

Quality Assurance Project Plan

Tracer Injection Study: French Gulch and Wellington-Oro Mine Site

Summit County, Colorado

Prepared For:



United States Environmental Protection Agency, Region 8

Ecosystem Protection and Remediation – Program Support

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A. Project Management

Project title: Tracer Injection Study: French Gulch and Wellington-Oro Mine Site
Summit County, Colorado

Date and revision: August 21, 2020

Organizations: U.S. Environmental Protection Agency, U.S. Geological Survey

Revision	Date	Primary Changes
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Revision 1	August 31, 2020	
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A1. Approval Sheet

EPA Remedial Project Manager:

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A3. Distribution List

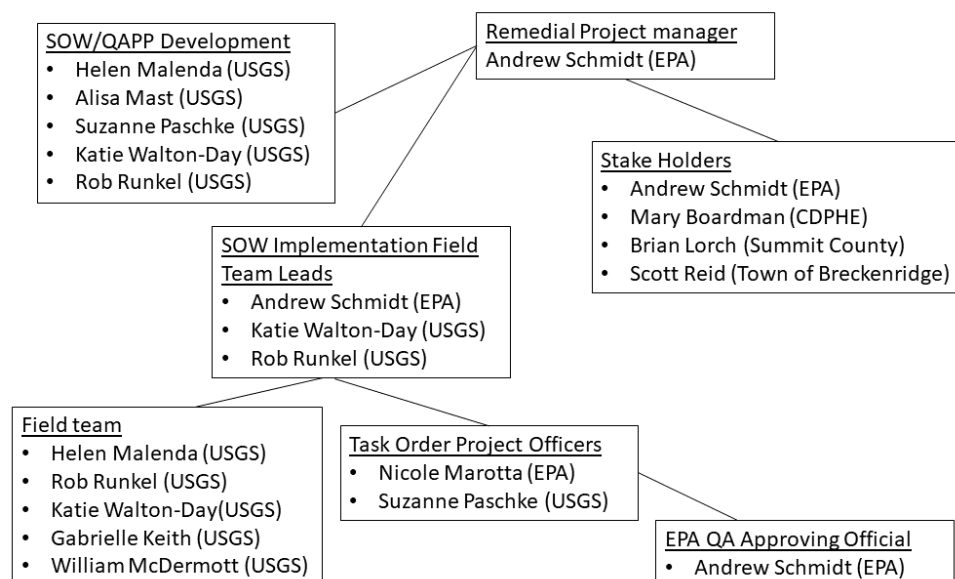
The following is a distribution list of personnel who will receive an electronic copy of the Sampling and Analysis Plan (SAP)/Quality Assurance Project Plan (QAPP) for the 2020 Geochemical sampling and analysis at the French Gulch site. The most current copies of the approved QA Project Plan will be distributed electronically by the SAP/QAPP preparer. The SAP/QAPP with original signatures will be placed in the Superfund administrative record. Agency and contractor affiliations are also listed for each individual.

Andrew Schmidt	United States Environmental Protection Agency (EPA) Remedial Project Manager (RPM)
Sherry Skipper	EPA Delegated Quality Assurance (QA) Approving Official
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Alex Hedgepath	Colorado Department of Public Health and Environment (CDPHE)
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Katie Walton-Day	USGS Hydrologist
Rob Runkel	USGS Hydrologist
Alisa Mast	USGS Hydrologist
Helen Malenda	USGS Hydrologist

A4. Project/Task Organization

The following is a chart of the federal project personnel involved in the implementation of the project plan, their respective agencies or contract affiliations, and general responsibilities.

Organizational Chart



A5. Problem Definition/Background

This document serves as the Sampling and Analysis Plan (SAP) and Quality Assurance Project Plan (QAPP) for tracer-injection studies and water-quality sampling to be conducted in September 2020 at the French Gulch Site located near the town of Breckenridge, Colorado. The proposed study is designed to evaluate current hydrologic conditions in the vicinity of the Wellington-Oro (W-O) Mine complex and to identify and quantify sources of metals to French Gulch with an emphasis on cadmium and zinc. This SAP/QAPP describes methods used for the tracer injections, water-quality sampling, discharge measurements, continuous water-quality measurements (pH, specific conductance, and temperature), and for selecting sampling locations. The data obtained from these investigations will be used in accordance with the provisions outlined in the data quality objectives (DQOs) and collected in accordance to applicable standard operating procedures (SOPs) presented in Section A.7.

The W-O Mine Site, located near Breckenridge, Colorado, has been the subject of hydrologic and water-quality studies since the late 1980s that have investigated sources of metal loading to French Gulch and its receiving stream, the Blue River. Patterns of groundwater discharge to French Gulch are complicated by upwelling along faults and fractures as well as disturbance to the shallow alluvial deposits caused by historic placer mining, channel realignment, remediation activities, and recent residential development. Remediation activities at the W-O Mine Site have included excavation, consolidation, and capping of waste rock and tailings, stream diversion, and construction of a water-treatment plant (TechLaw, Inc., 2012). The W-O water-treatment plant (WTP), which began operation in 2007, removes cadmium and zinc from water collected from a seep (identified as FG-6C), and the treated water is discharged to shallow alluvium between the plant and French Gulch via an injection well (Outfall 1 in Figure A5; Table A5 lists site references from previous studies and monitoring). The WTP utilizes a sulfide-precipitation process adding sodium hydrosulfide solution (NaHS) to precipitate zinc and cadmium as sulfides, and sodium bicarbonate solution (soda ash) to neutralize pH to discharge standards (BioteQ Environmental Technologies, Inc., 2010). Effluent from the WTP contains elevated concentrations of sodium, iron, and total dissolved solids (TDS; BioteQ Environmental Technologies, Inc., 2010). Water-quality data collected in 2017 provides some evidence that the WTP has been effective in reducing cadmium and zinc concentrations in the Blue River (Walton-Day and others, 2018).

Table A5 Reference Site Locations

Reference Surface Water Sites		
Name	latitude (dd)	longitude (dd)
FG-5	39.482056	-106.01420
FG-5.5	39.480303	-106.01804
FG-4	39.483608	-106.01096
FG-8	39.484829	-106.02861
FG-9A	39.486199	-106.03128
BR-1	39.493338	-106.04605
BR-2	39.494168	-106.04625
T2	39.48275	106.0131
Monitoring Wells		

Name	latitude (dd)	longitude (dd)
MW-2	39.4821	-106.0157
MW-3	39.4818	-106.0167
MW-4	39.4827	-106.0156
MW-7	39.4809	-106.0183
MW-9	39.4830	-106.0140
MW-11	39.4830	-106.0130
MW-14	39.4825	-106.0149
MW-20	39.4800	-106.0180
Seep FG-6C	39.481584	-106.0180

A previous tracer study of the W-O Mine Site identified and quantified metal loading to French Gulch (Kimball and others, 1999); however, site conditions have changed considerably since the study was conducted because the WTP was brought on-line, and the area has been regraded and redeveloped for residential housing. In the 1999 study, the reach of French Gulch upstream from the current WTP and FG-5 was described as a losing reach where flow “almost vanished” near the T2 transport site and MW-9 well. Downstream from FG-5, French Gulch was is a gaining reach due to groundwater discharge (Kimball and others, 1999). Current (2020) metal loading to French Gulch appears to occur primarily in this gaining reach between FG-5 and FG-5.5, and possible sources include: (1) upwelling of deep groundwater along faults, possibly from the W-O mine pool; (2) shallow groundwater flow from the alluvial aquifer; and (3) discharge of WTP effluent to the alluvium.

Because hydrologic and water-quality conditions likely have changed considerably since the 1999 study, new work has been proposed at the site, including tracer-injection studies and application of shallow geophysical techniques (previously described in a separate QAPP), to evaluate current hydrologic and water-quality loading along French Gulch. Tasks are designed to identify metals sources to the stream in the gaining reach of French Gulch bracketed by sites FG-5 and FG-5.5, as well as to characterize the losing reach of upstream from FG-5. The study described in this SAP/QAPP is designed to complement and expand upon routine environmental monitoring that has been performed at the W-O Mine Site by TechLaw, Inc. Environmental Services Assistant Team (ESAT) and EPA personnel since 2009 (TechLaw, Inc., 2019).

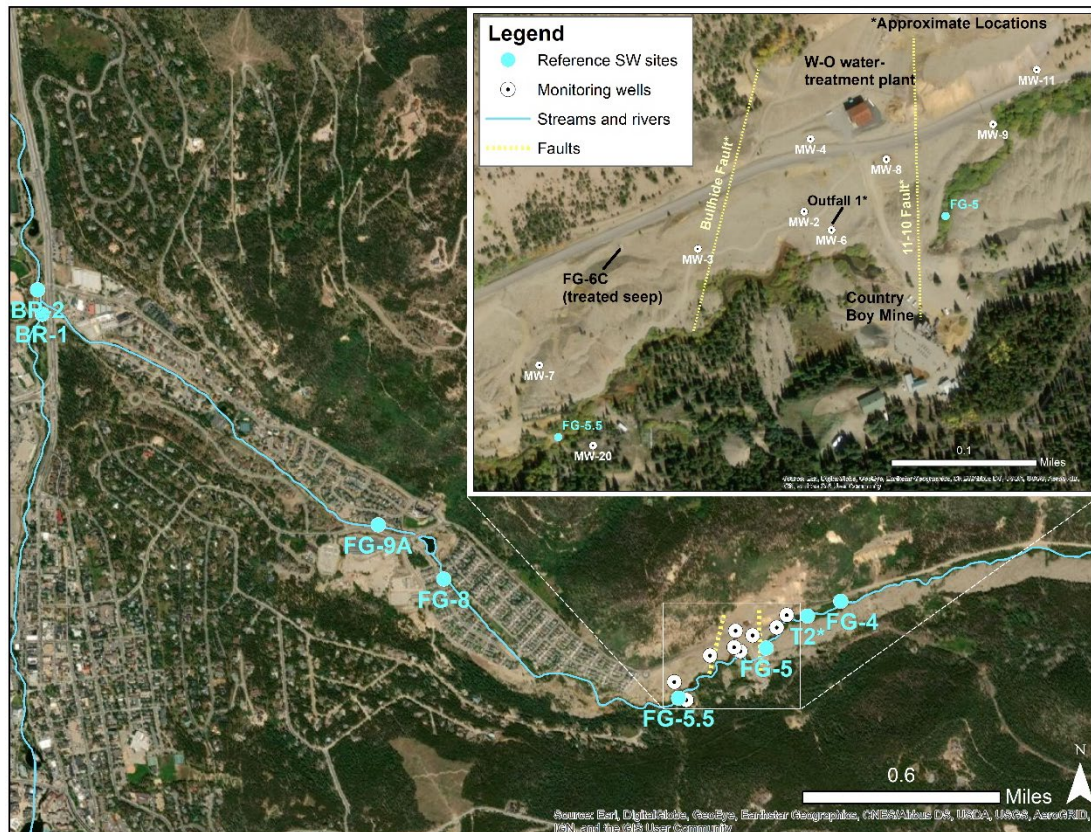


Figure A5: Overview map of study site with locations of sites referenced in previous studies and current monitoring activities. Streams are indicated by light blue lines, reference surface-water sites are indicated by light blue dots, monitoring wells are indicated by white dots, and faults are indicated by dashed yellow lines.

A6. Project/Task Description

This SAP/QAPP describes the tracer-injection studies to be conducted at the site in September 2020 and associated water-quality sampling and laboratory analyses. This study meets the goals of the inter-agency agreement between USGS and EPA to characterize the hydrology of the site and identify and quantify sources of cadmium and zinc to French Gulch. Table A6 summarized sampling activities and types of water-quality data to be collected.

Table A6 Summary of Sampling Activities and Approximate Number of Sites

Site Types	No. of sites	Data Types
Monitoring wells	8	H/O isotopes Iron speciation
Synoptic surface-water sampling	(40)	anions (including Br) alkalinity trace metals (total and filtered) Iron speciation H/O isotopes field QW parameters ¹
Continuous WQ parameters	(2)	field QW parameters ¹ (measured in 15 min increments)
Tracer autosampling	(3)	bromide (Br)
Stream gaging	(<10)	stream discharge

¹Includes temperature, pH, and specific conductivity

The work outlined in this SAP/QAPP addressed tasks 1 and 2 described in the 2019 French Gulch Site Data Analysis USGS Statement of Work- FY-2020, prepared by the USGS. Task 1 consists of tracer injection and synoptic sampling in two reaches of French Gulch, the losing reach upstream from FG-5, and the gaining reach between sites FG-5 and FG-5.5. Details of Task 1 are outlined in Section A.6.1. Task 2 consists of groundwater sampling and analysis as described in Section A.6.2.

A.6.1 Task 1. Tracer Injection and Synoptic Sampling

Injection of an inorganic tracer (sodium bromide, NaBr) combined with synoptic sampling of the stream and all visible inflows will be used to produce stream profiles of discharge and mass loading, which will be used to identify and quantify surface-water inflows, discrete groundwater inflows (seeps and springs), and diffuse groundwater inflows (by difference) (Kimball and others, 1999). Tracer injections in French Gulch will focus on the study reach comprised of (1) the suspected losing reach FG-4 to FG-5 and (2) the gaining reach between sites FG-5 to FG-5.5 (figure A6.1). The tracer will be conducted during baseflow conditions in September 2020, which is ideal because surface-water runoff is minimal, and groundwater is a large contributor to streamflow at this time making groundwater inflows easier to identify. Prior to the tracer injection, a field reconnaissance will be conducted to locate and flag potential inflow and stream sampling sites.

Continuous tracer injection and synoptic sampling in the reach of interest (FG-4 to FG-5.5) will occur over a 3 to 4-day period. On day 1, the tracer injection will be initiated upstream of the losing reach (figure A6.1) and water-quality samples will be collected from all inflows and springs. On day 2, after the tracer concentration in the stream reaches a steady state, discharge measurements and samples will be collected at the stream sites. On day 3, equipment will be dismantled, and samples will be transported to USGS offices in Lakewood, Colo. for log in and laboratory analyses.

For the suspected losing reach of French Gulch, up to four spot injections of sodium-chloride tracer will be made along with manual streamflow measurements to calculate discharge and stream loss for individual segments along this reach. In order to monitor changes in stream water quality during the tracer injection, pH, specific conductance, and water temperature will be continuously monitored at 2 locations along the study reach using multi-parameter sondes and data loggers.

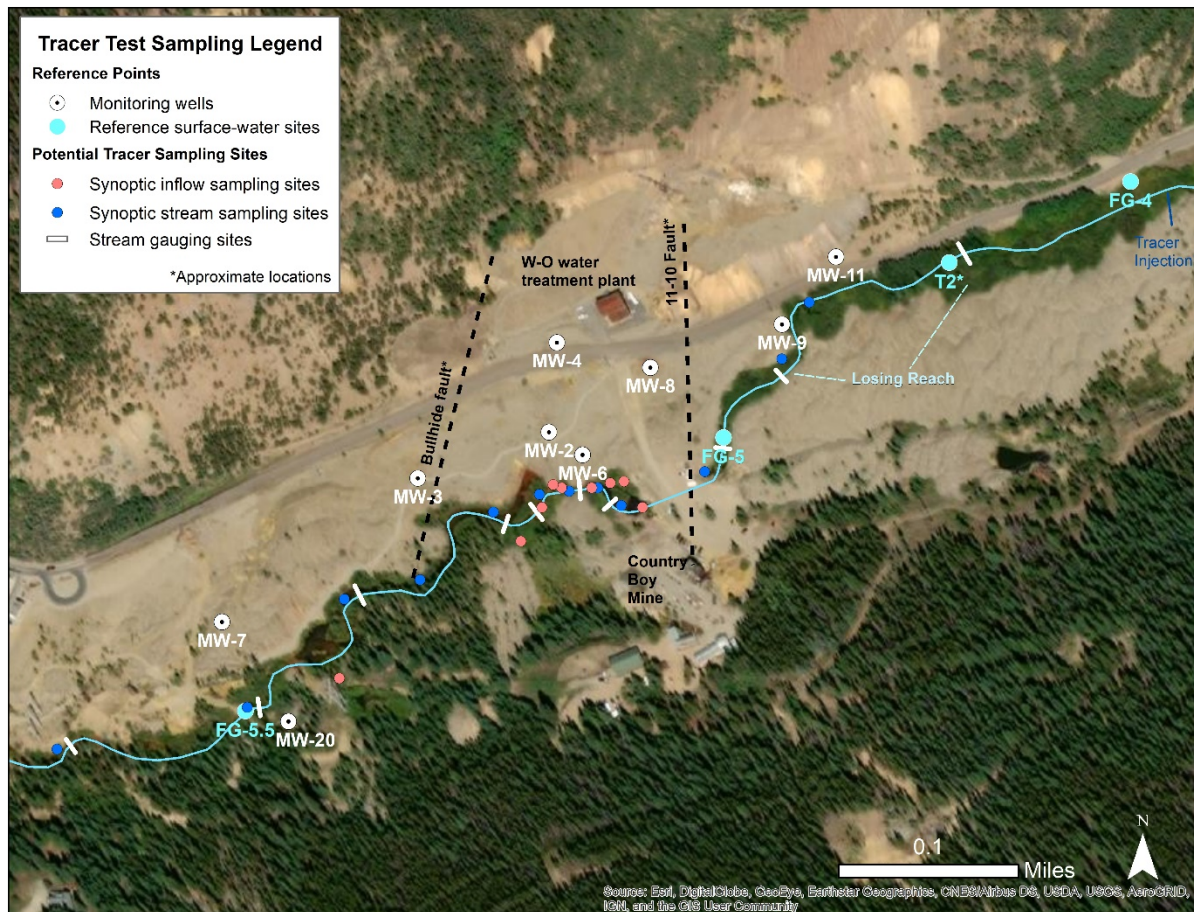


Figure A6.1 Overview of study reach of French Gulch with reference site locations and potential sampling and stream gaging locations identified during 2019 field reconnaissance. French Gulch indicated by light blue lines, reference surface-water sites indicated by light blue dots, and monitoring wells by white dots. Inflows identified during 2019 field reconnaissance indicated by red dots, and potential surface-water sites indicated by dark blue dots. Approximate fault locations indicated by dashed black lines. Additional reconnaissance before the 2020 field campaign will confirm sampling and stream gaging locations, as inflows and stream conditions can vary between seasons.

Surface-water samples from approximately 40 inflow and stream sites will be collected during the tracer-injection study. Samples will be analyzed for major anions, alkalinity, total and dissolved cations and trace elements, iron speciation, and hydrogen and oxygen (H/O) isotopes of water. The sites will be located: (1) on the main stem between FG-4 to FG-5.5; (2) at visible tributary inflows, seeps, and springs in the reach between FG-5 and FG-5.5; and (3) at downstream sites FG-8, FG-9A, BR-1, and BR-2. At 10 percent of sites, QA samples (replicates and blanks) will be collected. Samples will be filtered and preserved in the field on the day of collection and shipped or delivered to the laboratory for analysis.

Samples will also be collected hourly using an autosampler (about 140 samples) at three sites throughout the 36-hour tracer injection and analyzed for Br.

At all synoptic sampling sites, samples will be analyzed for major anions (Cl^- , F^- , NO_3^- and SO_4^{2-}), alkalinity, and total recoverable (unfiltered) and dissolved (filtered) cations and trace elements (Al, Ag, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, S, Sb, Se, SiO_2 , U, V, Zn) at the USGS Analytical Trace Elements Chemistry Laboratory in Boulder, Colo. (Appendix F1). Samples collected for iron speciation ($\text{Fe}^{2+}/\text{Fe}^{3+}$) will be analyzed at the USGS Redox Chemistry Laboratory in Boulder, Colo. (Appendix F2). Bromide in the autosamples will be analyzed by the USGS Analytical Trace Elements Chemistry Laboratory. Stable isotopes of water (H/O isotopes) will be analyzed at the USGS Reston Stable Isotopes Lab (RSIL) (Appendix F3).

A.6.2 Task 2. Groundwater Samples for Water Isotopes and Speciated Iron

There are several groundwater monitoring wells completed in alluvium and bedrock in the vicinity of the W-O Mine Site. Eight of these wells are presently sampled by EPA/TechLaw in June and again in September and analyzed for total and dissolved metals and anions (table A5) (TechLaw, Inc., 2020). During the September 2020 groundwater sampling by TechLaw, the USGS will provide bottles to collect samples for analysis of H/O isotopes and iron speciation. Analysis of H/O isotopes will be conducted at the USGS Reston Stable Isotope Laboratory (RSIL) according to the methods of Révész and Coplen (2008a,b).

A7. Quality Objectives and Criteria

This section discusses the data quality objectives (DQO) process. Specific topics addressed include the planning team and stakeholders, DQOs, and parameter metrics such as precision, accuracy, representativeness, completeness, comparability and sensitivity.

A7.1 Planning and Stakeholders

The planning team for this study includes personnel from EPA Region 8 (Andrew Schmidt and Ian Bowen), CDPHE (Alex Hedgepath), and the USGS Colorado Water Science Center (Suzanne Paschke, Katie Walton-Day, Rob Runkel, Alisa Mast, and Helen Malenda). In fall 2019, the USGS planning team visited the site for a reconnaissance to inspect the site and identify potential synoptic-sampling sites during the tracer-injection study. Personnel from EPA, CDPHE, and USGS have actively discussed possible field methods and their site-specific application, and the group determined analytical techniques that have the highest probability of success.

Stakeholders are parties who might be affected by the results of the study and persons who may later use the data resulting from this DQO process. For this study, stakeholder organizations and the individuals representing those organizations include EPA (Andrew Schmidt), CDPHE (Mary Boardman), Summit County (Brian Lorch), and the Town of Breckenridge (Scott Reid).

A7.2 Problem Statement

The mill site, mine workings, and alluvial material associated with the W-O Mine Site are possible sources of metal-rich waters entering French Gulch. Site hydrogeology is complicated by naturally complex structural geology and considerable site modifications, including mining operations, reworking of alluvial sediments, channel modification, residential development, and remediation efforts. Uncertainty related to the components of the hydrogeologic system (both natural and anthropogenic) has led to

unidentified sources of elevated cadmium and zinc and a lack of understanding behind the physical and geochemical conditions conducive to metal loading to French Gulch.

A7.3 Goals of the Study

- 1) Characterize the hydrology and geochemistry of the site to refine understanding of metal sources, especially cadmium and zinc, discharging to French Gulch.
- 2) Determine if the reach upstream from FG-5 is a losing reach and quantify the loss, to determine if the stream may be a potential source of recharge to the W-O mine pool
- 3) Evaluate the effect of effluent discharge from the W-O water-treatment plant on the stream chemistry of French Gulch.

A7.4 Information Inputs

- 1) Surface-water samples from French Gulch
- 2) Samples of inflows and seeps discharging to French Gulch including the WTP effluent
- 3) Streamflow measurements
- 4) Continuous field measurements of SC, pH, and temperature
- 5) Samples and water-level measurements from select observation wells (completed by EPA/TechLaw)

A7.5 Study Boundaries

A7.5.i Spatial Boundaries

The study will be focused on French Gulch and the adjacent alluvial aquifer in the vicinity of the W-O Mine Site but will also extend to the Blue River downstream from the confluence with French Gulch (figure A5).

A7.5.ii Temporal Boundaries

The study will be conducted in September 2020 in order to capture baseflow conditions in French Gulch and the observation wells.

A7.6 Performance and Acceptance Criteria

Field performance of sampling activities will be monitored according to standard techniques of the USGS, as described in the National Field Manual (U.S. Geological Survey, variously dated). Quality assurance and quality control for the project will be assessed as described by Mueller and others (2015) and Paul and others (2016). Specific attributes of the performance and acceptance criteria are detailed below.

A7.6.i Accuracy and Precision

Analytical precision and accuracy for water-quality constituents are sufficient to support the goals of the study. Typical method detection limits, accuracy, and analytical precision for each group of analytes are summarized in Table A7.6. Table A7.6 uses terminology typical of many quality-assurance (QA)/quality-control (QC) analyses. Accuracy is the closeness of a measured result to an accepted reference value. Accuracy is usually measured as a percent recovery. QC analyses used to measure accuracy include standard recoveries, laboratory control samples, spiked samples, and surrogates. Precision measures the agreement among a set of replicate measurements. Analytical precision is estimated by duplicate/replicate analyses, usually on laboratory control samples, spiked samples and/or field samples. The most commonly used estimates of precision are the relative standard deviation (RSD) and, when only two samples are available, the relative percent difference (RPD).

Table A7.6 Analytical Parameters and Typical Laboratory QA/QC Standards

Type of Analyte	Typical Detection Limit	Units of Measure	Typical Accuracy	Accuracy Units of Measure	Typical Precision	Precision Units of Measure
Major and Minor Cations/ Anions + REE	0.008 to 10	µg/L	90-110	% recovery of spikes	1-5	Relative % difference in concentration
H/O Isotopes	Not applicable ¹	per mil	0.07	per mil	0.2 _(O) to 2 _(H)	per mil
Iron Speciation	0.002 mg/L	mg/L	95-105 ²	% recovery of spikes	<5 ²	Relative % difference in concentration

¹ Results are presented as ratio of sample value to an international standard, there is no minimum detection limit

² To and others (1999); samples are reanalyzed if precision and accuracy fall out of this range

A7.6.ii Bias and Variability

Bias quantifies the tendency for environmental samples to either underestimate or overestimate a known quantity and can be the result of sampling, contamination analysis, or data-evaluation procedures. Bias will be addressed by selecting and adhering to proper sampling methods and employing laboratory calibration validation, laboratory replicates and control spikes as well as blank spikes and method blanks. Contamination will be evaluated using field blanks, which will test for positive bias caused by sample exposure during field sampling and processing, transport, and laboratory analytical procedures. Field blanks will be collected for 10% of the samples collected during the project, with the exception of H/O isotopes, for which it is not possible to produce a field blank. Laboratory bias is assessed by each individual laboratory as documented in appendices to this QAPP.

Field variability will be evaluated using field replicates and quantified using the relative percent difference (RPD) between replicate sample pairs (Eq. 1; Mueller and others, 2015). Field replicates will be collected for 10% of the samples collected during the project. The maximum acceptable RPD will be $\pm 20\%$ based on the 2020 QAPP for other activities at the site (TechLaw, Inc., 2020). Water-quality parameters with greater than 20% RPD will be subject to further quality control (Mueller and others, 2015; Paul and others, 2016), and usage of data will be dependent upon rigorous evaluation of bias and variability. The RPD is calculated according to:

$$RPD = \frac{|C_{ENV} - C_{REP}|}{(C_{ENV} + C_{REP}) * 0.5} \times 100 \quad (1)$$

where:

RPD = relative percent difference,
 C_{ENV} = concentration in the environmental sample, and
 C_{REP} = concentration in the replicate sample

A7.6.iii Representativeness

The goal of the study is to collect samples which are representative of the range of conditions observed on the site. The potential sampling locations were chosen (figures A.5 and A6.1) to represent the range of hydrologic and geochemical conditions, as detailed below in Section A7.7.

A7.6.iv Completeness

About 50 water-quality samples (including QA/QC samples) will be collected from approximately 40 stream sites and other inflows/seeps/effluent during September 2020. In addition, about 140 samples (for bromide analysis only) will be collected by three autosamplers during the 36-hour tracer injection. The project will be deemed complete if 90% of the proposed samples are collected. However, changing availability of sample sources (for example, reduced seep flow at baseflow or increased streamflow caused by precipitation events) are possible. Samples not collected because of these possibilities will not be considered a failure to collect a proposed sample.

A7.6.v Comparability

Water-quality samples collected during the project will be analyzed using field and laboratory methods comparable to previous sample collection efforts and studies. Accuracy and comparability of major-ion data will be evaluated by an electrical conductivity balance method, as described by McCleskey and others (2012) and McCleskey (2018) and charge balance (Appelo and Postma, 2005). Total and dissolved metals will be compared, total concentrations should be equal to or greater than dissolved. Water samples for H/O isotopes were previously collected at a handful of monitoring wells, surface-water sites, and seeps in French Gulch in early 1996 (AGS, 1999). Some of the sampling sites have been altered or destroyed (AGS, 1999), but where applicable, previously collected H/O isotope data will be compared to newly collected data.

A7.6.vi Method Sensitivity

The sensitivities of all laboratory methods (Table A7.6) are consistent with the expected range of concentrations at the site based on previous data.

A7.7 Sampling Locations

Surface-water samples from approximately 40 inflow and stream sites are anticipated for collection during the tracer injection and synoptic sampling of French Gulch. Sampling sites will be established during field reconnaissance and will be located as follows: (1) upstream of the tracer-injection site along the losing reach, as well as the lower reach bracketing inflows (FG-4 to FG-5.5); (2) at visible tributary inflows, seeps, and springs including effluent from the WTP; and (3) at downstream sites FG-8, FG-9A, BR-1, and BR-2. Inflows identified during the 2019 reconnaissance and potential sampling locations are shown in Figure A6.1. Three autosamplers will be located along the reach of interest to collect hourly samples during the tracer injection. Two YSI multiparameter sondes will also be deployed for continuous measurement of pH, specific conductance, and temperature. Potential streamflow measuring sites are depicted in Figure A6.1; however, 2020 reconnaissance will be used to determine final number and locations of streamflow measuring sites, as they are dependent on inflow locations and stream conditions, which can vary temporally. Once sampling and stream gaging locations for the 2020 field work are determined, the location coordinates will be recorded using a Garmin® handheld GPS.

A8. Special Training/Certifications

Collection of water-quality samples will be conducted by USGS hydrologists and hydrologic technicians under the supervision of experienced and specialized practitioners following USGS field methods (U.S. Geological Survey, variously dated). All field personnel who measure field parameters that are entered into NWIS will be up to date in their participation of the USGS National Field Quality Assurance Program, which evaluates the proficiency of personnel in measuring field parameters, such as pH, specific conductance, and alkalinity.

A9. Documentation and Records

All water-quality data (including groundwater, surface water, seeps, and WTP effluent) will be made publicly available. Field water-quality parameters, as well as data analyzed by the USGS Analytical Trace Elements Chemistry Lab (anions, alkalinity, and trace elements); the USGS Redox Chemistry Lab (iron speciation); and RSIL (H/O isotopes) will be uploaded to the National Water Information System (NWIS), <https://waterdata.usgs.gov/nwis>. These records will include the specific measurement values and pertinent metadata such as sample name, sample location, date and time, name of personnel collecting the sample or operating equipment, weather, analytical methods, and other relevant information. Electronic data collected in the field, such as water-quality data recorded by instruments with internal data loggers, will be downloaded to a laptop and concurrently backed up on external drives. Once back in the office, the data will be backed up on USGS servers. Both NWIS and the USGS servers are permanent data repositories. Electronic copies of any paper records, such as sample inventory sheets, field notebooks, chain of custody forms, will be made either by taking photographs onsite or by scanning the documents once back in the office and also placed in the project-specific folder on a USGS server.

B. Data Generation/Acquisition

B1. Sampling Process Design (Experimental Design)

The design of the sampling process is meant to provide geochemical and hydrologic information on the likely endmembers of the study system, namely streamflow of and inflows to French Gulch, groundwater discharged from naturally occurring rock fractures or mine workings, and effluent from the W-O WTP.

This study will employ tracer injection and synoptic water-quality sampling to evaluate surface-water quality, changes in streamflow, and sources of metals loading associated with French Gulch as described in section A.6.1. (figure A6.1).

B2. Sampling Methods

Sampling protocols that will be followed are described in the U.S. Geological Survey National Field Manual (U.S. Geological Survey, variously dated). Synoptic surface-water samples will be collected using grab-sampling methods (U.S. Geological Survey, 2008). Water temperature, pH, and specific conductance will be measured in-situ at the time of sample collection using handheld meters with methods described in the U.S. Geological Survey NFM (U.S. Geological Survey, variously dated; Wilde, 2008).

Grab samples will be collected in 1 liter precleaned Teflon bottles. If there is insufficient water present at a seep or inflow to collect a grab sample, a 60-mL syringe may be used to extract and transfer water to a sampling container. Samples for dissolved constituents will be filtered through disposable 0.45 micrometers (μm) capsule filters using a peristaltic pump and acid-rinsed Masterflex® C-Flex® tubing. Filtering procedures will follow USGS protocol (Skrobialowski, 2016). Filter and unfiltered aliquots for

trace elements will be collected in acid-rinsed 125 mL high density polyethylene (HDPE) bottles. Filtered aliquots for iron speciation will be collected into acid-rinsed, amber-colored HPDE bottles. Filtered aliquots for anions and alkalinity will be collected in pre-rinsed HDPE bottles. Unfiltered aliquots for H/O isotopes will be collected in 60 mL glass vials following RSIL guidelines (accessible at: <https://isotopes.usgs.gov/lab/instructions.html>), listed in Table B2.2.

Table B2. Guidance for Isotope Sampling Procedures

Sample Description	Bottle Recommendation
O-18/O-16 and/or H-2/H-1 of water	2 oz (60 mL) glass bottle with Polyseal cap
Treatment, Preservation, and Sample Amount	
Do not field rinse bottle. Do not add chemical treatment. Fill bottle two-thirds full with raw water so that if sample expands or freezes during shipping, bottle will not break. Cap bottle with Polyseal cap. Store at ambient temperature until shipped to laboratory.	

Streamflow will be measured at synoptic sampling sites using a Sontek© Flowtracker™ and following standard protocols described in the U.S. Geological Survey National Field Manual (Turnipseed and Sauer, 2010). Potential streamflow measurement sites are shown in figure A6.1, but streamflow conditions at the time of sample collection will determine the final number and locations of stream-gaging sites. Coordinates of all sampling sites will be recorded using a Garmin® handheld GPS.

If issues with sampling arise, such as issues with sample collection or instrumentation, detailed descriptions of the problems and corrective actions will be recorded by one of the field leads, either in a field notebook or in an electronic document. Any problems that affect the timing or quality of data collection will be reported on in the Technical Memo, along with any implications for data interpretation.

B3. Sample Handling and Custody

Sample handling will be completed according to standard methods of the USGS as described in U.S. Geological Survey (variously dated). Replicates will be assigned the same ID as the environmental sample with a time offset of 7 min. Custody will be tracked using a chain of custody form, an example of which can be found in Appendix F4.

Samples will be collected by one person in the field. Collection bottles will be labeled with the sampling site name, the date and collection time, and water temperature. The sampler will pass the sample to a runner, who will bring the water sample to a common processing location, where sample processing personnel will log the sample into an inventory sheet and process it into pre-prepared bottle kits labeled with the site name, sampling date and time, and a 15-digit unique site identifier. After processing, the sample processor will organize the labeled bottles into their respective analysis types, kept in separate coolers or boxes in a dedicated water-quality van. This van will be in sight of the common processing location and will be locked when not under supervision. Samples will be hand delivered to the Trace Elements Analytical Chemistry and Redox labs in Boulder, Colo., by a USGS staff member, and isotope samples will be shipped directly to RSIL overnight via FedEx, from the FedEx Ship Center near the field site.

Surface-water samples collected for analysis of trace elements (both total recoverable and dissolved) will be acidified to a pH less than 2 in the field using ultrapure nitric acid. Iron-speciation samples will be

preserved using hydrochloric acid (HCl) by adding HCl until the pH of the sample is less than 2. For each sample, the type, normality, and volume the acid added will be recorded. Samples for anions are not chemically preserved but kept chilled prior to analysis. Unless noted otherwise, non-preserved water-quality samples will be stored in coolers on ice and kept at or below four degrees Celsius for transport to the respective laboratory, in accordance with SOP FLD-12.00 *General Field Sampling Protocols* (EPA, 2012).

The maximum holding times differ depending on the target analytes or compound: 180 days for dissolved metals and total recoverable metals, 28 days for anions, and 14 days for alkalinity.

B4. Analytical Methods

Table B4 outlines the various laboratory analytical methods and standard procedure references.

Surface-water samples will be analyzed for anions, alkalinity, total recoverable and dissolved major and trace elements, iron speciation, and H/O isotopes. Analytical methods specific to each parameter are tabulated in the appendices to this SAP/QAPP. If issues arise with sample analysis, one or more of the field team leads will be notified directly, depending on the issue and the leads' expertise. Analytical issues and any corrective actions will be discussed and documented in emails between lab and USGS personnel. The EPA RPM will be notified as soon as possible if any problems with sample analyses could have substantial effects on data results and interpretation. If an issue has only a minor effect on the data quality of a single sample or subset of samples, corrective actions and possible implications will be included in the technical memorandum. On-site field water-quality measurements will include water temperature, pH, and specific conductance, and will following USGS procedures (U.S. Geological Survey, 2019; 2018; 2008). Specific conductance will be monitored downstream of each slug injection and increases in conductance will be used as a surrogate for chloride concentration.

Table B4 Analytical Laboratory Methods and Standard Procedure References

Analysis	Laboratory	Method	Method Procedures Reference
anions	USGS Trace Elements Analytical Chemistry Lab	ion chromatography	Brinton and others, 1995
alkalinity	USGS Trace Elements Analytical Chemistry Lab	autotitration	Barringer and Johnsson, 1996
total recoverable and dissolved trace metals	USGS Trace Elements Analytical Chemistry Lab	ICP-MS	Roth and others, 2014a
total recoverable and dissolved trace elements	USGS Trace Elements Analytical Chemistry Lab	ICP-OES	Roth and others, 2014b
iron speciation	USGS Redox Chemistry Lab	UV-VIS spectrophotometer	McCleskey and others, 2016

H isotopes	USGS Reston Stable Isotope Lab	dual-inlet isotope-ratio mass spectrometry	Révész and Coplen, 2008a
O isotopes	USGS Reston Stable Isotope Lab	dual-inlet isotope-ratio mass spectrometry	Révész and Coplen, 2008b

ICP-MS =Inductively Coupled Plasma-Mass Spectroscopy

ICP-OES=Inductively Coupled Plasma-Optical Emission Spectroscopy

B5. Quality Control

Samples will be analyzed for anions, alkalinity, total recoverable elements, dissolved elements, iron speciation, and H/O isotopes. Appendix tables provide the acceptable laboratory QA/QC criteria. The precision, accuracy, and comparability of all analytical data will be evaluated according to standard methods of the USGS (Mueller and others, 2015; Paul and others, 2016). Four replicate samples and 4 field blanks will be collected for trace elements, iron speciation, and alkalinity, while 4 replicate samples will be collected for H/O isotopes. Approximately 12 replicate samples (four from each autosampler) will be collected for bromide analysis.

Any calibration of field instruments will follow manufacturer specifications. All field equipment will be calibrated either immediately before use in the field, or on a schedule recommended by the manufacturer or as required by the U.S. Geological Survey National Field Manual (USGS, variously dated). Equipment will also be calibrated if repaired or if any parts are replaced. If multiple instruments are needed, the same manufacturer and model of instrument will be used whenever possible, and the specific instrument used will be recorded in order to identify and mitigate any instrument-specific bias. Field pH and specific conductance meters will have calibration checked every 10 samples. Recalibration will occur if meters have drifted outside tolerance (± 0.1 pH units; 3% specific conductance).

B6. Instrument/Equipment Testing, Inspection, and Maintenance

Instruments required for field-data collection include thermistors, pH probes, and SC sensors. All sensors will be obtained from the USGS Colorado Water Science Center or the USGS Hydrological Instrumentation Facility.

Instruments will be tested prior to their first use in the field and maintained thereafter according to standard methods described in U.S. Geological Survey (variously dated), which includes information on testing criteria, inspection procedures, and documentation of testing and maintenance. In addition to the instruments that will be used in the field, backups for instruments will be on hand, in case of equipment failure that cannot be corrected.

B7. Instrument/Equipment Calibration and Frequency

Instruments will be calibrated prior to each use in the field according to standard methods of the USGS as described in U.S. Geological Survey (variously dated) and by the laboratory procedures included in the appendix of this document.

B8. Inspection/Acceptance for Supplies and Consumables

All supplies used as part of sampling are obtained from the USGS National Water-Quality Laboratory, the USGS Analytical Redox Chemistry Lab, or other certified distributor. All sample materials and reagents

are tracked using the USGS Laboratory Information Management System (LIMS) using unique identifiers.

B9. Use of Existing Data (Non-Direct Measurements)

Water-quality data have been furnished to USGS by EPA. These data were used in informing this SAP/QAPP and may be utilized in further analysis. If further utilized, data will be evaluated according to standard methods (McCleskey and others, 2012; McCleskey, 2018; Mueller and others, 2015; Paul and others, 2016). If deemed appropriate, existing data will be used to further inform an understanding of the mine site (e.g. TechLaw, Inc., 2019; Apodaca and others, 2000; American Geological Services, 1999; Kimball and others, 1999) and supplement newly collected data.

B10. Data Management

All data will be managed by standard USGS systems including NWIS, in accordance with USGS Survey Manual 502.6 – Fundamental Science Practices: Scientific Data Management (accessible at: <https://www2.usgs.gov/usgs-manual/500/502-6.html>). All data will publicly accessible following appropriate QA/QC in accordance with USGS Survey Manual 502.7 – Fundamental Science Practices: Metadata for USGS Scientific Information Products Including Data (accessible at: <https://www2.usgs.gov/usgs-manual/500/502-7.html>) and USGS Survey Manual 502.8 – Fundamental Science Practices: Review and Approval of Scientific Data for Release (accessible at: <https://www2.usgs.gov/usgs-manual/500/502-8.html>).

Hardware and software configurations will depend on the data type being collected. In most cases, the USGS has recommended hardware and software that have been evaluated by the USGS Hydrologic Instrumentation Facility. In any other cases, industry standards for hardware and software will be used. In accordance with standard USGS field procedures, instruments will be connected to and updated using applicable software prior to field work.

Assessment and Oversight

C1. Assessments and Response Actions

C1.1 Field Assessments

USGS personnel will conduct data-collection activities. EPA personnel have the option to participate or oversee these data-collection activities at any time during the project. Field teams will be supervised by field leads with the appropriate expertise, and the Program Manager will be onsite, conducting daily spot checks of the field and sampling activities. Minor problems will be addressed onsite and documented.

Any significant modifications to sampling or measurement procedures, recalibration or replacement of equipment, significant changes to study design, reassignments of personnel, or necessary resampling will be reported in the final deliverables to the EPA RPM.

C1.2 Laboratory Assessments

All USGS laboratories undergo rigorous quality control and management assessments. Specifically, quality of data and laboratory procedures is maintained by the USGS Quality Management System, as described by <https://nwql.usgs.gov/quality.shtml> and <https://www.usgs.gov/about/organization/science-support/office-science-quality-and-integrity/quality-management-system>.

Additionally, the Boulder Redox and Trace Element Analytical Chemistry laboratories participate in the USGS Standard Reference Sample (SRS) program, which evaluates analytical accuracy of inorganic

constituents using USGS Standard Reference Water Samples (SRWS), which are prepared and used to ensure that the laboratories being used by USGS are producing analytical data that are of acceptable reliability (Schroder and others, 1980). Labs are evaluated twice a year, and results are available at <https://qsb.usgs.gov/srs/>. At least 3 supplemental SRWS samples, acquired from the SRS program, will be submitted as double blind samples along with the synoptic samples for QA/QC evaluation. Results will be evaluated by USGS personnel, and can be made available upon request by the EPA RPM.

C2. Reports to Management

All data will be managed and made publicly accessible through NWIS or USGS data releases in accordance with USGS Survey Manuals 502.4 – Fundamental Science Practices: Review, Approval, and Release of Information Products; 502.6 – Fundamental Science Practices: Scientific Data Management; 502.7 – Fundamental Science Practices: Metadata for USGS Scientific Information Products Including Data; and 502.7 – Fundamental Science Practices: Review and Approval of Scientific Data for Release (accessible at: <https://www.usgs.gov/about/organization/science-support/survey-manual/chapters-500-end>). Results will be presented as a technical memorandum and a peer-reviewed power-point presentation.

The results of the labs' biannual participation in the USGS SRS program are available online: <https://qsb.usgs.gov/srs/>, and the results from the supplemental SRS samples can be made available to the EPA RPM upon request. Any additional findings from water quality QA analysis that may impact the results of the study will be reported to the EPA RPM on an as-needed basis and will also be fully documented in the technical memorandum.

D. Data Validation and Usability

D1. Data Review, Verification, and Validation

All data collected will be reviewed using standard USGS methods including use of the R software tool WQReview (<https://github.com/USGS-R/WQ-Review>) and standard water-quality QA workflows (<https://doimsp.sharepoint.com/sites/usgs-portal/collaboration/wg/osd/SitePages/WQ-Review.aspx>). Verification and validation of data will be completed according to standard USGS protocols (Mueller and others, 2015; Paul and others, 2016).

Water quality data review and approval will follow USGS guidelines, as outlined here:

https://water.usgs.gov/osw/time-series-guidance/Approval_Guidance_WQ.pdf

D2. Verification and Validation Methods

Common techniques for data verification and validation include reviewing holding times, instrument calibration, and information on materials used (e.g., bottles, spikes, blanks, replicates). All appropriate data are tracked by the USGS LIMS and other QMS systems. Data quality and potential issues are addressed in the NWIS data approval process by data quality indicator (DQI) flags. If data are found to be affected by bias, improper hold times, or inaccuracies, the results can be flagged and remarks applied to document the problem. Only acceptable results will be made public, but if any data are rejected, the sample number, analyte, reason, and potential effect on result interpretations will be documented in the technical memorandum.

D3. Reconciliation with DQOs

Information obtained from the field investigation will be evaluated through the data-quality assessment

(DQA) process to determine if the data are of adequate quality and quantity to support their intended use. The intended use of data for this project is to provide necessary knowledge of the groundwater-flow system near the W-O Mine Site and to identify unaddressed sources of metal loading to French Gulch.

Specific evaluation of the DQOs will be approached using the following steps:

- 1) Review the project objectives and sampling design,
- 2) Conduct preliminary data review,
- 3) Select appropriate modeling or numerical methods (e.g., PREEQC; Parkhurst and Appelo, 2013), and
- 4) Assure that all applied methods are consistent with EPA requirements and understanding.
- 5) Limitations on data use will be outlined in the technical memorandum.

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F. Appendices

F1. Methods of the USGS Trace Elements Analytical Chemistry Lab, Boulder

Determination of Selected Trace Metals in Aqueous Media by Inductively Coupled Plasma-Mass Spectroscopy

Revised July 30, 2014

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Scope and Application

This inductively coupled plasma-mass spectrometry (ICP-MS) method is for the quantitative determination of Al, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Ga, Gd, Ho, La, Li, Lu, Mn, Mo, Nd, Ni, P, Pb, Pr, Rb, Re, Sb, Se, Sm, Sn, Sr, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn and Zr in aqueous media (natural waters, precipitation samples, and digestates with appropriate dilution) at concentrations generally less than 10 mg/L. Using clean handling techniques and purified reagents, method detection limits in the range of 0.0001-1 µg/L or below are routinely attainable. The major elements Ca, K, Mg, Na, and Si, along with Fe are also quantified using this method; however the reported concentrations are generally taken from alternant instrumentation determinations using inductively coupled plasma-optical emission spectroscopy (ICP-OES) methodology due to reduced interferences, typically higher analyte concentrations, or occasionally greater sensitivity. Other elements that are quantified against calibration standards include: Ag, Br, C, Cl, Ge, Hf, I, Pd, S, Sc and Ta but suffer from severe interferences or poor ionization efficiencies or are primarily used in interference correction calculations. Many elements in this group suffer from a lack of an appropriate standard reference material (SRM) and cannot be properly quality control (QC) checked, until a suitable standard becomes available, results for these elements are not normally reported. When suitable SRMs become available for these elements, they can be moved to the quantified list. Au, Hg, Nb, Os, Pa, Pt, Ru are truly semi-quantitative as they are not calibrated against standards but their concentrations are inferred based on their signal intensity response and their isotopic abundance. These elements are not reported but are monitored to alert us to rare instances where they show detectable concentration levels that can be further investigated if desired. The quantifiable elements, their measured isotopes, and their isotopic abundances are listed in Table 1.

Table 1. Isotopes and isotopic abundances used in the determination of concentrations for the quantifiable elements.

Element	Isotope	Isotopic abundance, %		Element	Isotope	Isotopic abundance, %
Aluminum	27	100.0		Molybdenum	95	15.92
Antimony	121	57.36		Neodymium	146	17.19
Arsenic	75	100		Nickel	60	26.2
Boron	11	80.2		Phosphorous	31	100
Barium	137	11.3		Praseodymium	141	100
Beryllium	9	100		Rubidium	85	72.165
Bismuth	209	100		Rhenium ¹	187	62.60
Cadmium ³	111 & 114	12.8 & 28.73		Selenium ³	77 & 82	7.63 & 8.73
Cerium	140	88.48		Samarium	147	15.0
Cobalt	59	100		Strontium	86	9.86
Chromium ³	52 & 53	83.8 & 9.50		Terbium	159	100
Cesium	133	100		Tellurium	126	18.95
Copper ³	63 & 65	69.17 & 30.9		Tin	118	24.23
Dysprosium	163	24.9		Thorium	232	100
Erbium	167	22.95		Titanium	47 & 49	7.3 & 5.5
Europium	151	47.8		Thallium	205	70.476
Gallium	71	60.1		Thulium	169	100
Gadolinium	158	24.84		Uranium	238	99.2745
Holmium	165	100		Vanadium	51	99.750
Lanthanum	139	99.91		Tungsten	182	26.3
Lead ²	206+207+208	24.1+22.1+52.4		Yttrium	89	100
Lithium	7	92.6		Ytterbium	174	31.8
Lutetium	175	97.41		Zinc ³	64 & 66	48.6 & 27.9
Manganese	55	100.0		Zirconium ¹	90	51.45

¹ Currently no reference standard available for these elements.

² '+' intensities of all three isotopes are summed to get one final sample intensity.

³ '&' indicates that multiple individual isotopes for the particular element are monitored and compared but not summed.

Summary of Method

It is important that samples are collected using ultra-clean sample handling protocols into rigorously cleaned polyethylene, Teflon, or appropriate type bottles and are preserved with 1% (v/v) double quartz-distilled nitric acid. Analysis is performed on a Perkin Elmer Sciex Elan DRC II ICP-MS or a Perkin Elmer Nexion 300Q ICP-MS using techniques based on those described in Garbarino and Taylor (1996) and Taylor (2001), except as modified below.

Reagents

Water: 18 megohm ultra-pure deionized water starting from a pre-purified (distilled, R.O., etc.) source. This water is produced from a Barnstead Nanopure II mixed bed deionizer. Both trace ionic species and trace organic compounds are removed from the processed water.

Nitric Acid: Trace-metal purified reagent HNO_3 is purchased and doubly-distilled in a quartz still in the laboratory (Kuehner, et al, 1972). Upon production of the purified acid, aliquots are sampled for quality-control purposes and those not passing are re-distilled or used for other purposes not requiring ultra-clean acid. Hydrochloric acid is purified using the same technique however it is used very little for ICP-MS analysis.

Stock standard solutions: Three certified multi-element solutions are purchased from High Purity Standards containing the following mixed standards: The first contains 200 mg/L Sr, 100 mg/L Al, 20 mg/L U and Zn, 10 mg/L As, Cu and Li, 5 mg/L Pb, Se and V, 2 mg/L Cd, 1 mg/L Cs, and 0.5 mg/L Be, Bi, Ce, Co, Eu, La, Lu, Pr, Sm, Th, Tl, Y and Yb in 10% nitric acid; the second solution contains 50 mg/L Ba, 2 mg/L Mo, Ni, W and Zr in 10% hydrochloric acid, a trace of nitric acid, and a trace of hydrofluoric acid; the third solution contains 100 mg/L B, 20 mg/L Mn, 5 mg/L Cr, 2 mg/L Rb, and 0.5 mg/L Dy, Er, Gd, Ho, Re, Rb, Tb and Tm in 10% nitric acid. These standards are certified to $\pm 0.5\%$ of their given concentrations and are purchased every other year (or more often, if necessary); they are commercially available. Sn and Zr secondary solutions are prepared from High Purity Standards single element standards and W secondary solutions are prepared from Nation Institute of Standards and Technology (NIST) standard 3163.

Mixed working standards: Mixed working standards for instrument calibration are prepared on a monthly basis from the stock standard mixed solutions by simple dilution and acidification of the stock and secondary standards.

QC SRM Samples: A variety of QC SRM samples are used during each analysis run to insure the accuracy of the analytical results. Generally, these QC SRM samples include National Institute of Standards and Technology (NIST) Standard Reference Material, both as water SRMs and digested solid SRMs and four to six U.S. Geological Survey standard reference water samples (USGS SRWS). The QC standards are changed as new suitable ones become available. Trace element standard reference materials from Environment Canada are used as needed.

Argon: Ultra-high purity argon is fractionally distilled from liquid argon stored in a cryogenic cylinder.

Bottle Cleaning Procedures for Trace Metals

It is imperative for accurate low-level concentration measurements that appropriately cleaned high density polyethylene or Teflon bottles with tight-fitting lids be used for all steps contacting the aqueous sample. Bottles have a capacity of 125 mL or 250 mL and are purchased pre-cleaned (acid rinsed) from the manufacturer; they are additionally cleaned in the laboratory prior to use by soaking them in a solution of

10% nitric acid and 10% hydrochloric acid for at least 24 hours. After acid soaking, bottles are rinsed a minimum of three times with ultra-clean water and filled with ultra-clean water for storage until use. Polyethylene sample bottles are never reused. All calibration standards and dilutions of SRM's are stored in dedicated Teflon bottles. These bottles are reused only for the same solution that was stored in them.

Equipment

The equipment and analytical methodology are described in Garbarino and Taylor (1996) and Taylor (2001) and are summarized here. Samples are analyzed using a Perkin-Elmer Sciex Elan DRC II ICP-MS or Perkin Elmer Nexion 300Q ICP-MS, equipped with a Perkin Elmer AS 91 or a Perkin Elmer S10 autosampler. Samples are pumped with a peristaltic pump from the autosampler, through a T-fitting to add an internal standard containing Rh, In, and Ir to a final concentration of approximately 2 ppb. This mixture is then sent to a Teflon Burgener T2100 nebulizer through PTFE tubing. Aerosol produced by the nebulizer is passed through a baffled quartz cyclonic spray chamber and then transported through an alumina injector and quartz plasma torch. Elemental constituents in the aerosol are ionized within the plasma and pass through nickel sampler and skimmer cones, focused with an ion lens, then directed into the mass spectrometer's quadrupole and then on to an ETP detector, which detects the mass-to-charge ratio (m/z) of each ion detected. Instrument conditions are optimized to favor the production of singly-charged species within the plasma ($z = 1$ mostly), and to minimize oxide formation so that mostly isotopic masses are detected and recorded. For example ^{60}Ni experiences a degree of minor molecular interference (mostly from $^{44}\text{Ca}^{16}\text{O}^+$) which is corrected empirically as described here and in more detail by Garbarino and Taylor (1996). Other molecular interferences are treated similarly and direct isotopic overlaps are corrected by measuring the intensities of the interfering element and subtracting the appropriate calculated isotopic abundance intensity from the analyte intensity. The system operating conditions are listed in Table 2.

Table 2. System operating conditions

Plasma gas	15 L/min
Auxiliary gas	1.0 L/min
Nebulizer gas	0.6-0.9 L/min (optimized)
Incident power	1300 W (optimized)
Reflected power	minimized (automatically tuned)
Sampling zone	X and Y: optimized; Z: fixed at 5 mm from end of torch
Torch	Quartz
Injector	Alumina
Nebulizer	Teflon Burgener T2100
Spray chamber	baffled quartz cyclonic
Sampler and skimmer cones	Nickel
Lens voltage	Optimized
Detector	thin-film ETP
Sweeps/replicate	15
Number of replicates	4

Points across peak	1 (peak hopping)
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Internal standards

In order to improve the overall quality of the analyses and to monitor the stability of the instrumental output, internal standards are added to all samples, blanks, calibrants and QC SRM standards prior to analysis. These internal standards consist of a solution of 1% nitric acid, a small amount of a non-ionic surfactant (0.0188 ml 30% Brij per 200 ml) and about 20 µg/L of three rare elements, Rh, In and Ir, which typically have undetectable occurrence in natural waters. The internal standard solution (IS) is added automatically using a peristaltic pump which employs different sized tubing for the samples (and standards, blanks, etc.) and the IS. The different diameter sizes of tubing are chosen so that the ratio between the sample volume passing through the peristaltic pump and the IS volume is about 9:1. The sample stream and IS stream are joined directly after the peristaltic pump and are subsequently passed through a mixing coil to thoroughly mix the solution prior to arrival at the nebulizer. The analyte signal is divided by the appropriate internal standard signal to compensate for slight changes in the nebulization efficiency due to a number of reasons. These can include partial clogging of the nebulizer or sampling cones, small changes in the viscosity of the samples, or fluctuations associated with the plasma.

Interference standards

Interferences can occur in a number of ways. A major problem is when an interfering species falls on the same mass as an analyte of interest. This can either be direct overlap of an isotope of one element having an indistinguishable mass of a different element. This is referred to as direct isobaric overlap. This is corrected by measuring the signal from an alternate isotopic mass from the interfering element, correcting it based on its natural isotopic abundances, then subtracting the resulting corrected signal from the analyte. An example of this is the correction of ^{114}Sn on ^{114}Cd , where Sn is measured using the isotope 118 and the intensity is corrected by applying the equation: $^{114}\text{Cd intensity} - ((\text{intensity of } ^{118}\text{Sn}) * 0.65/24.23)$. The ratio 0.65/24.23 is the isotopic abundance ratio of $^{114}\text{Sn}/^{118}\text{Sn}$ and multiplying this times the observed intensity of ^{118}Sn gives the apparent ^{114}Cd intensity contributed from Sn. The second type of interference is where a molecular species give the same apparent mass as the analyte ion. An example of this is $^{40}\text{Ar}^{35}\text{Cl}$ which gives the apparent mass of 75 which is the same as the ^{75}As . This is corrected empirically by observing the signal at mass 75 at different Cl concentrations then regressing the results to determine a relationship between the apparent As signal as a function of the chloride concentration at mass 75 which is subtracted from the total signal at mass 75 to give the signal due to As. Examples of these interferences are listed in Table 3 along with the isotope used to monitor the interference on the analyte of interest. Other interferences involve the performance of the sampling and plasma systems. These are generally compensated by matrix matching as closely as possible and the internal standard addition system.

Table 3. Isobaric and molecular interference corrections performed using this methodology. The “Possible Interference” column is not exhaustive, but only illustrative, of the possible molecular interferences that may be encountered during analysis. The “Monitored Ions” column indicates the ion measured to get the empirical apparent analyte concentration and includes all interfering molecular species related to the ion.

Element	Isotope	Possible Interference	Monitored Ions for Correction	
Aluminum	27	$^{12}\text{C}^{14}\text{N}^1\text{H}$, $^{12}\text{C}^{15}\text{N}$, $^{13}\text{C}^{14}\text{N}$	^{13}C	
Antimony	121	none		
Arsenic	75	$^{40}\text{Ar}^{35}\text{Cl}$	^{35}Cl	
Boron	11	none		
Barium	137	none		
Beryllium	9	none		
Bismuth	209	none		
Cadmium	111	$^{95}\text{Mo}^{16}\text{O}$	^{95}Mo	
Cadmium	114	$^{98}\text{Mo}^{16}\text{O}$, ^{114}Sn	^{95}Mo , ^{118}Sn	
Cerium	140	none		
Cobalt	59	$^{43}\text{Ca}^{16}\text{O}$	^{43}Ca	
Chromium	52	$^{40}\text{Ar}^{12}\text{C}$, $^{36}\text{Ar}^{16}\text{O}$, $^{35}\text{Cl}^{16}\text{O}^1\text{H}$	^{13}C , ^{35}Cl	
Chromium	53	$^{37}\text{Cl}^{16}\text{O}$, $^{40}\text{Ar}^{12}\text{C}^1\text{H}$	^{13}C , ^{35}Cl	
Cesium	133	none		
Copper	63	$^{40}\text{Ar}^{23}\text{Na}$	^{23}Na	
Copper	65	$^{32}\text{S}^{16}\text{O}_2^1\text{H}$, $^{33}\text{S}^{16}\text{O}_2$	^{34}S	
Dysprosium	163	$^{147}\text{Sm}^{16}\text{O}$	^{147}Sm	
Erbium	167	$^{151}\text{Eu}^{16}\text{O}$	^{151}Eu	
Europium	151	$^{135}\text{Ba}^{16}\text{O}$	^{137}Ba	
Gallium	71	$^{36}\text{Ar}^{35}\text{Cl}$, $^{55}\text{Mn}^{16}\text{O}$	^{35}Cl , ^{55}Mn	
Gadolinium	158	$^{142}\text{Nd}^{16}\text{O}$, $^{142}\text{Ce}^{16}\text{O}$	^{146}Nd , ^{140}Ce	
Holmium	165	$^{149}\text{Sm}^{16}\text{O}$	^{147}Sm	
Lanthanum	139	none		
Lead	206+207+208	none		
Lithium	7	none		
Lutetium	175	$^{159}\text{Tb}^{16}\text{O}$	^{159}Tb	
Manganese	55	none		
Molybdenum	95	none		
Neodymium	146	none		
Nickel	60	$^{44}\text{Ca}^{16}\text{O}$, $^{48}\text{Ca}^{12}\text{C}$	^{43}Ca , ^{13}C	
Phosphorous	31	none		
Praseodymium	141	none		
Rubidium	85	none		
Rhenium	187	$^{171}\text{Yb}^{16}\text{O}$	^{174}Yb	
Selenium	77	$^{40}\text{Ar}^{37}\text{Cl}$	^{35}Cl	

Selenium	82	$^{81}\text{Br}^{1}\text{H}$	^{81}Br	
Samarium	147	none		
Strontium	86	none		
Terbium	159	$^{143}\text{Nd}^{16}\text{O}$	^{146}Nd	
Tellurium	126	none		
Tin	118	none		
Thorium	232	none		
Titanium	47	$^{29}\text{Si}^{18}\text{O}, ^{31}\text{P}^{16}\text{O}$	$^{29}\text{Si}, ^{31}\text{P}$	
Titanium	49	$^{33}\text{S}^{16}\text{O}, ^{34}\text{S}^{14}\text{N}$	^{34}S	
Thallium	205	None		
Thulium	169	$^{153}\text{Eu}^{16}\text{O}$	^{151}Eu	
Uranium	238	None		
Vanadium	51	$^{35}\text{Cl}^{16}\text{O}$	^{35}Cl	
Tungsten	182	$^{166}\text{Er}^{16}\text{O}$	^{167}Er	
Yttrium	89	none		
Ytterbium	174	$^{158}\text{Gd}^{16}\text{O}$	^{158}Gd	
Zinc	64	$^{32}\text{S}^{16}\text{O}_2$	^{34}S	
Zinc	66	$^{34}\text{S}^{16}\text{O}_2, ^{132}\text{Ba}^{++}$	$^{34}\text{S}, ^{137}\text{Ba}$	
Zirconium	90	none		

Calibration

Typical calibration data consists of five calibrants and a reagent blank covering the following ranges: Sr: 20-2000 µg/L; Al and B: 10-1000 µg/L; Ba: 5-500 µg/L; Mn, U and Zn: 2-200 µg/L; As, Cu and Li: 1-100 µg/L; Cr, Pb, Se and V: 0.5-50 µg/L; Cd, Mo, Ni, Rb, W and Zr: 0.2-20 µg/L; Cs: 0.1-10 µg/L; Be, Bi, Ce, Co, Dy, Er, Eu, Gd, Ho, La, Lu, Pr, Re, Rb, Sm, Tb, Th, Tl, Tm, Y and Yb: 0.05-5 µg/L.

Calibration standard concentrations are arranged in a geometric pattern with the factors of 1, 3, 10, 30, and 100. If required for a particular analytical set of samples, a set of three multi-element standards are available at a concentration of 10 times the high standard concentrations previously listed in this section. For these calibration standards, regression r^2 values are determined, achieving values greater than 0.999. On those occasions upon which r^2 values are below 0.999, the calibration curves are scrutinized and incorrect calibrants are re-prepared. Calibration standards are analyzed producing a calibration curve for each analysis run. Samples whose concentrations fall above these ranges are diluted and reanalyzed. Tin is calibrated with a 2 point calibration using a single element solution due to the inability to stabilize it in a multi-element calibration solution. Table 4 shows typical r^2 values from twelve different analysis runs.

Table 4. Mean and median calibration r^2 values from indicated number of analysis runs.

Element	Mean r^2	Median r^2	n	Element	Mean r^2	Median r^2	n
Aluminum	0.9997	0.9997	12	Molybdenum	0.9999	1.0000	12
Antimony	0.9999	1.0000	12	Neodymium	0.9999	1.0000	12
Arsenic	0.9998	0.9998	12	Nickel	0.9999	1.0000	12
Boron	0.9998	0.9998	12	Phosphorous	0.9985	0.9999	10

Barium	0.9998	0.9999	12		Praseodymium	0.9999	0.9999	12
Beryllium	0.9998	0.9999	12		Rubidium	1.0000	1.0000	12
Bismuth	0.9999	0.9999	12		Rhenium	1.0000	1.0000	12
Cadmium	0.9998	0.9998	12		Selenium	0.9998	0.9998	12
Cerium	0.9999	0.9999	12		Samarium	0.9999	0.9999	12
Cobalt	0.9998	0.9999	12		Strontium	0.9999	0.9999	12
Chromium	0.9999	1.0000	12		Terbium	0.9999	0.9999	12
Cesium	0.9999	1.0000	12		Tellurium	0.9998	0.9998	12
Copper	0.9999	0.9999	12		Tin	2pt	calibration	12
Dysprosium	0.9999	1.0000	12		Thorium	0.9998	0.9998	12
Erbium	0.9999	0.9999	12		Titanium	0.9999	1.0000	12
Europium	0.9999	1.0000	12		Thallium	0.9999	0.9999	12
Gallium	0.9999	1.0000	12		Thulium	0.9999	0.9999	12
Gadolinium	0.9999	0.9999	12		Uranium	0.9983	0.9999	12
Holmium	0.9999	0.9999	12		Vanadium	0.9999	0.9999	12
Lanthanum	0.9999	1.0000	12		Tungsten	0.9998	0.9999	12
Lead	0.9999	0.9999	12		Yttrium	0.9998	0.9998	12
Lithium	0.9992	0.9994	12		Ytterbium	0.9999	0.9999	12
Lutetium	0.9998	0.9999	12		Zinc	0.9997	0.9997	12
Manganese	1.0000	1.0000	12		Zirconium	0.9994	0.9994	12

Blanks

Normally, a minimum of twelve laboratory blanks are analyzed during each analysis run to monitor instrument stability and blank levels. The blanks are interspersed throughout the analysis run. Additionally, these blanks are used to calculate detection limits for each analyte for each analysis run.

Method detection limits

The “Minimum Detection Limit” (MDL) is calculated according to the method of Skogerboe and Grant (1970). This method calculates the MDL as the standard deviation of n blanks multiplied by the Student t-statistic at the 98.5% confidence level for (n-1) degrees of freedom. Table 5 shows typical calculated detection limits using this methodology.

Table 5. Mean and Median detection limits for eleven separate analysis runs. Number of blanks used to calculate the detection for each run is 12.

Element	Mean	Median	Unit		Element	Mean	Median	Unit
Aluminum	0.02	0.01	µg/L		Molybdenum	0.1	0.1	µg/L
Antimony	0.03	0.02	µg/L		Neodymium	0.0003	0.0003	µg/L
Arsenic	0.03	0.02	µg/L		Nickel	0.01	0.005	µg/L
Boron	0.9	0.6	µg/L		Phosphorous	2	1	µg/L

Barium	0.02	0.01	µg/L		Praseodymium	0.00008	0.00008	µg/L
Beryllium	0.005	0.002	µg/L		Rubidium	0.003	0.002	µg/L
Bismuth	0.07	0.007	µg/L		Rhenium	0.0002	0.0001	µg/L
Cadmium	0.004	0.002	µg/L		Selenium	0.2	0.1	µg/L
Cerium	0.0002	0.0002	µg/L		Samarium	0.0003	0.0002	µg/L
Cobalt	0.003	0.001	µg/L		Strontium	0.09	0.06	µg/L
Chromium	0.2	0.08	µg/L		Terbium	0.00006	0.00004	µg/L
Cesium	0.0007	0.0008	µg/L		Tellurium	0.005	0.004	µg/L
Copper	0.02	0.01	µg/L		Tin	0.2	0.07	µg/L
Dysprosium	0.0002	0.00008	µg/L		Thorium	0.001	0.0004	µg/L
Erbium	0.0002	0.0001	µg/L		Titanium	0.1	0.02	µg/L
Europium	0.0001	0.00007	µg/L		Thallium	0.005	0.003	µg/L
Gallium	0.0008	0.0003	µg/L		Thulium	0.00008	0.00005	µg/L
Gadolinium	0.0002	0.0001	µg/L		Uranium	0.002	0.0006	µg/L
Holmium	0.00005	0.00003	µg/L		Vanadium	0.07	0.03	µg/L
Lanthanum	0.0001	0.0001	µg/L		Tungsten	0.02	0.008	µg/L
Lead	0.007	0.006	µg/L		Yttrium	0.0002	0.0002	µg/L
Lithium	0.02	0.01	µg/L		Ytterbium	0.0001	0.00007	µg/L
Lutetium	0.00007	0.00005	µg/L		Zinc	0.08	0.08	µg/L
Manganese	0.04	0.01	µg/L		Zirconium	0.005	0.004	µg/L

Quality Control

QC SRM samples are analyzed at a frequency which exceeds 30% of all analyses. These SRM standards are interspersed throughout the analysis run to determine precision, accuracy and instrument stability. Table 6 presents typical accuracy and precision results from various certified reference standards including National Institute of Standards and Technology (NIST) SRM 1643d, US Geological Survey (USGS) standard reference water samples T-135, T-173, and T-175, PPREE (a rare earth element standard, described in Antweiler (1998)), and two sediment samples NIST 8704 and Tibet sediment standard DC70317. As can be seen, precision is usually 3% or better, although this figure depends on the concentration and on the element in question. The average value for each QC sample is determined and is compared against its published certified value (in the case of NIST standards) or “most probable value” (MPV) to establish the accuracy of the results. Table 5 presents accuracy data for a reported analytes. As can be seen from these results, the observed values are very close to the MPV for all elements based on the calculated recoverys.

Table 6. Accuracy and precision results for this method; Mad is the median absolute deviation which is a robust analogue for standard deviation (Rousseeuw, 1990) and %Rmad is the percent relative median absolute deviation, an analogue for %RSD. Italicized elements indicate those elements which SRMs are in the evaluation phase or the SRM search is ongoing. All concentration in µg/L unless noted.

Element	MPV ¹	Median	Mad	% Recovery	% Rmad	Reference Standard
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Aluminum	12.76	13.0	0.2	102	1.3	NIST 1643d (1/10 dilution)
Antimony	5.41	5.34	0.15	99	2.8	NIST 1643d (1/10 dilution)
Arsenic	5.602	5.31	0.14	95	2.6	NIST 1643d (1/10 dilution)
Boron	14.48	14.9	0.2	103	1.7	NIST 1643d (1/10 dilution)
Barium	50.65	51.1	0.5	101	0.9	NIST 1643d (1/10 dilution)
Beryllium	1.253	1.23	0.04	98	2.8	NIST 1643d (1/10 dilution)
Bismuth	1.3	1.30	0.0003	100	0.02	NIST 1643d (1/10 dilution)
Cadmium	1.26	1.26	0.01	100	1.1	USGS SRWS T173
Cerium	1.63	1.63	0.003	100	0.2	PPREE (1/100 dilution)
Cobalt	2.500	2.50	0.04	100	1.5	NIST 1643d (1/10 dilution)
Chromium	1.853	1.85	0.02	100	0.9	NIST 1643d (1/10 dilution)
<i>Cesium¹</i>	<i>5.83</i>	<i>5.80</i>	<i>0.11</i>	<i>99</i>	<i>1.8</i>	<i>NIST Buff. R. Sed. 8704</i>
Copper	2.05	2.14	0.1	104	2.9	NIST 1643d (1/10 dilution)
Dysprosium	0.220	0.220	0.0004	100	0.2	PPREE (1/100 dilution)
Erbium	0.120	0.119	0.0007	99	0.6	PPREE (1/100 dilution)
Europium	0.0600	0.0599	0.0001	100	0.2	PPREE (1/100 dilution)
<i>Gallium</i>	<i>2.16</i>	<i>2.14</i>	<i>0.03</i>	<i>99</i>	<i>1.4</i>	<i>Env. Can. FP101T10</i>
Gadolinium	0.240	0.238	0.0003	99	0.1	PPREE (1/100 dilution)
Holmium	0.0443	0.0441	0.00005	100	0.1	PPREE (1/100 dilution)
Lanthanum	0.804	0.806	0.002	100	0.3	PPREE (1/100 dilution)
Lead	4.59	4.68	0.02	102	0.4	USGS SRWS T173
Lithium	1.650	1.70	0.05	103	3.0	NIST 1643d (1/10 dilution)
Lutetium	0.0111	0.0111	0.00002	100	0.2	PPREE (1/100 dilution)
Manganese	423	417	3	99	0.6	USGS SRWS T135
Molybdenum	11.29	11.5	0.2	102	1.5	NIST 1643d (1/10 dilution)
Neodymium	0.934	0.934	0.002	100	0.3	PPREE (1/100 dilution)
Nickel	5.81	5.90	0.13	102	2.2	NIST 1643d (1/10 dilution)
<i>Phosphorous¹</i>	<i>389</i>	<i>385</i>	<i>7</i>	<i>99</i>	<i>1.8</i>	<i>Tibet Sediment DC70317</i>
Praseodymium	0.212	0.212	0.001	100	0.5	PPREE (1/100 dilution)
Rubidium	1.2	1.14	0.04	93	3.2	NIST 1643d (1/10 dilution)
<i>Rhenium</i>						<i>No standard available</i>
Selenium	1.143	1.09	0.04	96	3.9	NIST 1643d (1/10 dilution)
Samarium	0.204	0.203	0.0003	100	0.2	PPREE (1/100 dilution)
Strontium	29.48	29.2	0.4	99	1.5	NIST 1643d (1/10 dilution)
Terbium	0.0367	0.0365	0.0001	99	0.3	PPREE (1/100 dilution)
Tellurium	0.1	0.098	0.002	98	2.2	NIST 1643d (1/10 dilution)
<i>Tin</i>	<i>15.6</i>	<i>15.7</i>	<i>0.3</i>	<i>101</i>	<i>1.9</i>	<i>Env. Can. FP101T08</i>
<i>Thorium¹</i>	<i>9.07</i>	<i>9.34</i>	<i>0.24</i>	<i>103</i>	<i>2.6</i>	<i>NIST Buff. R. Sed. 8704</i>
<i>Titanium¹</i>	<i>0.457</i>	<i>0.494</i>	<i>0.011</i>	<i>108</i>	<i>2.3</i>	<i>NIST Buff. R. Sed. 8704</i>
Thallium	0.728	0.763	0.006	105	0.8	NIST 1643d (1/10 dilution)
Thulium	0.0148	0.0148	0.00004	100	0.3	PPREE (1/100 dilution)
Uranium	1.48	1.49	0.005	101	0.3	USGS SRWS T175
Vanadium	3.51	3.44	0.09	98	2.5	NIST 1643d (1/10 dilution)

<i>Tungsten¹</i>	<i>9.2</i>	<i>10</i>	<i>1</i>	<i>106</i>	<i>10.9</i>	<i>Tibet Sediment DC70317</i>
Yttrium	1.348	1.345	0.001	100	0.1	PPREE (1/100 dilution)
Ytterbium	0.0818	0.0817	0.0004	100	0.5	PPREE (1/100 dilution)
Zinc	7.248	7.33	0.23	101	3.2	NIST 1643d (1/10 dilution)
<i>Zirconium</i>						<i>No standard available</i>

¹ Reference standard used is a digested sediment standard due to lack of water standard availability. Concentration is in µg/g except for Ti which is in wt%.

Sample Analysis

Each sample is analyzed in triplicate where they are systematically arranged to ensure that any particular sample pair is not analyzed back to back more than once. Furthermore, every sample has one replicate in each third of the analysis run following the calibration standards. The concentration value for each sample is the mean of these three separate analyses and the precision of the measurement is calculated as the standard deviation of the three analyses. Each of the three replicate analyses is compared for consistency. On those occasions for which one of the replicates substantially disagrees with the other two, it is discarded and the average and standard deviation of the remaining two are used for the concentration and precision. For those rare times when all three values substantially disagree, the sample is resubmitted for analysis.

Sample Pre-Processing

The raw sample data are run through a pre-processing macro to get the analytical results in to a suitable matrix form that has elements along the top of the table and sample (in chronological order) down the right side column. It is during this process that the best internal standard is chosen for each analyte and the internal standard ratioed intensities are generated.

Sample Processing

After analysis, the initial results from the instrumentation need to be processed to yield final results. These post-analysis processing steps are complex and thorough and will be briefly described below.

The initial step is to convert the raw instrument values into a preliminary concentration. For analyses from the ICP-MS, the instrument yields intensities that are in “counts per second” (cps) and these are generally proportional to the concentration. However, to remove gross instrument drift these values are first ratioed to the cps of internal standards which have been added to each sample. The internal standards are rhodium, indium and iridium. Generally, all element masses less than 135 (i.e., lower atomic number than barium) are ratioed to rhodium, and all those greater than this are ratioed to iridium. The indium internal standard is a back-up in case one of the other two is compromised in some way. These ratioed cps are converted to initial concentrations by using the calibration standards which are analyzed at the beginning of each analysis run. For most elements, the ratioed cps of five calibrants are regressed against their known concentrations; concentrations are geometrically spaced over two orders of magnitude, and span the range found in most samples. Regression R^2 values are normally at least 0.9995. Using the

regression parameters from these, all values for all elements are converted into a preliminary concentration.

The next step in the post-analysis processing is referred to as “blank subtraction”. In each analysis run, between 10 and 20 laboratory blank samples are analyzed, these blanks being interspersed throughout the run. The initial concentrations of these are regressed against the sample order (this latter being directly proportional to the time at which the sample was analyzed). The regression parameters from this step are used to “blank-subtract”: the initial concentrations of all samples (including these blanks) are adjusted by subtracting the sum of the slope value times the sample order number and the intercept value. It is thus the case that after this step the average value of the blanks throughout the run has a concentration of zero, and that there is no drift amongst the blanks across the run. The standard deviation of these blanks is used to calculate a detection limit for each line and is unique to the analysis run.

The third step is referred to as “interference correction”. ICP-MS analyses from one isotope may be subject to positive interferences from isotopes of other elements and molecules, and these must be removed to insure high-quality results. The elements whose isotopes can cause these interferences are analyzed at two different concentrations, and the effects that each of these have on the isotopes which are subject to interferences are used to determine the effect of the interference. Once this effect (per unit concentration) is calculated for each susceptible isotope, the concentrations of these isotopes are adjusted by subtracting the product of the effect times the concentration of the interfering isotope.

The fourth step is called “QC correction” and is a fine-tuned adjustment to the gross instrument drifts removed in the first step by utilizing the internal standards. In each analysis run, two separate “consistency standards” (C-standards) are analyzed as samples between eight and fifteen times interspersed throughout the run. These C-standards are prepared in the laboratory from single-element NIST-traceable standards; there are two C-standards because not all elements are compatible with each other. The ratios of the known concentration of the C-standard to its interference-corrected, blank-subtracted values within the analysis run are regressed against the sample number (proportional to the time at which the sample was analyzed). Under ideality, the slope of this regression is 0 (no instrument drift) and the intercept is 1; however, especially for elements whose atomic numbers are far from rhodium or iridium, there is almost always a non-zero slope, which indicates that there is still a residual drift. To correct for this drift (the “QC correction”), the interference corrected, blank subtracted concentrations of each sample are multiplied by the sum of the intercept and the product of the slope and the sample number. The consequence of this action insures that each element has been corrected so that there is no drift over the course of the analysis run.

The fifth step is called the “QC-adjustment”. In addition to the C-standards, every analysis run has six to eight different USGS SRWS and/or NIST SRMs, each of which is analyzed between three and six times interspersed throughout the run. The median value of every SRWS is calculated and this is plotted against its respective certified or most-probable value (MPV). Under ideality, these median observed values (MOV) should match the MPVs, and normally this is what is seen; however, at times there is either a positive or negative bias in which the MOVs are systematically greater or less than the MPVs. In this case, the MOVs are regressed against the MPVs by forcing the intercept through zero (since the blank-subtraction step has insured this), and the slope is used to adjust the concentrations of all samples to remove the bias.

The final step is referred to as “outlier removal”. Every sample is analyzed in triplicate, once in the first third of the analysis run, once in the middle third and once in the last third. In this step, the agreement of these is examined for each sample. In those cases in which one of the three is substantially different than the other two, it is removed. Whether a value has been removed or not, the mean and standard deviation are calculated for the sample either from the three values or from two if one has been removed. For those samples whose averaged concentration is less than the detection limit value calculated in the blank-subtraction step, the concentration is replaced by a “less than the detection limit value”. Thus for all samples and all lines, both an average concentration and a standard deviation are calculated.

The laboratory normally reports the concentrations of an element not an isotope or an analysis line. In the case in which the element has been analyzed using only on one line, this is what is reported. However, many elements have more than one isotope which has been analyzed; in addition, many elements are also analyzed other techniques such as ICP-OES as well as on the ICP-MS. In these cases there is frequently one emission line or atomic mass that is “preferred”, either because it has the greatest sensitivity or because it has the least amount of interferences, and this line is what is reported. This cross check using two different analysis techniques greatly enhances the confidence in the final result, but the analyst must be aware of the limitations and strengths of each technique. In spite of these generalizations, the analyst has to determine which of the multiple values represents the best one to report, and since the qualities of the various data are not equal, they simply cannot be averaged. Thus, the analyst must use his/her experience and judgment to select the one he/she feels represents the “best” value to report, and because of the intricacies of the analyses, there is no hard or fast rules which can be applied.

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Determination of Selected Trace and Major Elements, Dissolved Iron and Silica in Aqueous Media by Inductively Coupled Plasma-Optical Emission Spectroscopy

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Scope and Application

This inductively coupled plasma-optical emission spectroscopy (ICP-OES) method is primarily for the quantitative determination of Ca, Fe, K, Mg, Na, S, and SiO₂, including Cr, P, and Ti for digestates, in aqueous media (natural waters and precipitation samples, and with appropriately diluted digestates) at concentrations of less than 500 mg/L. The inclusion of Cr, P, and Ti are primarily for the determination of those elements in digestates of sediment, soil, vegetation and animal tissue due to the higher concentrations found in those liquids. In general, using clean handling techniques and purified reagents, method detection limits in the range of 0.002 - 0.05 mg/L for the major elements and a range of 0.3 – 13 µg/L the trace elements Cr, P, and Ti are routinely attainable. The trace elements Al, B, Ba, Cd, Co, Cu, Li, Mn, Mo, Ni, Sr, V, and Zn are also quantified using this method; however the reported concentrations are generally taken from alternant instrumental determinations using inductively coupled plasma-mass spectrometry (ICP-MS) methodology due to reduced interferences or better sensitivity. Detection limits for these elements range from 0.02 - 23 µg/L. As and Sc are also quantified against calibration standards but both suffers from a lack of an appropriate standard reference material (SRM) and cannot be properly quality control (QC) checked. Results for As and Sc will not normally be reported until a suitable SRM becomes available and it has been thoroughly tested. A single argon wavelength is monitored throughout the run as a global gage to indicate how well the analysis is progressing. The argon wavelength's intensity is an indicator of nebulizer performance, as it becomes clogged the intensity will show a significant positive deviation from its starting value. All wavelengths are monitored in the axial configuration except K, which is monitored both the axial and radial configurations. The quantifiable elements and their measured wavelengths are listed in Table 1.

Table 1. Spectroscopic wavelengths, in nanometers (nm), of elements used in the concentration determinations for the quantifiable elements and argon.

Element	Wavelength	Line Type		Element	Wavelength	Line Type
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	(nm)				(nm)	
Argon ^{1,2}	420.069	Atom		Magnesium	285.213	Atom
Aluminum	394.401	Atom		Manganese	257.610	Ion
Aluminum	396.153	Atom		Manganese	260.568	Ion
Arsenic	188.979	Atom		Molybdenum	204.597	Ion
Arsenic	193.696	Atom		Molybdenum	281.616	Ion
Boron	208.957	Atom		Sodium	330.237	Atom
Boron	249.772	Atom		Sodium	588.995	Atom
Barium	455.403	Ion		Sodium	589.592	Atom
Barium	493.408	Ion		Nickel	231.604	Ion
Cadmium	214.440	Ion		Nickel	232.003	Atom
Cadmium	226.502	Ion		Phosphorous	213.617	Atom
Calcium	315.887	Ion		Phosphorous	214.914	Atom
Calcium	317.933	Ion		Potassium ³	766.490	Atom
Calcium	396.847	Ion		Sulfur	180.669	Atom
Cobalt	228.616	Ion		Sulfur	181.975	Atom
Cobalt	230.786	Ion		Scandium ¹	361.383	Ion
Chromium	267.716	Ion		Scandium ¹	424.683	Ion
Chromium	357.869	Atom		Silica	251.611	Atom
Copper	224.700	Ion		Silica	288.158	Atom
Copper	324.752	Atom		Strontium	407.771	Ion
Copper	327.393	Atom		Strontium	460.733	Atom
Iron	238.204	Ion		Titanium	334.940	Ion
Iron	239.562	Ion		Titanium	336.121	Ion
Iron	259.939	Ion		Vanadium	292.402	Ion
Lithium	670.784	Atom		Vanadium	311.071	Ion
Magnesium	279.077	Ion		Zinc	206.200	Ion
Magnesium	279.553	Ion		Zinc	213.857	Atom

¹ Currently no reference standard available for these elements.

² Argon wavelength is used to indicate problems associated with the analytical run.

³ This wavelength for potassium is analyzed in both the axial mode and the radial mode to expand the linear range of the instrument.

Summary of Method

Samples are collected using ultra-clean sample handling protocols into rigorously cleaned polyethylene bottles and are preserved with 1% (v/v) double quartz-distilled nitric acid. Analysis is performed on a Perkin Elmer Optima 3300 DV ICP-OES using techniques based on those described by Garbarino and Taylor (1979), except as modified below.

Reagents

Water: 18 megohm ultra-pure deionized water starting from a pre-purified (distilled, R.O., etc.) source. This water is produced from a Barnstead Nanopure II mixed bed deionizer. Both trace ionic species and trace organic compounds are removed from the processed water.

Nitric Acid: Trace-metal purified reagent HNO₃ is purchased and doubly-distilled in a quartz still in the laboratory (Kuehner, et al, 1972). At monthly intervals, aliquots are sampled for quality-control purposes.

Stock standard solutions: Certified 10 mg/mL and 1 mg/mL standards are used as the basis of all lower concentration laboratory stock solutions. These solutions are commercially available.

Stock secondary mixed solutions: Six multi-element standards and three single element standards are prepared from the single element stock standard solutions, in 18 megohm ultra-pure deionized water and quartz-distilled nitric acid. Standard WMixA contains majors at 200 mg/L Na and 150 mg/L Ca, trace elements at 20 mg/L for Al, Li, and Sr, and 10 mg/L Ni and Cu. Standard WMixB contains majors at 100 mg/L Mg and 50 mg/L SiO₂, and trace elements at 20 mg/L Mn, 10 mg/L Fe and Zn, and 2 mg/L B and Ba. Standard WMixT contains only trace elements at 10 mg/L Be, Cd, Co, and Mo. These standards are then diluted 1/10, 1/50, and 1/250 to make up the calibration sets. The high major standard WC1 contains

250 mg/L Mg and 500 mg/L Na which is analyzed directly only. All of these stock solutions are prepared on a regular basis, usually about six times per year as needed. A single element set of 4 standards with a concentration range of 0.1 to 5 mg/L K are prepared from the certified stock for the calibration of K, and an additionally multi-element standard containing 10 mg/L K and 25 mg/L Fe is used when sample concentrations exceed 5 and 10 mg/L respectively. Four Sulfur standards ranging in concentration from 3 to 100 mg/L are prepared from a 1000 mg/L certified stock solution and a single 2 mg/L P standard (for a one point calibration, blank and 2 mg/L standard) is also prepared from a commercial certified stock solution. Lastly a single multi element standard for the trace elements As, Sc, and Ti at concentrations of 10, 1, 10 mg/L respectively is prepared and run as a single point calibration.

Mixed working standards: The mixed working standards described above for instrument calibration are prepared on a monthly basis from the stock secondary mixed solutions by simple dilution and acidification of the secondary standards.

Ionization Buffer: The ionization buffer is prepared from 99.999% CsCl solid by adding 1 gram CsCl solid to 1L of 1% HNO₃ (10 mL double distilled HNO₃ diluted to approximately 1L) with 18 megohm ultra-pure deionized water.

QC SRM Samples: A variety of quality control (QC SRM) samples are used during each analysis run to insure the accuracy of the analytical results. Generally, these QC SRM samples include 4 U.S. Geological Survey Standard Reference Water Samples (USGS SWRS) run six times, 3 USGS SRWS run 4 times and 4 USGS SRWS run 3 times per run. Occasionally (about every other month) a National Institute of Standards and Technology (NIST) standard is analyzed. In addition, these USGS SWRS standards are traceable to NIST certified samples (see Peart, et al, 1998). The QC standards are changed as new ones become available. Additionally, two laboratory made reference samples are run 17 times each during the run to monitor and account for drift during the run.

Argon: Ultra-high purity argon is fractionally distilled from liquid argon stored in a cryogenic cylinder.

Equipment

The equipment and analytical methodology are described in Garbarino and Taylor (1979) and are summarized here. Samples are analyzed on a Perkin Elmer Optima 3300 DV Inductively-Coupled Plasma Optical Emission Spectrophotometer, equipped with a Perkin Elmer AS-91 autosampler. The sample stream and ionization buffer (mixed realtime at approximately a 9:1 ratio) are pumped with a Perkin Elmer 3-channel peristaltic pump from the autosampler to a Burgener Teflon T2100 nebulizer and a cyclonic spray chamber. Aerosol produced by the nebulizer is then transported through an alumina injector and quartz plasma torch. Wavelengths and emission transition type (ie. atom line vs ion line) used

for the determination of the five elements were listed previously in Table 1. The typical system operating conditions for this method are listed below in Table 2.

Table 2. System operating conditions

Plasma	
Incident RF Power	1300 W
Coolant argon flow rate	15 L/min
Sample argon flow rate	0.850 L/min
Auxiliary argon flow rate	0.6 L/min
Sample pumping rate	1.25 mL/min
Vertical/Horizontal observation position	Mn optimized
Shear Gas	Purified Air
Spectrometer	
Purge Gas	Argon
UV detector range	165 – 403 nm
VIS detector range	404 – 782 nm
Grating (UV/VIS)	Echelle
Secondary dispersion device (UV)	Schmidt Cross Disperser
Secondary dispersion device (VIS)	Prism
Detectors (UV/VIS)	Segmented array CCD
Controller	
Min/Max Exposure time	0.2 – 20 sec
Replicate exposure/determination	5
Resolution	High

Calibration

Typical calibration data consists of four to six calibrants and a reagent blank covering the following ranges: major ions Ca: 0.6-150 mg/L; K: 0.1-10 mg/L; Mg: 0.4-250 mg/L; Na: 0.8-500 mg/L; S: 3.0-100

mg/L; and SiO₂: 0.2-50 mg/L. For trace elements B and Ba: 0.008-2 mg/L; Be, Cd, Co, Cr, Cu, Mo, Ni and Zn: 0.04-10 mg/L; Al, Li, Mn, and Sr: 0.08-20 mg/L; and Fe: 0.04-25 mg/L. Only one calibrant and a reagent blank are used for P, As, Sc, and Ti (concentrations for these elements can be found in the reagents section). For these calibration standards, regression r^2 values are determined, achieving values greater than 0.999. On those occasions upon which r^2 values are below 0.999, the calibration curves are scrutinized and incorrect calibrants are remade. Calibration standards are analyzed producing a calibration curve for each analysis run. Samples whose concentrations fall above these ranges are diluted and reanalyzed. Table 3 shows typical r^2 values from eleven different analysis runs.

Table 3. Mean and median calibration r^2 values from indicated number of analysis runs.

Element	Wavelength	Mean r^2	Median r^2	n	
Aluminum	394.401	0.99991	0.99990	11	
Aluminum	396.153	0.99998	0.99998	11	
Arsenic	188.979	2 point	calibration		
Arsenic	193.696	2 point	calibration		
Barium	455.403	0.99998	0.99999	11	
Barium	493.408	0.99998	0.99999	11	
Boron	208.957	0.99999	1.00000	10	
Boron	249.772	0.99999	1.00000	10	
Cadmium	214.440	0.99996	0.99998	11	
Cadmium	226.502	0.99998	0.99999	11	
Calcium	315.887	0.99998	0.99999	11	
Calcium	317.933	0.99996	0.99998	11	
Calcium	396.847	Experimental	Wavelength		
Chromium	267.716	0.99999	1.00000	11	
Chromium	357.869	1.00000	1.00000	11	
Cobalt	228.616	0.99999	1.00000	11	
Cobalt	230.786	0.99996	1.00000	11	
Copper	224.700	0.99970	0.99962	11	

Copper	324.752	0.99985	0.99988	11	
Copper	327.393	0.99987	0.99987	11	
Iron	238.204	0.99969	0.99991	11	
Iron	239.562	0.99958	0.99991	11	
Iron	259.939	0.99967	0.99980	11	
Lithium	670.784	0.99985	0.99996	11	
Magnesium	279.077	0.99988	0.99996	11	
Magnesium	279.553	Experimental	Wavelength		
Magnesium	285.213	0.99807	0.99811	11	
Manganese	257.610	0.99994	0.99995	11	
Manganese	260.568	0.99997	0.99998	11	
Molybdenum	204.597	0.99997	0.99998	11	
Molybdenum	281.616	0.99997	0.99998	11	
Nickel	231.604	0.99998	0.99998	11	
Nickel	232.003	0.99999	1.00000	11	
Phosphorous	213.617	2 point	calibration		
Phosphorous	214.914	2 point	calibration		
Potassium (axial)	766.490	0.99991	0.99992	10	
Potassium (radial)	766.490	0.99958	0.99971	10	
Scandium	361.383	2 point	calibration		
Scandium	424.683	2 point	calibration		
Silica	251.611	0.99938	0.99999	11	
Silica	288.158	0.99938	0.99999	11	
Sodium	330.237	0.99988	0.99989	11	
Sodium	588.995	0.99993	0.99995	11	
Sodium	589.592	0.99974	0.99975	11	
Strontium	407.771	0.99999	0.99999	11	
Strontium	460.733	0.99992	0.99993	11	

Sulfur	180.669	0.99930	0.99970	11	
Sulfur	181.975	0.99950	0.99983	11	
Titanium	334.940	2 point	calibration		
Titanium	336.121	2 point	calibration		
Vanadium	292.402	0.99999	1.00000	11	
Vanadium	311.071	0.99999	1.00000	11	
Zinc	206.200	0.99995	0.99997	11	
Zinc	213.857	0.99990	0.99992	11	

Blanks

Eighteen laboratory blanks are analyzed during each analysis run to monitor instrument stability, contamination issues, and carry-over problems. The blanks are interspersed throughout the analysis run. Additionally, these blanks are used to calculate detection limits for each analyte for each analysis run.

Detection Limits

The “Minimum Detection Limit” (MDL) is calculated according to the method of Skogerboe and Grant (1970). This method calculates the MDL as the standard deviation of n blanks multiplied by the Student t-statistic at the 97.5% confidence level for (n-1) degrees of freedom. Table 4 shows calculated detection limits and number of blanks analyzed for eight separate analysis runs.

Table 4. Mean and Median detection limits for eleven separate analysis runs (n). Number of blanks used to calculate the detection for each run is 18.

Element	Wavelength	Mean	Median	Units	n	
Aluminum	394.401	4	3	µg/L	11	
Aluminum	396.153	2	2	µg/L	11	
Arsenic	188.979	18	17	µg/L	11	
Arsenic	193.696	24	23	µg/L	11	
Barium	455.403	0.04	0.04	µg/L	11	

Barium	493.408	0.05	0.05	µg/L	11	
Boron	208.957	3	2	µg/L	11	
Boron	249.772	0.8	0.5	µg/L	11	
Cadmium	214.440	0.4	0.3	µg/L	11	
Cadmium	226.502	0.4	0.4	µg/L	11	
Calcium	315.887	0.008	0.008	mg/L	11	
Calcium	317.933	0.006	0.005	mg/L	11	
Calcium	396.847	experimental	wavelength	mg/L		
Chromium	267.716	0.3	0.3	µg/L	11	
Chromium	357.869	1	1	µg/L	11	
Cobalt	228.616	0.6	0.6	µg/L	11	
Cobalt	230.786	1	1	µg/L	11	
Copper	224.700	2	2	µg/L	11	
Copper	324.752	2	2	µg/L	11	
Copper	327.393	0.8	0.2	µg/L	11	
Iron	238.204	4	4	µg/L	11	
Iron	239.562	4	4	µg/L	11	
Iron	259.939	3	2	µg/L	11	
Lithium	670.784	0.05	0.05	µg/L	11	
Magnesium	279.077	0.003	0.002	mg/L	11	
Magnesium	279.553	experimental	wavelength	mg/L	11	
Magnesium	285.213	0.002	0.002	mg/L	11	
Manganese	257.610	0.09	0.08	µg/L	11	
Manganese	260.568	0.1	0.1	µg/L	11	
Molybdenum	204.597	8	7	µg/L	11	
Molybdenum	281.616	6	5	µg/L	11	
Nickel	231.604	1	1	µg/L	11	
Nickel	232.003	3	2	µg/L	11	

Phosphorous	213.617	13	10	µg/L	11	
Phosphorous	214.914	14	13	µg/L	11	
Potassium (axial)	766.490	0.004	0.003	mg/L	11	
Potassium (radial)	766.490	0.2	0.1	mg/L	11	
Scandium	361.383	0.1	0.1	µg/L	11	
Scandium	424.683	0.1	0.1	µg/L	11	
Silica	251.611	0.006	0.005	mg/L	11	
Silica	288.158	0.02	0.02	mg/L	11	
Sodium	330.237	0.3	0.3	mg/L	11	
Sodium	588.995	0.02	0.009	mg/L	11	
Sodium	589.592	0.02	0.007	mg/L	11	
Strontium	407.771	0.03	0.02	µg/L	11	
Strontium	460.733	0.7	0.5	µg/L	11	
Sulfur	180.669	0.05	0.05	mg/L	11	
Sulfur	181.975	0.09	0.08	mg/L	11	
Titanium	334.940	0.4	0.3	µg/L	11	
Titanium	336.121	0.4	0.4	µg/L	11	
Vanadium	292.402	0.3	0.2	µg/L	11	
Vanadium	311.071	0.6	0.2	µg/L	11	
Zinc	206.200	1	1	µg/L	11	
Zinc	213.857	0.5	0.6	µg/L	11	

Quality Control

QC SRM samples are analyzed at a frequency which exceeds 30% of all analyses. These check standards are interspersed throughout the analysis run to determine precision, accuracy and instrument stability. Table 5 presents typical precision and accuracy results from various USGS SRWS standards for trace elements and major ions for eleven separate analysis runs. For the elements B and Mn, NIST SRM 1643d water reference sample is used to determine accuracy and precision. For Ti a NIST SRM sediment (8704) is used due to no suitable water reference samples. The median value for each QC sample is determined

and is compared against its published “most probable value” (MPV) to establish the accuracy of the results. As can be seen, accuracy is better than 5% as the percent recoveries are between 98 and 102 percent with the exception of Ti which used the digested NIST Buffalo River 8704 reference standard. Precision is evaluated by the %Rmad which is an robust analog to % relative standard deviation (% RSD). Over the course of these 11 analysis runs, the %Rmad is less than 4% for each of the elements evaluated.

Table 5. Accuracy and precision results for this method; Mad is the median absolute deviation which is a robust analogue for standard deviation (Rousseeuw, 1990) and %Rmad is the percent relative median absolute deviation, an analogue for %RSD. Italicized elements indicate those elements which SRMs are in the evaluation phase or the SRM search is ongoing. All concentration in µg/L unless noted.

Element	MPV ³	Median	Mad	% Recovery	% Rmad	Reference Standard
Aluminum	62.9	61.7	0.5	98	0.9	USGS SRWS T187
Arsenic						<i>No standard available</i>
Barium	29.9	29.9	0.08	100	0.3	USGS SRWS T195
Boron	14.48	14.5	0.01	100	0.1	NIST 1643d (1/10 dilution)
Cadmium	8.2	8.34	0.07	102	0.8	USGS SRWS T175
Calcium ²	3.90	3.89	0.02	100	0.4	USGS SRWS T187
Chromium	2.62	2.68	0.06	102	2.2	USGS SRWS T211
Cobalt	5.55	5.47	0.11	99	2.0	USGS SRWS T197
Copper	7.50	7.37	0.08	98	1.1	USGS SRWS T173
Iron	66.9	67.1	1.29	100	1.9	USGS SRWS T205
Lithium	17.1	16.8	0.09	98	0.5	USGS SRWS T173
Magnesium ²	4.91	4.88	0.06	99	1.3	USGS SRWS T209
Manganese	3.766	3.77	0.09	100	2.3	NIST 1643d (1/10 dilution)
Molybdenum	41.4	41.2	1.5	99	3.7	USGS SRWS T159
Nickel	18.9	19.1	0.3	101	1.6	USGS SRWS T197
Phosphorous	162	166	1	102	0.6	USGS SRWS M206
Potassium ²	2.66	2.62	0.06	99	2.1	USGS SRWS T209
Scandium						<i>No standard available</i>

Silica ²	8.78	8.68	0.04	99	0.5	USGS SRWS T205
Sodium ²	6.56	6.46	0.07	98	1.1	USGS SRWS T195
Strontium	23.5	24.0	0.1	102	0.6	USGS SRWS T187
Sulfur ²	10.8	11.0	0.2	102	2.1	USGS SRWS M206
Titanium ¹	0.457	0.49	0.01	108	2.3	<i>NIST Buff. R. Sed. 8704</i>
Vanadium	4.31	4.33	0.06	100	1.5	USGS SRWS T173
Zinc	71.6	71.5	1.6	100	2.3	USGS SRWS T175

¹ Reference standard used is a digested sediment standard due to lack of water standard availability. Concentration is in µg/g except for Ti which is in wt%.

² Concentration is in mg/L.

² MVP is Most Probable Value, except for NIST concentrations which are certified.

Sample Analysis

Each sample is analyzed in triplicate, again interspersed throughout the analysis run such that one replicate for each sample is analyzed in every third of the analysis run. The concentration value for each sample is the mean of these three separate analyses and the precision of the measurement is calculated as the standard deviation of the three analyses. Each of the three replicate analyses are compared for consistency. On those occasions for which one of the replicates substantially disagrees with the other two, it is discarded and the average and standard deviation of the remaining two are used for the concentration and precision. For those rare times when all three values substantially disagree, the sample is reanalyzed.

Sample Pre-Processing

The raw sample data are run through a pre-processing macro to get the analytical results in to a suitable matrix form that has elements along the top of the table and sample (in chronological order) down the right side column. It is during this process that the run is initially evaluated using preliminary data to warrant passing it on the next processing step.

Sample Processing

After analysis, the initial results from the instrumentation need to be processed to yield final results. These post-analysis processing steps are complex and thorough and will be briefly described below. The wavelengths are chosen so that interferences are minimized and multiple wavelengths are analyzed for each analyte so at least one of the wavelengths will be generally unaffected by the same interfering substance.

The initial step is to convert the raw instrument values into a preliminary concentration. For analyses performed on the ICP-OES, there are generally more than one wavelength of sufficient intensity per element to provide concentration values, and therefore there is generally more than one estimate of concentration per element. The instrument yields wavelength intensities that are “counts per second” (cps) and they are generally proportional to the concentration of the element. These cps are converted to initial concentrations by using the calibration standards which are analyzed at the beginning of each analysis run. For most elements, the cps of the calibrants are regressed against their known concentrations; concentrations of the standards are biased towards the lower end of the calibration curve, extend for more than two orders of magnitude, and span the range found in most samples. Regression R^2 values are normally at least 0.9995. Using the regression parameters from these, all values for all elements are converted into a preliminary concentration.

The next step in the post-analysis processing is referred to as “blank subtraction”. In each analysis run, between 10 and 20 laboratory blank samples are analyzed, these blanks being interspersed throughout the run. The initial concentrations of these are regressed against the sample order (this latter being directly proportional to the time at which the sample was analyzed). The regression parameters from this step are used to “blank-subtract”: the initial concentrations of all samples (including these blanks) are adjusted by subtracting the sum of the slope value times the sample order number and the intercept value. It is thus the case that after this step the average value of the blanks throughout the run has a concentration of zero, and that there is no drift amongst the blanks across the run. The standard deviation of these blanks is used to calculate a detection limit for each line and is unique to the analysis run.

The third step is called “drift-correction” and is a fine-tuned adjustment to account for instrument drifts. In each analysis run, two separate “consistency standards” (C-standards) are analyzed as samples between ten and twenty times interspersed throughout the run. These C-standards are prepared in the laboratory from single-element NIST-traceable standards; there are two C-standards because not all elements are compatible with each other. The ratios of the known concentration of the C-standard to its blank-subtracted values within the analysis run are regressed against the sample number (proportional to the time at which the sample was analyzed). Under ideality, the slope of this regression is 0 (no instrument drift) and the intercept is 1; however, there is almost always a non-zero slope indicating an instrument drift. To correct for this drift (the “QC correction”), blank subtracted concentrations of each sample are multiplied by the sum of the intercept and the product of the slope and the sample number. The consequence of this action insures that each element has been corrected so that there is no drift over the course of the analysis run.

The fourth step is called the “final-adjustment”. In addition to the C-standards, every analysis run has six to twelve different USGS, Environment Canada, and/or NIST standard reference water samples (SRWS) each of which is analyzed between three and six times interspersed throughout the run. The median value of every SRWS is calculated and this is plotted against its respective certified or most-probable value

(MPV). Under ideality, these median observed values (MOV_s) should match the MPV_s, and normally this is what is seen; however, at times there is either a positive or negative bias in which the MOV_s are systematically greater or less than the MPV_s. In this case, the MOV_s are regressed against the MPV_s by forcing the intercept through zero (since the blank-subtraction step has insured this), and the slope is used to adjust the concentrations of all samples to remove the bias.

The final step is referred to as “outlier removal”. Every sample is analyzed in triplicate, once in the first third of the analysis run, once in the middle third and once in the last third. In this step, the agreement of these is examined for each sample. In those cases in which one of the three is substantially different than the other two, it is removed. Whether a value has been removed or not, the mean and standard deviation are calculated for the sample either from the three values or from two if one has been removed. For those samples whose averaged concentration is less than the detection limit value calculated in the blank-subtraction step, the concentration is replaced by a “less than the detection limit value”. Thus for all samples and all lines, both an average concentration and a standard deviation are calculated.

The laboratory normally reports the concentrations of an element not an isotope or an analysis line. In the case in which the element has been analyzed using only on one wavelength, this is what is reported. However, many elements have more than one wavelength which has been analyzed; in addition, many elements are also analyzed other techniques such as ICP-MS as well as on the ICP-OES. In these cases there is frequently one emission wavelength or atomic mass that is “preferred”, either because it has the greatest sensitivity or because it has the least amount of interferences, and this line is what is reported. This cross check using two different analysis techniques greatly enhances the confidence in the final result, but the analyst must be aware of the limitations and strengths of each technique. In spite of these generalizations, the analyst has to determine which of the multiple values represents the best one to report, and since the qualities of the various data are not equal, they simply cannot be averaged. Thus, the analyst must use his/her experience and judgment to select the one he/she feels represents the “best” value to report, and because of the intricacies of the analyses, there is no hard or fast rules which can be applied.

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F2. Methods of the USGS Redox Chemistry Laboratory, Boulder, Colorado

Standard Operating Procedure: Ferrous Iron and Total Iron in Aqueous Samples

December, 2016

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Scope and Application

This SOP describes the procedure for assaying ferrous iron (Fe(II)) and total iron (Fe(T)) in aqueous samples. Samples are filtered, collected in acid-washed, amber plastic bottles and preserved with 6M redistilled hydrochloric acid in the field at the time of collection, and quantified via the FerroZine colorimetric analysis. During sample collection, the bottles are rinsed three times with sample after a minimum of 500mL have passed through the filter. Samples are stored at 4°C for up to 6 months without significant changes in the Fe redox distribution because microbial catalysts are removed, the pH is low enough to keep metals solubilized, and the iron oxidation rate is negligible (To and others, 1999). This procedure was developed from previously published methods (Stookey, 1970; To and others, 1999).

Method Summary

The method is based on the specific binding of the FerroZine reagent to Fe(II) in the presence of an ammonium acetate buffer, reacting to form a purple complex that can be quantitated by measuring absorbance of the solution at 562 nm with a UV-VIS spectrophotometer. Total Fe can be measured by adding a reducing agent (hydroxylamine chloride) to the reaction. Each sample is typically split into two analyses: (1) in the absence of hydroxylamine for Fe(II) determination, and (2) in the presence of hydroxylamine for Fe(T) determination. The calculated difference between these two measurements is Fe(III).

Reagents

Water: 18 megohm ultra-pure deionized water starting from a pre-purified source. This water is produced from a Barnstead E-Pure mixed bed deionizer. Both trace ionic species and trace organic compounds are removed from the processed water.

Hydrochloric Acid: Trace-metal grade 6M hydrochloric acid is used for preservation of sample, in blanks, and standards.

FerroZine reagents:

FerroZine iron reagent (3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine-4',4''-disulfonic acid sodium) is prepared by diluting 2g in 1L of deionized water.

Ammonium acetate buffer solution (pH 7-7.5) is prepared by diluting 455mL redistilled NH_4OH and 340mL ultrapure glacial acetic acid in deionized water to 1L, and adjusting the final pH to the appropriate range with either ammonium hydroxide or acetic acid.

Hydroxylamine chloride is prepared by diluting a 20% solution with equal parts deionized water.

Total iron (Fe(T)) standards: A 1000ppm standard solution (High Purity Standard) is used for calibration curve.

Sample, Standard, Blank Preparation

Samples, blanks, and standards are prepared in acid-washed, 25mL volumetric flasks. The appropriate amount of acidified sample is pipetted into a volumetric flask to be within the range of the calibration curve when diluted to 25mL total volume. For Fe(II) determination, 0.5mL of FerroZine reagent and 1.25mL of ammonium acetate buffer solution are added to the flask. Deionized water is added to fill the flask to 25mL. For Fe(T) determination, 0.25mL hydroxylamine chloride solution is added along with FerroZine reagent and buffer. Samples are analyzed within hours of preparation.

Equipment

In addition to reagents, acid washed 25mL volumetric flasks, pipettes and tips, and a UV/VIS spectrophotometer with an autosampler, flow-through cuvette, and data capture are required for analysis.

Calibration

The calibration range is 0.25-20 $\mu\text{g Fe} / 25\text{mL}$. Calibration standards are prepared by dilution from certified Fe(T) standard solution, and hydroxylamine is added to all calibration standards during preparation. Calibration standards are analyzed twice per analytical run. A calibration linear regression is performed, and regression r^2 values are determined; values less than 0.99 indicate a rerun of the standards and samples are necessary.

Blanks and Detection Limits

Laboratory blanks are analyzed during each analysis run to monitor instrument stability, and are interspersed throughout the run. Blanks consist of laboratory deionized water and the analytical reagents, as described above. The blanks are also used to determine the detection limit (MDL) for each analysis run. The MDL is defined as the minimum concentration of a substance that can be measured with 99% confidence that the analyte concentration is greater than zero. This method calculates the MDL as the standard deviation of n blanks multiplied by the Student t-statistic at the 97.5% confidence level for (n-1) degrees of freedom (Skogerboe and Grant, 1970). The method detection limit is typically 0.002 mg/L, but may vary depending on the analytical run, cuvette path length, and sample dilutions performed. Consistent with ICP-OES SOP, when low-level Fe(II) or Fe(T) concentrations need to be reported at higher accuracy, the minimum reporting level (MRL) will be used and for this method is the MRL is equal to 10 times the MDL.

Quality Control

In addition to blank and standard analysis, at least three USGS standard reference water samples (SRWS, trace metal series) that contain a known amount of Fe(T) are analyzed in at least triplicate in each analytical run. Because Fe(II) is not stable in SRWS, only Fe(T) is analyzed for SRWSs.

Sample Analysis

Prepared sample is pumped through a 1cm cuvette and the absorbance at 562nm is measured. Each sample is analyzed in triplicate at one dilution. Sample concentrations are determined using the calibration curve(s) generated during the same analytical run and are calculated by linear regression. Triplicate samples are averaged for reporting, and the standard deviation is calculated for each sample; for samples greater than 10µg/L with relative standard deviations within triplicate analysis greater than 5% are reanalyzed. Fe(T) values are compared to ICP-OES Fe values, and any discrepancy >10% between the two values requires reanalysis.

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F3. Methods of the Reston Stable Isotope Lab, Reston, Virginia for stable isotopes of water

$\delta^2\text{H}$ replicate analysis of water by dual-inlet isotope-ratio mass spectrometry: Sample preparation by equilibration with gaseous hydrogen and automated analysis; requires 1 to 2 milliliters of water. Isotopic analysis by laser absorption spectrometry is avoided as a primary analytical technique for all USGS water samples because this method can produce anomalous results that will not hold up in court. The "gold standard" for $\delta^2\text{H}$ determination on water is dual-inlet isotope-ratio mass spectrometry. For 2-mL samples, the estimated expanded uncertainty of replicate hydrogen-isotope measurements is 2 per mil. This means that if the same sample were resubmitted for isotopic analysis, the newly measured value would lie within the uncertainty bounds 95 percent of the time. See the reference below for additional details

Révész, Kinga, and Coplen, T.B., 2008, Determination of the $\delta(2\text{H}/1\text{H})$ of water: RSIL lab code 1574, chap. C1 of Révész, Kinga, and Coplen, T.B., eds., *Methods of the Reston Stable Isotope Laboratory: U.S. Geological Survey Techniques and Methods 10–C1*, 27 p.

$\delta^{18}\text{O}$ replicate analysis of water by dual-inlet isotope-ratio mass spectrometry: Sample preparation by equilibration with carbon dioxide and automated analysis; requires 0.2 to 2.0 milliliters of water. Isotopic analysis by laser absorption spectrometry is avoided as a primary analytical technique for all USGS water samples because this method can produce anomalous results that will not hold up in court. The "gold standard" for $\delta^{18}\text{O}$ determination on water is dual-inlet isotope-ratio mass spectrometry. For 2-mL samples, the estimated expanded uncertainty of replicate oxygen-isotope measurements is 0.2 per mil. This means that if the same sample were resubmitted for isotopic analysis, the newly measured value would lie within the uncertainty bounds 95 percent of the time. See the reference below for additional details

Révész, Kinga, and Coplen, T.B., 2008, Determination of the $\delta(18\text{O}/16\text{O})$ of water: RSIL lab code 489, chap. C2 of Révész, Kinga, and Coplen, Tyler B., eds., *Methods of the Reston Stable Isotope Laboratory: U.S. Geological Survey Techniques and Methods, 10–C2*, 28 p.

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