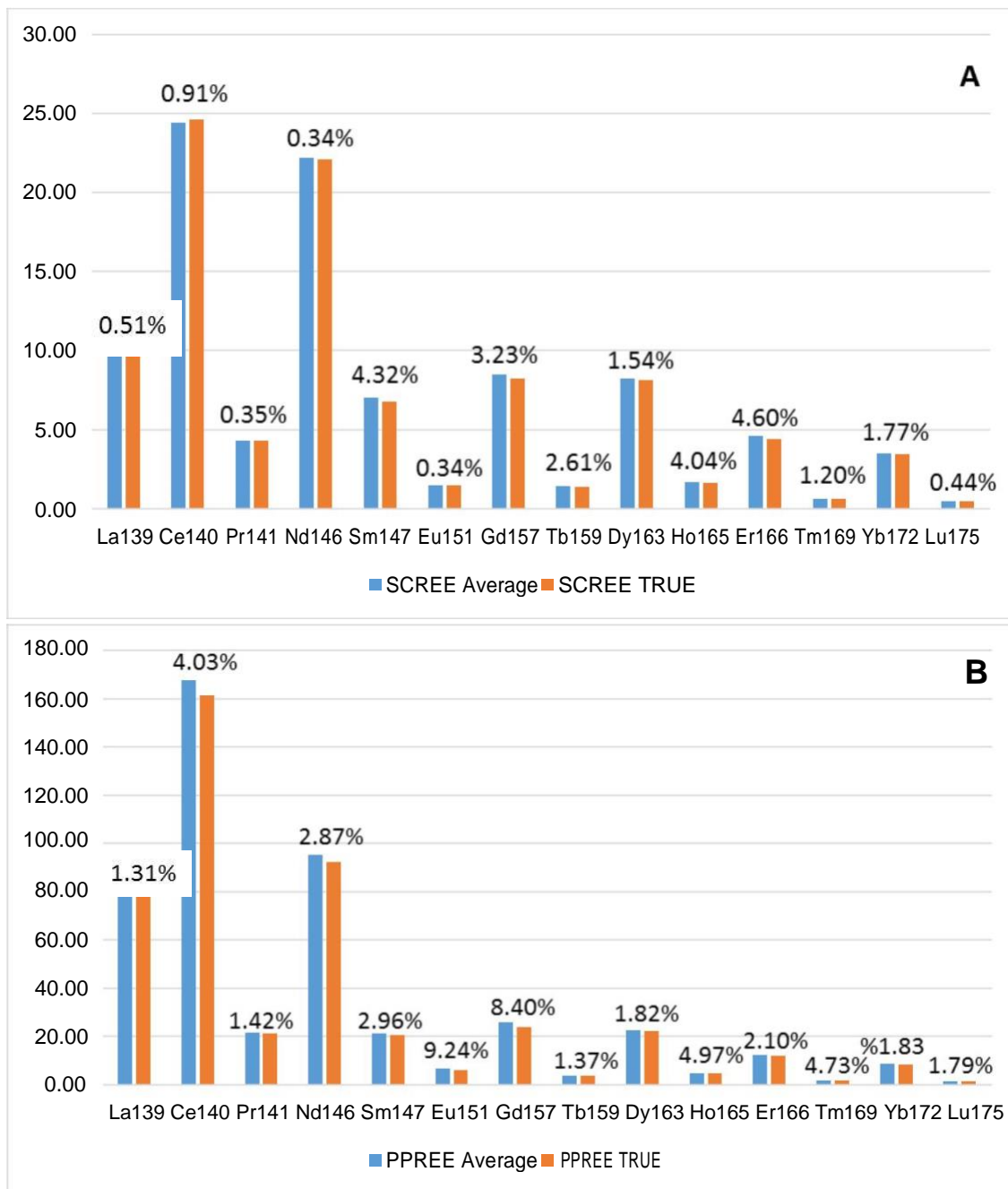


Figure 1. Results of USGS REE reference waters (µg/L, SCREE [A] and PPREE [B]; using REE HR v1.met). Blue bars show values from this method (n=2; SCREE 50x dilution, PPREE 100x dilution) and orange bars are the most probable values provided by Verplank et al. (1999); % error shown.

9 REVISION HISTORY

Revision #	Description	Effective Date
0	Initial Version	Date Management Approves

Appendix 9

Seeps and Springs Site Locations and Coordinates

Site ID	AREA	LAT	LONG
SS001	Eureka_Gulch	37.905365	-107.61578
SS002	Eureka_Gulch	37.905117	-107.615672
SS003	Eureka_Gulch	37.904255	-107.614295
SS004	Eureka_Gulch	37.904122	-107.614155
SS005	Eureka_Gulch	37.904122	-107.614155
SS006	Eureka_Gulch	37.895306	-107.618645
SS007	Eureka_Gulch	37.92052	-107.633544
SS008	Cement_Creek	37.920468	-107.632023
SS009	Cement_Creek	37.920056	-107.630744
SS010	Cement_Creek	37.91965	-107.6307
SS011	Cement_Creek	37.918808	-107.630075
SS012	Cement_Creek	37.86854	-107.643707
SS013	Cement_Creek	37.86952	-107.644713
SS014	Cement_Creek	37.871164	-107.642219
SS015	Cement_Creek	37.881573	-107.646016
SS016	Cement_Creek	37.8819	-107.645897
SS017	Cement_Creek	37.883718	-107.646793
SS018	Cement_Creek	37.886621	-107.64851
SS019	Cement_Creek	37.90706	-107.632797
SS020	Cement_Creek	37.906326	-107.630939
SS021	Cement_Creek	37.905258	-107.630635
SS022	Cement_Creek	37.90493	-107.630232
SS023	Cement_Creek	37.904364	-107.629131
SS024	Cement_Creek	37.903941	-107.626835
SS025	Cement_Creek	37.90822	-107.623109
SS026	Cement_Creek	37.913774	-107.629268
SS027	Cement_Creek	37.91265	-107.632752
SS028	Cement_Creek	37.912872	-107.632396
SS029	Cement_Creek	37.894614	-107.614796
SS030	Eureka_Gulch	37.894083	-107.615165
SS031	Eureka_Gulch	37.893836	-107.614318
SS032	Eureka_Gulch	37.894679	-107.613936
SS033	Eureka_Gulch	37.894703	-107.613267
SS034	Eureka_Gulch	37.894494	-107.612788
SS036	Eureka_Gulch	37.891128	-107.607551
SS037	Eureka_Gulch	37.893231	-107.609872

Site ID	AREA	LAT	LONG
SS038	Eureka_Gulch	37.895748	-107.606359
SS039	Eureka_Gulch	37.893643	-107.606734
SS040	Eureka_Gulch	37.891882	-107.60492
SS041	Eureka_Gulch	37.892134	-107.602922
SS042	Eureka_Gulch	37.892317	-107.60237
SS043	Eureka_Gulch	37.893254	-107.601083
SS044	Cement_Creek	37.908677	-107.639612
SS045	Cement_Creek	37.907822	-107.640522
SS046	Cement_Creek	37.907521	-107.640225
SS047	Cement_Creek	37.888791	-107.632963
SS048	Cement_Creek	37.890559	-107.632656
SS049	Cement_Creek	37.886676	-107.634941
SS050	Cement_Creek	37.887072	-107.635941
SS051	Cement_Creek	37.887235	-107.637596
SS052	Cement_Creek	37.887021	-107.637859
SS053	Cement_Creek	37.881428	-107.637774
SS054	Cement_Creek	37.882417	-107.638575
SS055	Cement_Creek	37.889338	-107.6479
SS056	Cement_Creek	37.90606	-107.643794
SS057	Cement_Creek	37.910964	-107.636868
SS058	Cement_Creek	37.90994	-107.633296
SS059	Cement_Creek	37.907486	-107.641738
SS060	Cement_Creek	37.906085	-107.642411
SS061	Cement_Creek	37.904061	-107.644002
SS062	Cement_Creek	37.897621	-107.645047
SS063	Cement_Creek	37.897425	-107.627271
SS064	Cement_Creek	37.897346	-107.627702
SS065	Cement_Creek	37.891519	-107.648381
SS066	Cement_Creek	37.891911	-107.648525
SS067	Cement_Creek	37.896249	-107.646373
SS068	Cement_Creek	37.89591	-107.646335
SS069	Cement_Creek	37.900564	-107.644423
SS070	Cement_Creek	37.901871	-107.644353
SS071	SF_Animas	37.876719	-107.602423
SS072	SF_Animas	37.881232	-107.600445
SS073	SF_Animas	37.880884	-107.599078
SS074	SF_Animas	37.881676	-107.598683
SS075	SF_Animas	37.88253	-107.598205
SS076	Cement_Creek	37.886801	-107.608403

Site ID	AREA	LAT	LONG
SS077	Cement_Creek	37.886933	-107.614588
SS079	Cement_Creek	37.885515	-107.608237
SS080	Cement_Creek	37.887026	-107.605265
SS083	Cement_Creek	37.894344	-107.639765
SS084	Cement_Creek	37.894308	-107.639741
SS085	Cement_Creek	37.894842	-107.642207
SS086	Cement_Creek	37.894184	-107.647306
SS087	Prospect_Gulch	37.898073	-107.685949
SS088	Prospect_Gulch	37.895996	-107.68289
SS089	Prospect_Gulch	37.893865	-107.692072
SS090	Prospect_Gulch	37.894855	-107.692081
SS091	Prospect_Gulch	37.892556	-107.688036
SS092	Prospect_Gulch	37.89066	-107.692453
SS093	Prospect_Gulch	37.890349	-107.692983
SS094	Prospect_Gulch	37.888435	-107.688413
SS095	Prospect_Gulch	37.89032	-107.689131
SS096	Prospect_Gulch	37.892169	-107.68216
SS097	Prospect_Gulch	37.891842	-107.681224
SS098	Prospect_Gulch	37.891849	-107.680724
SS103	Cement_Creek	37.914474	-107.63048
SS105	Cement_Creek	37.90833	-107.63843
SS110	Eureka_Gulch	37.894485	-107.60795
SS111	Cement_Creek	37.8768	-107.646645
SS117	Cement_Creek	37.892864	-107.60425
SS120	Prospect_Gulch	37.882233	-107.635605
SS121	Prospect_Gulch	37.909832	-107.63089
SS122	Prospect_Gulch	37.891876	-107.68951
SS123	Prospect_Gulch	37.89096	-107.682816
SS124	Prospect_Gulch	37.89174	-107.68248
SS125	Prospect_Gulch	37.89341	-107.68113
SS126	Prospect_Gulch	37.891502	-107.67908
SS127	Cement_Creek	37.90022	-107.64235
SS128	Cement_Creek	37.903637	-107.6412
SS129	Cement_Creek	37.90305	-107.64193
SS133	Cement_Creek	37.89318	-107.63208
SS140	Cement_Creek	37.916872	-107.626769
SS200	Cement_Creek	37.89559767	-107.6473548
SS201	Cement_Creek	37.8919025	-107.6485027
SS203	Prospect_Gulch	37.89306787	-107.6821467

Site ID	AREA	LAT	LONG
SS204	Prospect_Gulch	37.89160156	-107.6824265
SS205	Prospect_Gulch	37.89373779	-107.6891861
SS206	Prospect_Gulch	37.8941695	-107.690042
SS207	Prospect_Gulch	37.89505005	-107.6889572
SS208	Prospect_Gulch	37.89477002	-107.6905918
SS210	Cement_Creek	37.91337204	-107.6293182
SS211	Cement_Creek	37.91905933	-107.6303397
SS213	Eureka_Gulch	37.89300919	-107.6064987
SS214	Eureka_Gulch	37.90233994	-107.6140747
SS215	Cement_Creek	37.9099095	-107.63323
SS216	Cement_Creek	37.90997633	-107.6379537
SS217	Cement_Creek	37.88510132	-107.6160126
SS218	Cement_Creek	37.88356781	-107.6179581
SS219	WF_Animas_CG	37.91635895	-107.6135635
SS220	WF_Animas_CG	37.91812515	-107.6113663
SS221	WF_Animas_CG	37.918504	-107.611049
SS222	WF_Animas_CG	37.91915021	-107.6107264
SS223	Placer_Gulch	37.91265106	-107.5986176
SS224	Placer_Gulch	37.90810776	-107.5969009
SS225	Placer_Gulch	37.90847778	-107.5949783
SS226	Placer_Gulch	37.90955972	-107.6016434
SS227	Cement_Creek	37.87120183	-107.6427552
SS228	Cement_Creek	37.889615	-107.649714
SS229	Eureka_Gulch	37.90252783	-107.6139597
SS230	Cement_Creek	37.890528	-107.634048
SS231	Eureka_Gulch	37.895265	-107.607211
SS232	Eureka_Gulch	37.91060822	-107.6348909
SS235	Placer_Gulch	37.9165655	-107.5922943
SS236	Cement_Creek	37.89742939	-107.6459215
SS237	SF_Animas	37.87164367	-107.6066807
SS238	Eureka_Gulch	37.88187267	-107.598426
SS250	Cement_Creek	37.905767	-107.643516