

## STANDARD OPERATING PROCEDURE NO. 30

### ICP-OES ANALYSIS

REVISION LOG		
Revision Number	Description	Date
30v0	Original SOP (Bonnie Frey author)	02/01/05
30v1	Preliminary edits LMK	02/02/05
30v1	Comments-GMLR	02/10/05
30v2	Edits and comments LMK	2/21/05
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30v4	Incorporated GMLR comments,	3/8/05
30v5	Incorporated GMLR comments (phone) and Bonnie Frey edits; Fixed gaps, reposted to Granite FTP, Resent to Jack Hamilton - LMK	3/9/05
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30v7	Further edits by Bonnie Frey and LMK	04/20/06
	Note: Send Bonnie these edits, then Hold until Bonnie finalizes before posting to Grannite and sending to Jack Hamilton	
30v7	Finalized by LMK for posting to project website and to send to George Robinson for lab audit	3/29/07
30v8	Editorial by SKA	10/23/08

## 1.0 PURPOSE AND SCOPE

This Standard Operating Procedure (SOP) provides technical guidance and procedures for the analysis of solid and water samples by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), specifically on a PerkinElmer Optima 5300 DV. This SOP addresses sample preparation, equipment used, laboratory and instrument procedures, personnel responsibilities, and quality control.

The primary purpose for conducting metals analysis by ICP-OES for this project is because it provides a stable instrument that can handle complicated matrices of up to 5% dissolved solids as is expected for many of the Molycorp rock pile samples. A secondary purpose for analyzing these samples by ICP-OES is to screen them before trace element analysis that will be conducted by ICP-MS. This screening process is necessary to prevent overloading the ICP-MS detector and to reduce the amount of maintenance required when analyzing high-solids samples.

Analysis by ICP-OES will follow US EPA Method 6010 – Inductively Coupled Plasma-Atomic Emission Spectrometry. Sample digestion will follow Briggs method (see References section). Any deviations from these methods will be noted in this SOP.

Currently 39 elements are targeted for ICP-OES analysis. US EPA Method 6010b provides details for analysis of 30 of these elements: aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, phosphorus, potassium, selenium, silica, silver, sodium, strontium, thallium, tin, titanium, vanadium and zinc. The NMBMMR Chemistry Lab (hereafter referred to as the Chem Lab) has added the following elements for analysis by ICP-OES: bismuth, gallium, sulfur, tungsten, yttrium and zirconium. Boron, lithium, mercury and thallium are included in Method 6010b but will not be included in the Chem Lab ICP-OES analysis package. The following target analytes will be analyzed by ICP-MS additionally or instead of ICP-OES: arsenic, beryllium, cobalt, gallium, lead, molybdenum, nickel, rubidium, silver, tellurium, thorium, uranium, vanadium and the rare earth elements. Because of the volatile nature of silica during open-vessel digestion, no silicon analyses will be completed on solids by ICP-OES. Table 1 (Appendix 1) lists the target analytes, their wavelengths, their expected method detection limits (MDLs), and their plasma viewing positions.

## 2.0 RESPONSIBILITIES AND QUALIFICATIONS

The Laboratory Manager, under the direction of the Team Leader and Characterization Team, will have the overall responsibility for implementing this SOP. They will be responsible for assigning appropriate staff to implement this SOP and for ensuring that the procedures are followed accurately.

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

regarding these procedures, if necessary. Personnel trained to use the Environmental Express HotBlock and the associated hazardous acids will undertake the procedures outlined in the sample preparation section of this SOP. Qualified personnel include the Chem Lab manager, lab technicians, and selected student workers. The Chem Lab manager and lab technicians will undertake the procedures outlined in the ICP-OES section of this protocol when conducting analyses on the PerkinElmer Optima 5300 DV.

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

### **3.0 DATA QUALITY OBJECTIVES**

This SOP addresses the following objectives in the data quality objectives outlined in the "Geological and Hydrological Characterization work plan at the Molycorp Questa Mine, Taos County, New Mexico":

1. To provide principle investigator (PI) researchers with quality analytical laboratory data that have been verified and validated.
2. To provide PI researchers with analytical data that have appropriate detection limits and that have been conducted in accordance with acceptable procedures.
3. To provide PI researchers with confidence that the data have been generated and transferred to the centralized database utilizing the procedures outlined in the project SOPs.

### **4.0 RELATED STANDARD OPERATING PROCEDURES**

The procedures for providing analyses by ICP-OES set forth in this SOP are intended for use with the following SOPs:

- SOP 1 Data management (including verification and validation)
- SOP 2 Sample management (including chain of custody)
- SOP 5 Sampling outcrops, rock piles, and drill core (solids)
- SOP 8 Sample preparation (solids)
- SOP 15 Surface water and seep sampling
- SOP 16 Ground-water sampling
- SOP 22 Analytical data validation
- SOP 31 ICP-MS analysis
- SOP 36 Sample preservation, storage, shipping and custody
- SOP 68 Water analyses
- SOP 78 Humidity cell testing

- SOP 79 Humidity cell sample preparation

## 5.0 EQUIPMENT LIST

The following materials and equipment are needed for sample preparation and analysis by ICP-OES:

### 5.1 Preservation of water samples:

- Dropper bottle filled with concentrated, ultra-high-purity nitric acid ( $\text{HNO}_3$ ) to be added by laboratory personnel 16 hours prior to performing the sample analysis.

### 5.2 Briggs four-acid digestion for solid samples (hereafter referred to as the Briggs method)

- Environmental Express 36-well HotBlock™ SC100
- Two 18-place polycarbonate racks for HotBlock
- 36 60-mL Teflon HotBlock vessels with caps
- Digital plastic coated temperature probe
- perchloric acid ( $\text{HClO}_4$ ) fume hood
- Milestone Duopur acid distillation unit
- Milestone TraceClean acid washer
- Ohaus Voyager balance accurate to four decimal places
- Stainless steel laboratory scoops
- Trace-element grade  $\text{HNO}_3$ ,  $\text{HClO}_4$ , hydrofluoric acid (HF) and hydrochloric acid (HCl)
- Water purified to 18.2 MOhm by reverse osmosis, hereafter referred to as RO water
- Safety gear (Safety goggles, lab coat, etc.)
- Whatman ashless filters (grade 40)
- Polypropylene funnels
- Funnel holders
- 50-mL graduated centrifuge tubes
- 14-mL graduated centrifuge tubes
- 60-place plastic centrifuge tube rack
- National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 2780 (Appendix 2), *Hard Rock Mine Waste*
- Molycorp Capulin sample 104, to be treated as an ongoing laboratory control sample
- Standard solutions for matrix spikes
- Laboratory notebook and indelible pens

### 5.3 Analysis for metals and other cations

- PerkinElmer ICP-OES Optima 5300 DV
  - Computer-controlled emission spectrometer with background correction
  - Echelle grating optical system
  - Radial and axial viewing capability

- Radio-frequency generator compliant with FCC regulations
- High purity argon gas
- Volumetric flasks and pipettes
- Ultrapure HNO<sub>3</sub> and HCl
- RO water
- Single element standard solutions, mixed calibration standards, calibration blank (for establishing calibration curve), method blank (used to identify contamination from sample preparation), initial calibration verification, continuous calibration verification, internal standard (scandium), interference check solution, and spiking standards

## **6.0 PROCEDURES**

Analysis by ICP-OES will follow US EPA Method 6010b – Inductively Coupled Plasma-Atomic Emission Spectrometry. Sample digestion will follow Briggs method. Any deviations from these methods will be noted in this SOP.

### **6.1 Sample preservation and preparation**

Sample collection, preservation, and preparation techniques are critical for successful analysis on any laboratory instrument. For this reason, criteria in SOPs 5, 8, 15, 16, 36, 78, and 79 must be accurately followed and documented during sample preservation and preparation.

#### **6.1.1 Preparation of water samples**

Water samples must be filtered to less than 0.45 um and preserved in the field by cooling to less than 4 degrees C within four hours of sampling. Lab personnel will acidify water samples to a pH less than 2 with ultrapure HNO<sub>3</sub> 16 hours before ICP-OES analysis (USEPA Method 200.7). Acid preservation is not necessary in the field. Acid preservation will be done in the laboratory as described above. Water samples will be analyzed initially without dilutions. If concentrations are found to be above the highest calibration standards, subsequent dilutions will be required and appropriately documented.

Preparation of samples from humidity cells need alternative and additional handling that is detailed in SOPs 78 and 79.

### 6.1.2 Preparation of solid samples

Solid samples will be digested by HotBlock following the Briggs digestion method, a four-acid method requiring HCl, HClO<sub>4</sub>, HNO<sub>3</sub> and HF. The procedure takes approximately two days and must be completed under a perchloric-acid fume hood. Details of each digestion will be recorded in a laboratory notebook designated for Molycorp digestions.

Prior to digestion, solid samples must be ground to a powder following SOP 8. Samples are then dried overnight at 110 degrees C, and 0.200 g of sample is weighed into a Teflon HotBlock vessel. The sample names and weights are recorded in the laboratory notebook.

The sides of the sample vessels are rinsed down with RO before adding reagents. The initial reagent mixture is 3 mL HCl, 2 mL HNO<sub>3</sub>, 1 mL HClO<sub>4</sub>, and 2 mL HF. The sample mixtures are heated on the HotBlock at 110 degrees C under an HClO<sub>4</sub> fume hood until the solution is dried completely. The samples are then removed from the heat until they are cool to touch. Another milliliter of HClO<sub>4</sub> and 2 mL of RO water are added to each sample, and the solution is evaporated to dryness at 160 degrees C. The samples are cooled again, then 1 mL of aqua regia (3 parts HCl to 1 part HNO<sub>3</sub>) is added to each sample and allowed to react for 15 minutes. A solution of 9 mL 1% HNO<sub>3</sub> is added to each sample, the vessel is capped, and the vessel is heated in a drying oven for 1 hour at 95 degrees C. The solution is cooled again. If there is no evidence of remaining solids, the samples are rinsed into 50-mL graduated centrifuge tubes and brought to volume. These tubes will also serve as the permanent storage containers for the samples.

Digested samples are then diluted at least 1:5 for ICP-OES analysis and at least 1:20 for ICP-MS analysis. Subsequent dilutions may be required if analyte concentrations are above the instrument's linear range.

## 6.2 ICP-OES Procedures

Prior to sample analysis, interference corrections will be established and an initial instrument performance demonstration must be documented and kept on file. This laboratory document will include instrument detection limits (IDLs), method detection limits (MDLs), and the linear dynamic range of the instrument. A list of MDLs are included in Table 1, Appendix 1. These tasks are detailed in Method 6010b, but a review is provided in the quality control section of this SOP. QA/QC procedures are conducted in accordance with SOP 22 Analytical Data Validation.

The following solutions must be prepared prior to analysis:

- A sample probe rinse solution of 1% ultrapure HNO<sub>3</sub>
- An internal standard solution of 10 ppm Sc in 1% ultrapure HNO<sub>3</sub>
- A calibration blank and calibration standards for a three-point calibration
- A calibration check blank solution

- Calibration verification solutions made from stock solutions independent of the calibration standard stock solutions
- An interference check solution, when necessary (see quality control section)
- Water samples preserved with 1% ultrapure HNO<sub>3</sub> can be analyzed directly unless earlier analyses suggest dilutions are necessary. Solid samples digested by Briggs method must be diluted at least 1:5 with RO water.

All samples will be analyzed with a Scotts spray chamber and a gem cone nebulizer.

## 7.0 MAINTENANCE

Maintenance is completed on daily and periodic levels. Although occasional users of the ICP-OES will only conduct daily maintenance, they must be aware of how recently periodic maintenance tasks have been conducted.

Immediately after installation of the ICP-OES, the wavelengths were aligned by a PerkinElmer technician. This maintenance item will be repeated by a PerkinElmer technician whenever the spectrometer is serviced.

Periodic maintenance includes an argon purge after the argon tank has been disconnected from the spectrometer. When running the instrument for the first time after the argon tank has been reconnected, an argon purge is necessary and the spectrometer must be warmed up for 70 minutes. After this warm-up, turn on the pump to flush the lines. If a month has passed since last firing the torch, purge the plasma, auxiliary and nebulizer gas lines before lighting the plasma. If the last firing occurred within the last month, the gas lines will be purged automatically when the plasma is turned on.

Several other periodic tasks are required after lighting the torch; however, the plasma must be allowed to equilibrate for about 30 to 60 minutes before proceeding with these tasks. The nebulizer flow and plasma power must be optimized every month, especially when high salt solutions are analyzed on a regular basis, and whenever maintenance on the sample introduction section has been conducted. A solution of As (5 ppm), Mn (1 ppm), Sc (0.1 ppm), K (5 ppm), and Ba (0.1 ppm) is pumped through the torch during optimization. Optimization involves the adjustment of the plasma power between 1300 and 1400 W while observing the element's signal strength in the continuous graphics window. Each of these five elements will react differently to the power adjustments. The power that provides the best signal for all five elements must be established and that wattage used during analysis. Next, adjust the nebulizer flow incrementally between 0.90 and 0.60 L/min for radial and axial plasmas, in that order. After observing each element's change in intensity, the best flow will be established and used for the analyses.

Once a month or after torch maintenance, the plasma view must be realigned. The torch is first aligned in the radial view while pumping a 10 ppm solution of Mn. The "align-view" command is given from the spectrometer control window. Record the alignment settings and peak intensity upon completion of the alignment. Repeat this procedure for the axial view while pumping a 1 ppm solution of Mn.

All pump tubing must be changed on a weekly basis.

The Background Equivalent Concentration must be checked daily.

The mercury lamp must be realigned daily. Pump a solution of 1% ultrapure  $\text{HNO}_3$  through the sample introduction system and give the “Hg realign” command from the spectrometer control window. The final intensity, which must be at least 7 million counts per second, must be recorded upon completion of the realignment.

## **8.0 LABORATORY SAFETY**

Several safety aspects must be observed by all laboratory personnel: the proper and safe handling of acids, especially perchloric acid and hydrofluoric acid, and all other general safe laboratory practices detailed in New Mexico Tech’s Laboratory Safety Manual. Hydrofluoric acid and perchloric acid are among the most dangerous chemicals used in the Chem Lab. Special precautions must be taken during their use. The most important and basic of these precautions are posted in the vicinity of the perchloric acid fume hood, which will be used for all HotBlock procedures. Basic first aid (instruction posted near fume hood) should be administered if any personnel become exposed to these acids through skin contact, eye contact, inhalation, or ingestion.

## **9.0 QUALITY ASSURANCE/QUALITY CONTROL**

The analyst must make an initial demonstration of the ability to generate acceptable accuracy and precision following EPA Method 6010b. This demonstration will result in the documentation of detection limits, initial precision and recovery, linear dynamic range for each wavelength used, and the first analysis of an ongoing laboratory control sample with a reference sample.

In addition, quality control samples will be analyzed including:

- samples used to evaluate solid sample preparation methods.
- samples to evaluate analytical precision.

### **9.1 Interference corrections**

Two techniques will be employed to correct interferences on the PerkinElmer Optima 5300 DV. The first is a multi-component spectral fitting (MSF) file. To develop this file, a single element standard of each element of interest is diluted with 1% ultrapure  $\text{HNO}_3$  and analyzed on the instrument. After the run, the peaks and baselines are reset, the blanks are identified as global blanks, any interfering elements are identified for



subsequent subtraction, and the elements of interest are identified as analytes. These corrections are tested with interferent-check standards for five consecutive days to within 20 percent of the target concentration. These checks must be completed every six months (EPA Method 6010B). After this file has been tested sufficiently, an inter-element correction (IEC) file may be developed. An interference check solution will be run every six months.

The second interference correction test used is a dilution test and post-digestion spike described in Method 6010B. This test will be performed periodically to check for matrix interferences:

1. When completing initial analyses of the Molycorp laboratory control sample and NIST SRM 2780 (Appendix 1).
2. When completing the first analyses of Questa samples.
3. When analyzing an unusual sample.

## **9.2 Detection limits**

Instrument detection limits (IDLs) and method detection limits (MDLs) will be calculated for the ICP-OES following the USEPA SW-846 manual, Chapter 1, and USEPA Method 6010b and kept as in-house documentation. Only the MDLs will be reported in an updated draft of SOP 30.

The IDL is estimated by taking the average standard deviations of three runs of seven blank measurements each on three nonconsecutive days. An IDL analysis will be conducted annually.

MDLs will be calculated for all elements from standards that are 3 to 5 times the expected MDLs. Calculations of this parameter will follow US-EPA Manual SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods Chapter 1. Subsequent sample concentrations below the reported MDL will not be reported as data points, but as less-than values. New MDLs will be determined annually.

### **9.3.1 Internal standard**

Scandium is the internal standard being used on this instrument. If the intensity of the internal standard falls below 30 percent for a particular sample, a matrix effect must be suspected. To correct the problem, first recalibrate the instrument and reanalyze the sample to be sure the problem was not the result of instrument drift. If the problem has

still not been corrected, dilute the sample 1:5 and reanalyze, repeating analysis with increasing dilutions until the internal standard is within 30 percent of the blank intensity.

#### 9.4 Quality control samples

Reagent blanks, sample duplicates, matrix spikes, and NIST standards will be prepared at the digestion level for solids. For each HotBlock batch, one reagent blank will be prepared per every 10 samples and one duplicate and one NIST standard will be prepared per every 20 samples. The Molycorp ongoing control sample will be analyzed once a month to monitor sample precision throughout the project. Sample spikes will be prepared before any Molycorp samples are analyzed and whenever a particular sample does not digest easily or produces unusual data. The following guidelines should be met for these quality control solutions:

- Reagent blanks should be less than the method detection limit.
- The relative percent difference of duplicates and standards should be within 15 percent.
- The percent recovery of matrix spikes should be within 25 percent.

Reagent blanks, sample duplicates and matrix spikes will be prepared for the analysis of water samples and should meet the guidelines listed above.

ICP-OES runs will include an initial calibration verification solution and a blank solution at the beginning and end of every run. A calibration verification solution will be analyzed after every 10 samples throughout the run. The verification measurements must be within 10 percent of the expected value. If they are not, the problem should be corrected before continuing with analyses.

During the analysis, every element will be analyzed in triplicate for every sample and used by the instrument to calculate relative standard deviation (RSD) automatically. Analyses above the method detection limit with a RSD greater than 5 % should be discontinued and the problem corrected before continuing with the analyses.

From these quality control samples, the following parameters can be calculated to evaluate precision and accuracy within the parameters listed above:

1) Relative percent difference (RPD) =  $100 * [(A-B)/((A+B)/2)]$ , where A = measured concentration of a sample and B = measured concentration of sample replicate.

2) Percent recovery (%R) of spiked samples =  $100 * (x_s - x_u) / K$ , where  $x_s$  = measured concentration of the spiked sample,  $x_u$  = measured concentration of the unspiked sample, and  $K$  = known concentration of spike.

3) Percent recovery (%R) for standard reference materials =  $100 * (x) / K$ , where  $x$  = measured concentration of the NIST standard or ICV, and  $K$  = known concentration of NIST standard or ICV.

4) Standard deviation – calculated from the NIST standard in the case of solid analysis and calculated from the ICV in the case of water samples.

### 9.5 Ion balance for water samples

Major and minor cations analyzed by ICP-OES and ICP-MS (SOP 31) will be used in conjunction with anions analyzed by IC (SOP 68) to calculate ion balance as described in SOP 22. The ion balance calculations will be performed within the database. An ion balance report will be provided to the lab manager, project manager and auditor.

## 10.0 DOCUMENTATION

- Documentation to track samples through the laboratory will be as follows:
- Upon sample delivery to the Chem Lab, a chain of custody form will be signed by the person delivering the samples and by the person receiving the samples. In addition to the samples and the chain of custody form, a copy of the conductivity, pH, and alkalinity field data will be delivered to the lab.
- Samples will be logged in to the Chem Lab's log book detailing the date received, Molycorp sample ID, lab ID and required analyses.
- The lab ID will be written on sample bottles and bags with black Sharpie (indelible pen).
- Throughout the digestion process, the lab ID for solid samples will be transferred to the Prep Lab notebook, to the bottles containing the digested sample, and to the bottles containing the diluted sample.
- The sample ID and lab ID will be entered into the sample introduction file on the ICP-OES software before analysis begins.
- The numeric results of the analyses are reported to three significant figures.

- After analysis, an electronic version of the data will be transferred to the Molycorp Project database.
- In addition, an analysis report detailing the samples transferred and the quality of the analyses will automatically be sent to the project manager, the Chem Lab manager and the project auditor.
- Any unused solid sample material will be returned to the sampler with the proper chain of custody forms filled out and signed.
- Water samples and sample digestate will be stored in the Chem Lab for a period of 12 months after digestion. After that period, they will be disposed of following the protocols of the New Mexico Tech safety office.

## 11.0 FORMS

Forms are not applicable to this SOP as the data is output by the machinery in the form of Excel spreadsheets that are directly entered into the Molycorp Database.

## 12.0 DATA ANALYSIS AND VERIFICATION

In addition to the checks conducted by the analyst during and after an ICP-OES run to assure proper calibration and instrument stability, an automated analysis report will be generated during the data transfer to the project database. This report will be sent automatically by email to the lab manager, project manager and auditor. A filter will be set up to flag and hold any analyses that do not meet project specifications so the sample can be reanalyzed, if necessary. The report will include failures of the calibration checks, blanks, duplicates, and standard reference materials, as well as failures of relative percent difference, percent recovery, and relative standard deviations.

Data provided to the customer will include a data quality report documenting that all accepted data has met the quality protocols detailed in this SOP. All NIST standard and ICV data will be entered into the Molycorp Project database as samples and will be used to generate standard errors on solid and water data tables. Standard deviation errors will be included with all data reports.

The database technician will be responsible for verifying that the data has transferred to the database correctly.

## 13.0 REFERENCES

U.S. Environmental Protection Agency, 1996, Inductively Coupled Plasma-Atomic Emission Spectrometry, Method 6010B, Revision 2.0, SW-846 Manual, 3<sup>rd</sup> edition, Office of Solid Waste and Emergency Response.

Briggs, P.H., (2001 version) The Determination of Forty Elements in Geological and Botanical Samples by Inductively Coupled Plasma-Atomic Emission Spectrometry, U.S. Geological Survey Open File Report 02-223-G, Analytical Methods for Chemical Analysis of Geologic and Other Materials, U.S. Geological Survey.

U.S. Environmental Protection Agency, 1987, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 Manual, 3<sup>rd</sup> edition, Office of Solid Waste and Emergency Response.

U.S. Environmental Protection Agency, 2001, Trace Elements in Water, Solids, and Biosolids by Inductively Coupled Plasma-Atomic Emission Spectrometry, Method 200.7, EPA-821-R-01-010, Revision 5.0.

Certificate of Analysis, Standard Reference Material 2780, Hard Rock Mine Waste, National Institute of Standards & Technology, January 31, 2003.

Boss, C.B., Fredeen, K.J., Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry, PerkinElmer, 2004.

New Mexico Tech Safety Manual.

**APPENDIX 1. Table 1**

**Table 1.** Analytes and their associated wavelengths, detection limits (ppm), linear dynamic ranges (ppm) and plasma viewing positions on the PerkinElmer Optima 5300 DV.

Analyte	Wavelength (nm)	Method detection limits (water)	Method detection limits (solids)	Linear dynamic range	Plasma viewing position
Ag	328.068	0.003	5.36	50	Axial
Al	396.153	0.008	4787	1000	Radial
As	188.979	0.006	25.1	100	Axial
Ba	455.403	0.0004	73.4	10	Radial
Be	313.107	0.0006	0.163	100	Radial
Ca	317.933	0.020	108	3000	Radial
Cd	214.440	0.0005	1.50	50	Axial
Co	228.616	0.0005	1.15	50	Axial
Cr	205.560	0.001	6.68	100	Axial
Cu	324.752	0.008	11.9	50	Axial
Fe	238.204	0.022	1984	1000	Radial
Ga	294.364	0.003	2.94	1000	Axial
K	766.490	0.048	1762	3000	Radial
Mg	279.553	0.013	370	100	Radial
Mn	257.610	0.002	35.3	500	Radial
Na	589.592	0.054	105	100	Radial
Ni	231.604	0.001	4.18	500	Axial
P	177.434	0.056	112	1000	Axial
P	213.617	0.037	66.6	1000	Axial
Pb	220.353	0.002	467	1000	Axial
S	180.669	0.012	904	1000	Axial
S	181.975	0.019	888	1000	Axial
Sb	206.836	0.004	9.81	100	Axial
Se	196.026	0.010	8.95	100	Axial
Si	212.412	0.014	NA		Axial
Si	251.611	0.014	NA		Axial
Sr	421.552	0.0007	18.3	10	Radial
Th	401.913	0.0014	2.07	10	Axial
Ti	334.940	0.0003	654	100	Axial
V	292.402	0.0002	20.7	500	Axial
W	239.708	0.0026	14.4	10	Axial
Zn	202.548	0.0009	91.9	100	Axial
Zn	213.857	0.0017		100	Axial
Ar	420.069	plasma gas	plasma gas		Radial
Sc	361.383	internal standard	internal standard		Axial
Sc	361.383	internal standard	internal standard		Radial

**APPENDIX 2. Certificate of analysis, NIST Standard Reference Material 2780**

# National Institute of Standards & Technology

## Certificate of Analysis

### Standard Reference Material 2780

#### Hard Rock Mine Waste

This Standard Reference Material (SRM) is intended for use in the evaluation of methods and for the calibration of apparatus used to determine heavy metals and other elements in hard rock mine waste and materials of a similar matrix. SRM 2780 is composed of material collected from a waste pile of an abandoned mine site near Silverton, CO. A unit consists of approximately 50 g of material of which 90 % passes a 150  $\mu\text{m}$  (No. 100) sieve.

**Certified Values and Uncertainties:** Certified mass fraction values for 12 elements are listed in Table 1. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST. All values are reported as mass fractions [1], on a dry mass basis (see *Instructions for Drying*), and are based on measurements using a sample mass of at least 250 mg.

**Reference Values and Uncertainties:** Reference mass fraction values for seven elements are given in Table 2. Reference values are noncertified values that are the best estimate of the true value; however, the values **DO NOT** meet the NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty. Mass fraction values are on a dry mass basis.

**Information Values:** Information mass fraction values for 28 elements are provided in Table 3. An information value is considered to be a value that will be of interest and use to the SRM user, but insufficient information is available to assess the uncertainty associated with the value.

**Expiration of Certification:** The certification of this SRM lot is valid within the measurement uncertainties specified until **31 December 2012**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see *Instruction for Use* section). However, the certification will be nullified if the SRM is contaminated or modified.

**Stability:** This material is considered to be stable. NIST will monitor this material and will report any substantive changes in certification to the purchaser. Return of the attached registration card will facilitate notification.

The overall direction and coordination of the technical measurements leading to the certification of this SRM were performed by G.C. Turk of the NIST Analytical Chemistry Division.

Analytical measurements from NIST were performed by C.M. Beck II, W.R. Kelly, S.E. Long, J.L. Mann, A.F. Marlow, J.R. Sieber, R.D. Vocke, Jr., and L.L. Yu of the Analytical Chemistry Division.

Statistical consultation was provided by S.D. Leigh and D.D. Leber of the NIST Statistical Engineering Division.

Mine waste sample collection, preparation of the SRM, and contributing chemical analyses were performed by the U.S. Geological Survey (USGS) under the direction of S.A. Wilson. Details are described [4] in USGS Open-File Report 99-370, which is available from USGS Information Services, Box 25286, Federal Center, Denver, CO 80225 (telephone: (303) 202-4210; e-mail: [infoservices@usgs.gov](mailto:infoservices@usgs.gov)).

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by B.S. MacDonald.

Willie E. May, Chief  
Analytical Chemistry Division

Gaithersburg, MD 20899 John Rumble, Jr., Chief

Certificate Issue Date: 31 January 2003 Measurement Services Division

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Partial financial support for the development of this SRM was provided by the U.S. Environmental Protection Agency (EPA) under the direction of project manager B.A. Schumacher of the EPA National Exposure Research Laboratory, Characterization Research Division, Las Vegas, NV.

#### INSTRUCTIONS FOR USE

To relate analytical determinations to the certified values on this certificate, a minimum sample mass of 250 mg should be used. Sampling and sample preparation procedures should be designed to avoid material segregation on the basis of particle size. It is recommended to mix the contents of the bottle prior to sampling by turning the bottle end over end for two minutes. The sample should be dried according to the Instructions for Drying. If particle size reduction is performed, it is the user's responsibility to prevent contamination or loss of material. This SRM must be stored in an air-conditioned or similar cool and dry environment away from light and fumes.

Instructions for Drying: Analyses should be performed on samples as received; separate samples should be weighed before and after drying to obtain a correction factor for moisture. Samples may be dried in an oven at 107 °C under clean, dry inert gas, or in a dessicator over fresh anhydrous  $\text{Mg}(\text{ClO}_4)_2$ , or by other equivalent method which reaches a constant dry weight.

#### Table 1. Certified Mass Fractions

Element Mass Fraction k (%)

Aluminum	$8.87 \pm 0.33$	2.3
Calcium	$0.195 \pm 0.020$	2.6
Iron	$2.784 \pm 0.080$	2.4
Lead	$0.577 \pm 0.041$	2.4



Magnesium  $0.533 \pm 0.020$  2.8Potassium  $3.38 \pm 0.26$  2.8Sodium  $0.221 \pm 0.018$  2.8Sulfur  $1.263 \pm 0.042$  2.6Zinc  $0.257 \pm 0.016$  2.6

## Element Mass Fraction k (mg/kg)

Arsenic  $48.8 \pm 3.3$  2.0Cadmium  $12.10 \pm 0.24$  2.8Mercury  $0.710 \pm 0.042$  2.6

The certified values for mercury and sulfur are the means of results obtained by NIST using isotope dilution mass spectrometry (IDMS). The expanded uncertainty is calculated as  $U = ku_c$ , where  $u_c$  is intended to represent, at the level of one standard deviation, the combined standard uncertainty calculated according to the ISO Guide [2]. The coverage factor,  $k$ , is determined from the Student's  $t$ -distribution for the appropriate degrees of freedom to yield 95 % confidence. The certified values and uncertainties for the remaining elements are derived from the results of at least one analysis performed at NIST and independent results from one or more methods provided by the U.S. Geological Survey (USGS) using the approach described by Levenson et al. [3] for combining results for multiple methods. Multiple method results from USGS were first combined to give a single value and uncertainty before being combined with the NIST results. The certified value is an unweighted mean of the results from NIST and USGS. The uncertainty listed with each value is an expanded uncertainty about the mean,  $U = ku_c$ , with a coverage factor,  $k$ , determined from the Student's  $t$ -distribution for the appropriate degrees of freedom to yield 95 % confidence. Each  $u_c$  is calculated by combining a between-method variance [3] with a pooled, within-method variance following the ISO/NIST Guide [2]. Analytical methods are listed in Table 4.

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**Table 2. Reference Mass Fractions**

## Element Mass Fraction k (%)

Titanium  $0.699 \pm 0.019$  2.8

## Element Mass Fraction k (mg/kg)

Barium  $993 \pm 71$  2.1Copper  $215.5 \pm 7.8$  2.4Manganese  $462 \pm 21$  2.6Phosphorus  $427 \pm 40$  2.3Strontium  $217 \pm 18$  2.2Vanadium  $268 \pm 13$  2.4

The reference values are based on the results of a single NIST method and one or more USGS methods. Reference values and uncertainties were derived from multiple results in the same manner as was done for the certified values and uncertainties. Analytical methods are listed in Table 4.

**Table 3. Information Mass Fractions**

Element Mass Fraction (%)

Silicon 31

Element Mass Fraction (mg/kg)

Antimony 160	Niobium 18
Cerium 64	Rubidium 175
Cesium 13	Scandium 23
Chromium 44	Selenium 5
Cobalt 2.2	Silver 27
Gallium 26	Tellurium 5
Gold 0.18	Terbium 0.58
Hafnium 4.4	Thallium 5
Holmium 0.84	Thorium 12
Lanthanum 38	Thulium 0.4
Lithium 18	Tungsten 24
Molybdenum 11	Uranium 4
Neodymium 28	Zirconium 176
Nickel 12	

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**Table 4. Methods Used in Elemental Determinations**

Method Elements Determined

Cold Vapor Isotope Dilution Inductively Hg  
 Coupled Plasma Mass Spectrometry (CV-ID-ICP-MS) at NIST  
 Isotope Dilution Thermal Ionization Mass Spectrometry (ID-TIMS) at NIST S  
 Standard Additions Inductively Coupled Plasma As, Cd, Cu, Pb, Zn  
 Mass Spectrometry (ICP-MS) at NIST  
 Wavelength Dispersive X-ray Fluorescence Al, As, Ba, Ca, Fe, K, Mg, Mn,  
 Spectrometry (WDXRF) at NIST Na, P, Pb, Sr, Ti, V, Zn, Zr  
 Wavelength Dispersive X-ray Fluorescence Al, Ca, Fe, K, Mg, Ti  
 Spectrometry (WDXRF) at USGS  
 Inductively Coupled Plasma Atomic Emission Al, Ba, Ca, Cd, Cu, Fe, K, Mg,  
 Spectrometry (ICP-AES) at USGS Mn, Na, P, Pb, Sr, V, Zn  
 Instrumental Neutron Activation Analysis (INAA) at USGS As, Ba, Cd, Fe, Na, Zn  
 Hydride Generation Atomic Absorption Spectrometry (HGAAS) at USGS As

## REFERENCES

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- [3] Levenson, M.S.; Banks, D.L.; Eberhardt, K.R.; Gill, L.M.; Guthrie, W.F.; Liu, H.K.; Vangel, M.G.; Yen, J.H.; Zhang, N.F.; An Approach to Combining Results from Multiple Methods Motivated by the ISO GUM; Res. Natl. Inst. Stand. Technol. 105, pp. 571-579 (2000).
- [4] Wilson, S.A.; Briggs, P.H.; Brown, Z.A.; Taggart, J.E.; Knight, R.; Collection, Preparation and Testing of NIST Hard Rock Mine Waste Reference Material SRM 2780; SGS Open-File Report 99-370, U.S. Geological Survey, Denver, CO (1999).  
Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail [srminfo@nist.gov](mailto:srminfo@nist.gov); or via the Internet <http://www.nist.gov/srm>.