



September 9, 2021

Joni Sandoval
EPA On-Scene Coordinator
U.S. Environmental Protection Agency Region 8
1595 Wynkoop St.
Denver, Colorado 80202

Subject: **Sampling, Monitoring, and Analysis Plan for Fluvial San Miguel Removal
Assessment Support, Telluride, Colorado
U.S. EPA Region 8 START 5, Contract No. 68HE0820D0001
Task Order No. 68HE0820F0071
Technical Direction No. 2071-2106-09
Document Tracking No. 0462a**

Dear Joni:

As required by Technical Direction Form No. 2071-2106-09, Tetra Tech, Inc. is submitting the attached Sampling, Monitoring, and Analysis Plan for activities at the Fluvial San Miguel Site in Telluride, San Miguel County, Colorado. If you have any questions or comments, please contact the START Project Manager at 720-999-8519.

Sincerely,

Billy Bol
START Technical Direction Manager

Enclosures

cc: Joyce Ackerman, START Contracting Officer's Representative (cover letter only)
 Kevin Scott, Rob Tisdale, Clayton Longest, TD file

SAMPLING, MONITORING, AND ANALYSIS PLAN

**REMOVAL ASSESSMENT SUPPORT
AT THE FLUVIAL SAN MIGUEL SITE
TELLURIDE, SAN MIGUEL COUNTY, COLORADO**

**Region 8 Superfund Technical Assessment and Response Team (START) 5
Contract No. 68HE0820D0001, Task Order 68HE0820F0071, Technical Direction 2071-2106-09
Document Tracking Number (DTN): 0462a**

Prepared For:

U.S. Environmental Protection Agency
Region 8
Superfund Division
1595 Wynkoop Street
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September 9, 2021

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ATTACHMENT 4 NIST CERTIFICATE OF ANALYSIS,
STANDARD REFERENCE MATERIAL 2710A

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STANDARD REFERENCE MATERIAL 2711A

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) Region 8 Superfund Division tasked the Tetra Tech, Inc. (Tetra Tech) Superfund Technical Assessment and Response Team (START), under contract number 68HE0820D0001, Task Order Number 68HE0820F0071, Technical Direction number 2071-2106-09, to assist with removal assessment activities at the Fluvial San Miguel Site in Telluride, San Miguel, County, Colorado.

The Site consists of five tailings piles on the bank of the San Miguel River, approximately 3 miles west of Telluride, Colorado. The tailings piles have accumulated from runoff from a former mill approximately 5.5 miles east of the Site.

Removal assessment tasks for START include collecting soil samples from the tailings piles, collecting global positioning system (GPS) coordinates from the perimeter of the tailings piles, data management, and documentation of Site activities. This site-specific Sampling, Monitoring, and Analysis Plan (SMAP) identifies site-specific features and addresses elements of the sampling strategy and analytical methods proposed for the investigation. Billy Bol is the START Technical Direction Manager (TDM) for this activity, and Joni Sandoval is the EPA On-Scene Coordinator (OSC).

SITE BACKGROUND INFORMATION

This section discusses the information regarding the Site's location, description, and operational and investigative history.

Site Location/Description

The Site is approximately 3 miles west of Telluride, Colorado (Figure 1), in a semi-developed commercial area along the San Miguel River. The Site includes five tailings piles on the bank of the river. The Site is adjacent to a public road that is accessed by recreational users daily. The approximate coordinates, acreage, and elevation of the Site are identified in Table 1.

TABLE 1
SITE LOCATION

Site	Latitude	Longitude	Acreage	Elevation (feet above mean sea level)
Fluvial San Miguel	37.947422	-107.876149	3	8,645

Site Operational and Investigative History

The Site was referred to the EPA by the U.S. Forest Service (USFS) in the fall of 2020, after sampling conducted by the USFS and the responsible party found mine tailings on the Site contained high levels of lead and arsenic (EPA 2021).

Actions completed as part of the emergency response include:

- Installation of erosion controls to mitigate runoff from the excavation and stockpile operations.
- Removal of approximately 3,000 cubic yards of tailings and stabilization/reinforcement of the riverbank area.
- Installation of low water crossing for moving equipment and material.
- Stabilization of a hiking/biking area by placing a thin cap of gravel over the tailings.
- Placement of barriers around the contaminated areas pending mitigation of cleanup.
- Transportation of excavated material to a state-designated, responsible party-owned on-site repository

Metal contaminants associated with the tailings are a potential source of harmful exposure to human health and the environment. Lead and arsenic are considered contaminants of concern (COC) at the fluvial San Miguel Site. The COCs must be addressed by a cleanup action because they are a potential threat to human health or the environment (EPA 2021).

SAMPLING STRATEGY AND METHODOLOGY

START will collect 10 soil samples (one of which will be duplicated) from the five tailings piles on the bank of the San Miguel River. Using a hand auger, START will collect five aliquots from depths of 0-2 feet below ground surface (bgs) and a second group of five aliquots from 2-4 feet bgs. The aliquots will be from random locations on each tailings pile. A composite sample from each layer will be homogenized in a stainless-steel mixing bowl, then placed in an appropriate sample container. Figure 2 indicates the proposed sample locations.

Sample nomenclature will be based on an identifier established by START for each tailings pile. Additional sample information such as date, time, and location will be recorded on electronic sample collection forms (Tetra Tech SOP 024-3). The samples will be prepared and analyzed in the EPA Region 8 warehouse laboratory using X-ray fluorescence (XRF) technology following Superfund Guidance Document

SFDGUID-001-R0. To confirm the accuracy of the XRF results, ten percent of samples will be delivered to and analyzed by a formal laboratory and analyzed for total metals using method SW-846 6010B.

Tetra Tech START will follow SOP and chain-of-custody procedures referenced in the SMAP throughout sampling activities to verify the sample's integrity from the time of collection until submittal to the laboratory.

XRF Screening

XRF screening will be used in conjunction with visual identification of the surface soil material to determine tailings locations. To determine the demarcation between tailings material and native soil, START will look for heterogenous differences in color and texture between the two materials. START will conduct in-situ XRF screenings at random locations in the suspected tailing piles area to determine if lead and arsenic are present in the soil. The results of the XRF screenings will help the field team confirm their proposed soil sampling locations are within the tailings piles footprint. START will operate a handheld Innov-X Omega XRF to analyze lead and arsenic concentrations in soil. XRF screening data will be verbally relayed by START to the EPA OSC. The OSC will determine if the sample location is within the tailing piles boundary. No XRF screening data will be recorded.

A summary of anticipated samples for this project is provided in Table A-1 of the attached site-specific addendum to the Quality Assurance Project Plan (QAPP) (Appendix A). Tetra Tech START will follow standard operating procedures (SOP) referenced in the SMAP throughout sampling activities to verify the integrity of the samples.

Blank samples, reference standards, and duplicates will be performed using the XRF in accordance with SFDGUID-001-R0, Superfund X-Ray Fluorescence Field Operations Guide (Attachments 2 through 5). Table 2 identifies the quality assurance/quality control (QA/QC) checks for the XRF device.

TABLE 2

X-RAY FLUORESCENCE QUALITY ASSURANCE AND QUALITY CONTROL CHECKS

QA/QC Check	Frequency	Standards Used	Comparison for Approval
Standard Check	At the beginning and end of the workday and every 5 hours of analysis time	NIST 2709a, 2710a, 2711a, Silica/Sand Blank	The mean of the 4 readings should be within 20% of the known value of the standard.
Duplicate Reading	Every 20 sample bags	Current sample	2 of 3 readings should be within 95% confidence limit based on reported instrument error

Notes:

%	Percent
NIST	National Institute of Standards and Technology
QA	Quality assurance
QC	Quality control

QUALITY CONTROL

Collection of field QC samples is required for this project. START will collect one duplicate sample every 10 samples. One duplicate sample is anticipated to be collected to ensure precise field collection methods. START will also collect one matrix spike/matrix spike duplicate (MS/MSD) sample for every 20 samples collected to ensure quality laboratory analytical procedures. START anticipates collecting one MS/MSD sample. START will also collect one equipment rinsate sample to assess the cleanliness of sampling equipment and the effectiveness of equipment decontamination (Tetra Tech 2020).

INVESTIGATION-DERIVED WASTES

Disposal of investigation-derived wastes (IDW) and equipment, and personal decontamination procedures will be addressed in a site-specific health and safety plan prepared by Tetra Tech START. IDW is expected to consist primarily of disposable sampling supplies (for example, gloves, and paper towels). Disposal of those materials will occur off-site as uncontaminated solid waste.

REFERENCES

- National Institute for Occupational Safety and Health (NIOSH). 2007. "NIOSH Pocket Guide to Chemical Hazards." <https://www.cdc.gov/niosh/docs/2005-149/pdfs/2005-149.pdf>.
- U.S. Environmental Protection Agency (EPA) Region 8. 2021. "Action Memorandum: Approval and Funding for a Removal Action at the Telluride Valley Floor Site, Telluride, San Miguel County, Colorado." <https://response.epa.gov/sites/14971/files/Telluride%20Valley%20Floor%20TC%20AM%20SIG%20NED.pdf>.

APPENDIX A

SITE-SPECIFIC ADDENDUM TO THE QAPP

(Eight Pages)

Region 8 Superfund Program
Addendum to the QAPP for Superfund Site Assessment and Response Team (updated October 2020)
for the Fluvial San Miguel Site

Project Information:	
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Site Name: Fluvial San Miguel			Location: Telluride	State: Colorado
U.S. Environmental Protection Agency (EPA) Project Manager: Joni Sandoval			Superfund Technical Assessment and Response Team (START) Project Manager: Billy Bol	
Prepared By:	Billy Bol		Prepared For: EPA Region 8 Superfund Division	
Title:	START SMAP Preparer	Date: 9/9/2021		
Approved By:	Heather Wood			
Title:	START QCC Reviewer	Date:		
Approved By:	Billy Bol			
Title:	START Project Manager	Date:		
Approved By:	Kevin Scott			
Title:	START Program Manager	Date:	Prepared By: Billy Bol Date: 9/9/2021	
Approved By:				
Title:	START Quality Assurance (QA) Manager	Date:		
Approved By:	Joni Sandoval			
Title:	EPA Project Manager	Date:	Tetra Tech START Project Number: 103X903520F0071210609	
Approved By:				
Title:	EPA Region 8 QA Manager	Date:		

Distribution List									
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EPA—Region 8:	Joni Sandoval, EPA OSC	Tetra Tech START:	Billy Bol, Technical Direction Manager Rob Tisdale, OA Manager
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Project/Task Organization

Joni Sandoval of the EPA Region 8 Superfund Division serves as the EPA OSC for the activities described in this SMAP. Billy Bol of Tetra Tech, Inc. (Tetra Tech) will serve as the START Project Manager.

1.0 Project Management:

1.1	Project Scope
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U.S. EPA in conjunction with USFS is conducting a joint Removal Action at the Telluride Valley Floor Site, which is in Telluride, CO. EPA is the lead Agency conducting the cleanup and has assigned Federal On-Scene Coordinator, Joni Sandoval, to oversee field activities. The Removal Action will be conducted in two phases. The first phase was an Emergency Response to stabilize eroding tailings in the San Miguel Riverdust and erosion control in an area containing mill tailings that is frequently trespassed by bikers and hikers. This area will be closed off by signage. The Emergency Response phase was conducted in November 2020. The second phase is the Time Critical Removal Action, which will be conducted in 2021 and is still in the planning phase. This second phase will be conducted to mitigate the remaining tailings that pose a threat to human health and the environment.

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for the Fluvial San Miguel Site

1.2 Objectives and Critical Decisions

No.	Incident Objective	Critical Decisions	Data Deliverables
1	Removal Assessment – Sample five tailings piles to be analyzed for total metals	<ul style="list-style-type: none"> Determine the presence or absence of metals in tailings piles. Determine extent/volume of contaminated material 	<ul style="list-style-type: none"> Survey 123 forms will be used to collect sample collection info to be posted on the response website, viewer, and Story Map. Analytical data package will be generated by the laboratory. Values will be verbally reported to EPA.
2	Removal Assessment – Collect GPS coordinates of the tailings piles	<ul style="list-style-type: none"> Delineate the tailings footprint. 	<ul style="list-style-type: none"> Survey 123 with GPS coordinates of tailing boundaries will be uploaded to Viewer and appropriate platforms.
3	Communication with stakeholders, including the community.	<ul style="list-style-type: none"> Provide updates to the public and stakeholders through a central website (response.epa.gov) in accordance with the Region 8 Response Playbook. <p>Updates will work progress, access to particulate monitoring data, photos, videos, sampling data, metrics on the number of truckloads/runs, and a map viewer.</p> <ul style="list-style-type: none"> Provide recurring public meetings and a process for accessing the meeting. 	<ul style="list-style-type: none"> Response.epa.gov will be used as a central website for sharing updates with the public and stakeholders. An Experience Builder Application, including a Story Map, a Real-Time Air Monitoring Charting Application, and a Contact Section will be embedded on the Site Profile section of the website. The Story Map will include the following sections: <ul style="list-style-type: none"> Overview – Description of what work will be completed on-site and the location of the Site. Background – Description of the site history, a site layout map, and other related content helping the reader understand why EPA is on-site. Operational Objectives – Description of current operational objectives. It is anticipated that the operational period will be on a weekly schedule, and this section will be updated accordingly. Current Activities – A summary of current activities completed during the operational period. This section will be updated for each operational period. Safety Issues – Description of safety issues/considerations during the operational period. This section will be updated for each operational period. Planned Activities – Description of activities expected to be completed during the next operational period. This section will be updated for each operational period. Timeline – Graphic depicting the project progression (updated each operational period). Map Viewer – Link to the public map viewer. More Information – Links to archived Story Maps and the EPA response website. Real-time Air Monitoring Charting Application – Interactive charting application for the public displaying real-time particulate monitoring (time-weighted average [TWA] of respirable particulates). Public Meeting RSVP Form – Online public form for RSVP'ing to the scheduled meetings. Public Meeting Posters/Maps – Content will be requested/provided to the Superfund Technical Assessment and Response Team (START) by EPA for printing prior to public meetings.

1.3 Problem Definition/Background:

Description: This site-specific SMAP and addendum to the QAPP for Superfund Site Assessment and Response Team Programs (updated October 2020) specifies site-specific data quality objectives for the sampling, monitoring, and analysis activities described herein.

☒ Description in the main body of this plan above.

☐ Description in referenced report: _____ Title _____ Date _____

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for the Fluvial San Miguel Site

1.4 Project/Task Description:

- ☒ Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)
☐ CERCLA Site Investigation (SI) ☐ Brownfields Assessment ☒ Removal Action
☐ Other (description attached): ☐ Pre-CERCLIS Site Screening ☒ Removal Site Evaluation

Other Description:

Schedule: Field activities are anticipated to be in September of 2021.

☐ Description in referenced report: _____
Title
Date

1.5 Quality Objectives and Criteria for Measurement Data:

- | | |
|------------------------|---|
| a. Accuracy: | <input checked="" type="checkbox"/> Identified in attached table. |
| b. Precision: | <input checked="" type="checkbox"/> Identified in attached table. |
| c. Representativeness: | <input checked="" type="checkbox"/> Identified in attached table. |
| d. Completeness*: | <input checked="" type="checkbox"/> Identified in attached table. |
| e. Comparability: | <input checked="" type="checkbox"/> Identified in attached table. |

Other Description:

*A completeness goal of 100 percent has been established for this project. However, if the completeness goal is not met, EPA may still be able to make site decisions based on any or all of the remaining validated data. Critical samples include air samples for arsenic and lead along highway 145 at the entrance of the Site, in town, and at the entrance of the repository to ensure there are no airborne tailings exceeding site-defined screening levels during transport.

1.6 Special Training/Certification Requirements:

- ☒ Occupational Safety and Health Administration (OSHA) 1910
☐ Special Equipment/Instrument Operator (describe below): _____
 ☒ Other (describe below): Lead Awareness Training

1.7 Documentation and Records:

- ☒ Field Sheets ☒ Site Log ☐ Trip Report ☒ Site Maps ☐ Video
☒ Chain of Custody ☒ Health and Safety Plan ☒ Letter Report ☒ Photos
- ☒ Sample documentation will follow Tetra Tech Standard Operating Procedure (SOP) 024-3 "Recording Notes in Field Logbooks" and be documented using site-specific Survey 123 forms.
☒ A copy of this QAPP and any future amendments will be available to all personnel throughout sampling and monitoring activities. EPA will maintain original documents.
☒ Other: Analytical information will be handled according to procedures identified in Table 2.

2.0 Measurement and Data Acquisition:

2.1 Sampling Process Design:

- | | | |
|--|---|---|
| <input type="checkbox"/> Random Sampling
<input checked="" type="checkbox"/> Stratified Random Sampling
<input type="checkbox"/> Systematic Random Sampling
<input checked="" type="checkbox"/> Screening w/ Definitive Confirmation
<input type="checkbox"/> Other (Provide rationale behind each sample): See Appendix A for additional sampling and monitoring information. | <input type="checkbox"/> Transect Sampling
<input type="checkbox"/> Search Sampling
<input type="checkbox"/> Definitive Sampling
<input type="checkbox"/> Incremental Sampling Methodology | <input checked="" type="checkbox"/> Biased/Judgmental Sampling
<input type="checkbox"/> Systematic Grid
<input type="checkbox"/> Screening w/o Definitive Confirmation
<input checked="" type="checkbox"/> Sample Map Attached |
|--|---|---|

Sample or Monitor Location Summary	Matrix	# of Samples or Monitoring instruments*	Sample Analysis or Parameter Monitored
Soil samples from tailings piles	Surface Soil	10	Lead and arsenic / Innov-X Omega XRF, and SW-846 6010B, SFDGUID-001-R0

* See Table A-1 for a complete sample summary.

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2.2 Sample Methods Requirements:

Matrix	Sampling Method	EPA SOP or other Method
Soil	Hand Auger	Tetra Tech SOP: 005, Revision 3, Soil Sampling

2.3 Sample Handling and Custody Requirements:

- ☐ Samples will be packaged and preserved in accordance with procedures described in Tetra Tech SOP 019-8 "Packaging and Shipping Samples." If shipment of samples by commercial service is required, each cooler lid will be securely taped shut, and two custody seals will be signed, dated, and placed across the lid opening. Samples will be submitted to the laboratory in a time-efficient manner to ensure no exceedances of applicable holding times. Chain of custody (COC) will be maintained as directed by the following SOP (as well as any additional contract requirements):
- ☐ EPA ERT SOP 2004. ☒ Tetra Tech SOP 019 (Revision 8), Packaging and Shipping Samples.
- ☐ The EPA Region 8 laboratory will accept samples according to Region 8 EPA SOPs.
- ☒ Other (Describe): Soil samples will be screened on-site using the Innov-X Omega XRF. Fully processed and prepared samples will be analyzed in the Region 8 EPA warehouse laboratory. Ten percent will be sent to a third-party laboratory for confirmation.

2.4 Analytical Methods Requirements:

- ☒ Identified in attached Table A-3.
- ☐ Rationale: The requested analyses have been selected based on historical information about the site and program experience with similar sites.
- ☐ Other (Describe):

2.5 Quality Control Requirements

- ☐ Not Applicable
- ☐ Identified in attached table.
- ☒ In accordance with the QAPP for Superfund Site Assessment and Response Team (updated October 2020).
- Field quality control (QC) samples:
- Field duplicates: ☒ Field duplicates will be collected to assess total method precision.
☐ Because assessment of total method precision will not be required for this project, no field duplicates will be collected.
- Equipment rinsate blanks: ☒ Equipment rinsate blanks will be collected to assess potential effects on accuracy from field equipment contamination.
☐ Because only disposable sampling supplies will be used, no equipment rinsate blank will be required.
- Trip blanks: ☐ Trip blanks will be collected to assess potential effects on accuracy from volatile organic compound (VOC) contamination.
☒ Because VOC sampling is not planned, no trip blanks will be required.
- Matrix spike/method spike duplicate (MS/MSD): ☒ MS/MSD samples will be collected to assess precision and accuracy.
☐ Because assessment of total method precision and accuracy will not be required for this project, MS/MSD samples will not be collected to assess precision and accuracy.
- Additional samples: ☐ Additional QC samples are required.
☒ No additional QC samples are required.
- ☐ Other (Describe):

2.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements:

- ☐ Not Applicable
- ☒ In accordance with the QAPP for Superfund Site Assessment and Response Team (updated October 2020).
- ☒ Testing, inspection, and maintenance of analytical instrumentation will accord with the previously referenced SOPs and/or manufacturers' recommendations.

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2.7 Instrument Calibration and Frequency:

- ☐ Not Applicable
☒ In accordance with the QAPP for Superfund Site Assessment and Response Team (updated October 2020).
☒ Calibration of laboratory equipment will proceed as described in the previously referenced SOPs and/or manufacturers' recommendations.
☒ Other (Describe): Field instrument calibration checks will occur daily, as specified in the manufacturers' recommendations.

2.8 Inspection/Acceptance Requirements for Supplies and Consumables:

- ☐ Not Applicable
☒ In accordance with the QAPP for Superfund Site Assessment and Response Team (updated October 2020).
☒ All sample containers will meet EPA criteria for cleaning procedures for low-level chemical analysis. The manufacturer will provide sample containers with Level II certifications in accordance with pre-cleaning criteria established by EPA in *Specifications and Guidelines for Obtaining Contaminant-Free Containers*.
☐ Other (Describe):

2.9 Data Acquisition Requirements:

- ☐ Not Applicable
☒ In accordance with the QAPP for Superfund Site Assessment and Response Team (updated October 2020).
☐ EPA and/or its contractor(s) have compiled from other sources data or information pertaining to the Site (including other analytical data, reports, photos, maps, etc., that are referenced in this QAPP). Some of those data have not been verified by EPA and/or its contractor(s); however, EPA will not use that unverified information for decision-making purposes without verification by an independent professional qualified to verify such data or information.
☐ Other (Describe):

2.10 Data Management:

- ☐ The EPA Region 8 laboratory will manage all data acquired there in accordance with Region 8 EPA SOPs.
☐ Other (Describe): The START-subcontracted laboratory will manage all data acquired there in accordance with the laboratory's established procedures.
☒ All data will be managed in accordance with the site-specific data management plan.

3.0 Assessment and Oversight:

3.1 Assessment and Response Actions:

- ☒ Peer Review ☒ Management Review ☐ Field Audit ☐ Lab Audit
☒ Assessment and response actions pertaining to analytical phases of the project associated with the EPA Region 8 laboratory are addressed in Region 8 EPA SOPs.
☐ Other (Describe):

3.1A Corrective Action:

- ☒ Corrective actions will be at the discretion of the EPA Project Manager whenever problems appear that could adversely affect data quality and/or resulting decisions affecting future response actions pertaining to the Site.
☐ Other (Describe):

3.2 Reports to Management:

- ☐ Audit Report ☐ Data Validation Report ☐ Project Status Report ☐ None Required
☐ START will prepare and submit to EPA a letter report describing sampling and monitoring techniques, locations, problems encountered (with resolutions to those problems), and interpretation of analytical results.
☒ Preparation of reports will accord with the QAPP for Superfund Site Assessment and Response Team (updated October 2020).
☐ Other (Describe):

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4.0 Data Validation and Usability:

4.1 Data Review, Validation, and Verification Requirements:

- ☐ Identified in attached table.
- ☒ Data review and verification will accord with the QAPP for Superfund Site Assessment and Response Team (updated October 2020).
- ☐ A qualified analyst and the EPA Region 8 laboratory's Section Manager will conduct data review and verify analytical results generated by that laboratory, as described in Region 8 EPA SOPs.
- ☐ Other (Describe):

4.2 Validation and Verification Methods:

- ☐ Identified in attached table.
- ☒ Validation of data generated by the laboratory will accord with Region 8 EPA SOPs.
- ☐ The EPA Project Manager will inspect the data to provide a final review. The EPA Project Manager will review the data, if applicable, for laboratory spikes and duplicates, laboratory blanks, and field duplicates to ensure the data are acceptable. The EPA Project Manager will also compare the sample descriptions with field sheets for consistency and will ensure appropriate documentation of any anomalies in the data.
- ☐ Other (Describe):

4.3 Reconciliation with User Requirements:

- ☐ Identified in attached table.
- ☒ If data quality indicators do not meet the project's requirements as outlined in this QAPP, the data may be discarded, and re-sampling, re-monitoring, or re-analysis of the subject samples may be required by the EPA Project Manager.
- ☐ Other (Describe):

Region 8 Superfund Program Addendum to the QAPP for Superfund Site Assessment and Response Team (updated October 2020) for the Fluvial San Miguel Site							
Table A-1: Sample Summary							
Site Name: Fluvial San Miguel				Location: Telluride, San Miguel County, Colorado			
START Project Manager: Billy Bol				Activity/ASR #: Removal Assessment / Removal Action		Date: 9/2/2021	
No. of Samples	Matrix	Location	Purpose	Depth or other Descriptor	Requested Analysis	Sampling Methods	Analytical Method
10	Soil	Tailings Piles	Characterize for removal	0-2' and 2'-4' below ground surface	Lead and Arsenic	Hand Auger	SW-846 6010B SFDGUID-001-R0
1	Soil	Tailings Pile, duplicate	Assess precision of analytical and sampling methods	Not applicable	Lead and Arsenic	Hand Auger	SW-846 6010B SFDGUID-001-R0

Region 8 Superfund Program Addendum to the QAPP for Superfund Site Assessment and Response Team (updated October 2020) for the Fluvial San Miguel Site						
Table A-2: Monitoring Summary						
Site Name: Fluvial San Miguel				Location: Telluride, San Miguel County, Colorado		
START Project Manager: Billy Bol				Activity/ASR #: Removal Assessment / Removal Action		Date: 9/2/2021
No. of Field monitors	Matrix	Location	Purpose	Depth or other Descriptor	Parameters Monitored	
N/A	N/A	N/A	N/A	N/A	N/A	

Region 8 Superfund Program Addendum to the QAPP for Superfund Site Assessment and Response Team (updated October 2020) for the Fluvial San Miguel Site								
Table A-3: Data Quality Objectives Summary								
Site Name: Fluvial San Miguel					Location: Telluride, San Miguel County, Colorado			
START Project Manager: Billy Bol					Activity/ASR #: Removal Assessment / Removal Action			Date: 9/2/2021
Analysis	Analytical Method	Data Quality Measurements					Sample Handling Procedures	Data Management Procedures
		Accuracy	Precision	Representativeness	Completeness	Comparability		
Soil Samples								
Total Metals Lead & Arsenic	SFDGUID-001-R0	Will collect a rinsate blank and MS/MSD	Field Duplicate with an RPD ≤ 70%	Standardized procedures for sample collection and analysis will be used.	Goal of 90% not qualified as rejected	Standardized procedures for sample collection and analysis will be used.	See Section 2.3 of SMAP form.	See Section 2.10 of SMAP form.

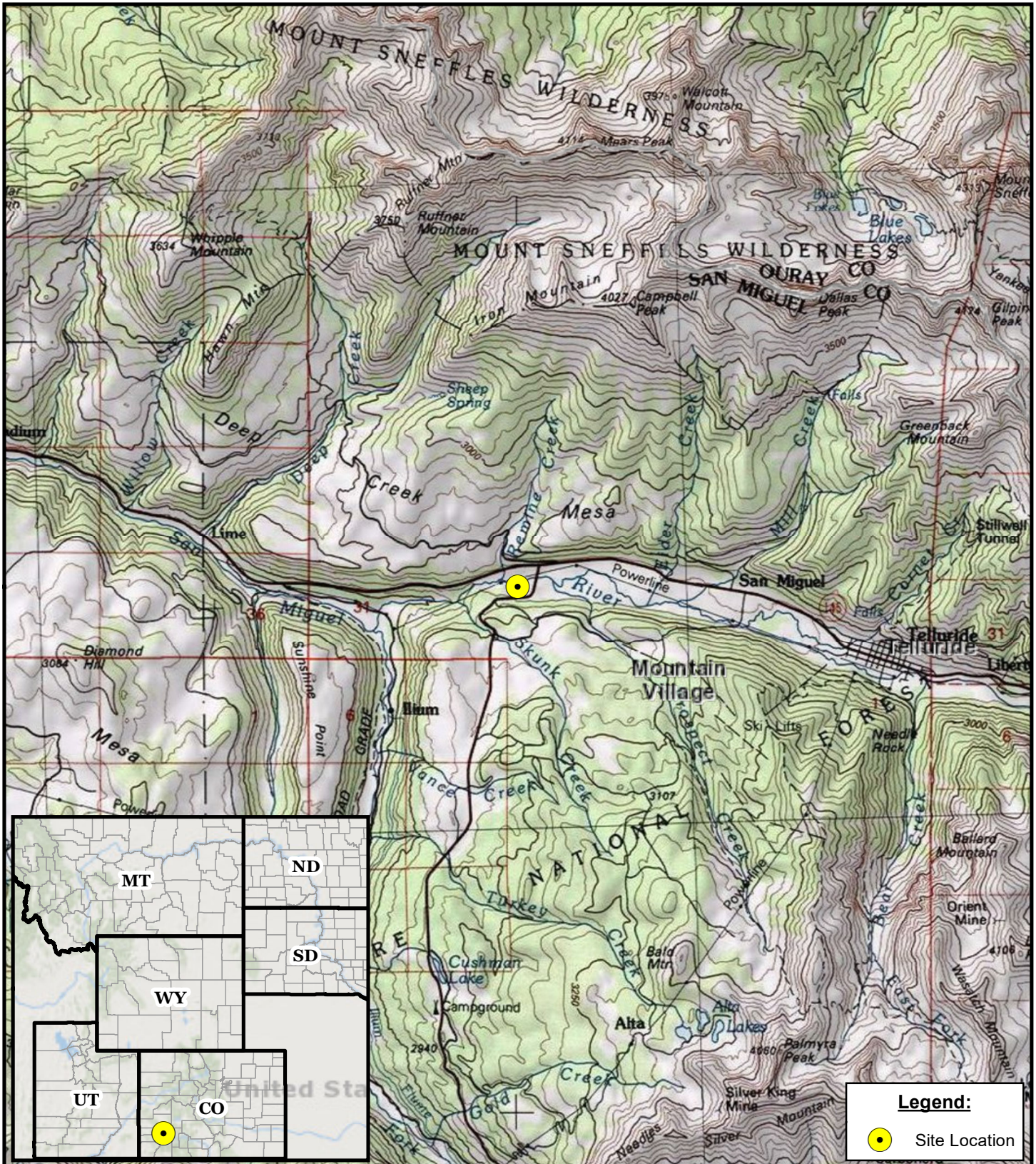
Notes:
MS/MSD – Matrix Spike/Matrix Spike Duplicate
RPD - Relative Percent Difference

APPENDIX B

FIGURES

(Two Pages)

Path: C:\R8Projects\TellurideValley\Floor\ArcGIS_Desktop\Maps_Reports\Figure 1 Site Location SanMiguelFluvial.mxd



Coordinate System: WGS 1984 Web Mercator Auxiliary Sphere
Projection: Mercator Auxiliary Sphere
Datum: WGS 1984

Source:
Background: ESRI USA Topo Maps (2020)

0 0.75 1.5 3 Miles



Prepared for:
U.S. EPA - Region 8



Contract: 68HE0820D0001
TO/TD: 2071-2106-09

Prepared By:
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1560 Broadway
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**FIGURE 1
SITE LOCATION MAP
FLUVIAL SAN MIGUEL TAILINGS RS
SAN MIGUEL COUNTY, COLORADO**

Date: 7/20/2021



Coordinate System: WGS 1984 Web Mercator Auxiliary Sphere
Projection: Mercator Auxiliary Sphere
Datum: WGS 1984

Source:
Background: ESRI World Imagery (2021)
Parcels: San Miguel County Assessor's Office (2021)

0 375 750 1,500 Feet



Prepared for:
U.S. EPA - Region 8

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FIGURE 2
PROPOSED SAMPLE LOCATIONS
FLUVIAL SAN MIGUEL TAILINGS RS
SAN MIGUEL COUNTY, COLORADO

Date: 9/3/2021

ATTACHMENT 1

NIOSH METHOD 7303 ELEMENTS BY ICP

(Six Pages)

ELEMENTS by ICP (Hot Block/HCl/HNO₃ Digestion)

7303

MW: Table 1

CAS: Table 2

RTECS: Table 2

METHOD: 7303, Issue 1		EVALUATION: PARTIAL		Issue 1: 15 March 2003	
OSHA: Table 2 NIOSH: Table 2 ACGIH: Table 2			PROPERTIES: Table 1		
ELEMENTS: aluminum cadmium indium nickel strontium zinc antimony* calcium iron palladium tellurium arsenic chromium lead* phosphorus thallium barium cobalt magnesium platinum tin* beryllium copper manganese potassium titanium bismuth* gallium molybdenum selenium vanadium boron gold neodymium sodium yttrium					
* With certain restrictions (see Table 3)					
SAMPLING			MEASUREMENT		
SAMPLER: FILTER (0.8-µm, cellulose ester membrane)			TECHNIQUE: INDUCTIVELY COUPLED ARGON PLASMA, ATOMIC EMISSION SPECTROSCOPY		
FLOW RATE: 1 to 4 L/min			ANALYTE: See element list above		
VOL-MIN: Table 1 -MAX: Table 1			REAGENTS: Conc. HCl, 1.25 mL; and conc. HNO ₃ , 1.25 mL		
SHIPMENT: Routine			FINAL SOLUTION: 5% HCl and 5% HNO ₃ , 25 mL		
SAMPLE STABILITY: Stable			WAVELENGTH: Element and instrument specific		
BLANKS: 2 to 10 field blanks per set			BACKGROUND CORRECTION: Spectral wavelength shift		
ACCURACY			CALIBRATION: Elements in 5% HCl, 5% HNO ₃		
RANGE STUDIED: 5,000 to 50,000 µg/sample			RANGE: LOQ to 50,000 µg/sample [1]		
BIAS: Not determined			ESTIMATED LOD: Varies with element; Table 1		
OVERALL PRECISION: Not determined			PRECISION (Š): Not evaluated		
ACCURACY: Not determined					
APPLICABILITY: The working range of this method is up to 100 mg/m ³ for each element in a 500-L sample (the minimum range depends on the LOD for each sample; see Table 1). The analysis is not compound specific. Certain elemental compounds are known to be acceptable or unacceptable by this method (see Table 3). For unverified compounds, a test run should be conducted using a known amount of the compound in question to determine acceptability.					
INTERFERENCES: Interferences are spectral in nature and are accounted for by choosing appropriate wavelengths, applying interelement correction factors, and background correction.					
OTHER METHODS: Alternative, more sensitive methods exist for some elements by graphite furnace atomic absorption spectroscopy. This method is similar to NIOSH Method 7301, differing only in the use of the hot block for digestion of the sampler.					

REAGENTS:

1. Hydrochloric acid,* conc., ultra pure.
2. Nitric acid,* conc., ultra pure.
3. Calibration stock solutions, 50-1000 µg/mL. Commercially available single element solutions or multielement solutions prepared as instructed by the instrument manufacturer.
4. Argon, prepurified.
5. Distilled, deionized, Type II water.
6. Diluting solution: 5% HCl : 5% HNO₃. To about 600 mL of deionized water in a 1-L volumetric flask, slowly add 50 mL conc. HCl and 50 mL conc. HNO₃. Dilute to the mark with deionized water.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler: cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter; in cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Inductively coupled argon plasma-atomic emission spectrometer, equipped as specified by the manufacturer for analysis of elements of interest.
4. Hot block apparatus at 95 °C.
5. Digestion vessels and caps, 50-mL.
6. Watchglasses.
7. Pipettes, electronic and mechanical.
8. Regulator, two-stage, for argon.
9. Forceps.

SPECIAL PRECAUTIONS: Concentrated acids are powerful oxidizers, toxic, and corrosive liquids. Wear protective clothing and work in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 200 to 2000 L for TWA measurements. Do not exceed a filter loading of approximately 2 mg total dust.

SAMPLE PREPARATION:

3. Open the cassette filter holder and with forceps remove the sample filter. Fold the filter into quarters taking care not to lose any sample, and transfer to a clean, 50-mL hot block digestion tube.
4. Add 1.25 mL HCl. Cover with a plastic watchglass. Place in the hot block and heat at an internal temperature of 95 °C for 15 minutes.
NOTE: The internal temperature may vary from the digital readout. Calibrate the hot block prior to digestion.
5. Remove the sample from the hot block and cool for 5 minutes. Remove watchglass and add 1.25 mL HNO₃. Replace watchglass and return to hot block at 95 °C for 15 minutes.
6. Remove the sample from the hot block and cool for at least 5 minutes. Rinse watchglass into the sample container and discard watchglass.
7. Dilute to 25-mL final volume with distilled, deionized Type II water.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate the spectrometer according to the manufacturer's recommendations. Use standards consisting of the same 5% HCl : 5% HNO₃ matrix as the samples.
9. Analyze a standard every 10 samples.
10. Analyze a media blank every 20 samples, and a reagent blank every 10 samples.
11. Analyze a set of two laboratory control samples every 40 samples of a given matrix for a given analyte.
12. Check recoveries with at least two spiked media blanks per ten samples.
NOTE: In the determination of lead, there may be a measurement interference (for example, samples with high aluminum levels). More recent instruments have a correction for this.

MEASUREMENT:

13. Set spectrometer to conditions specified by manufacturer.

14. Analyze standards, samples and quality control checks.

NOTE: If the elemental value for a sample is above the linear range of the element(s) in question, dilute the sample solution with 5% HCl: 5% HNO₃ diluting solution, reanalyze and apply the appropriate dilution factor in the calculations.

CALCULATIONS:

15. Obtain the solution concentrations for the sample, C_s (µg/mL), and the average media blank, C_b (µg/mL), from the instrument.

16. Using the solution volumes of sample, V_s (mL), and media blank, V_b (mL), calculate the concentration, C (mg/m³), of each element in the air volume sampled, V (L):

$$C = \frac{C_s V_s - C_b V_b}{V}, \text{mg} / \text{m}^3$$

NOTE: µg/L = mg/m³

EVALUATION OF METHOD:

The method was evaluated for all elements and compounds listed in Table 1 and Table 2 between 1999 and 2001 using known amounts of bulk material [4]. Evaluation is ongoing for additional elements and compounds. The limits of detection and quantitation were also determined for each element. Two ICP instruments were used in the evaluation, a Thermal Jarrell Ash Model 61E [5] and a TJA IRIS [6], operated according to the manufacturer's instructions.

REFERENCES:

- [1] WOHL [2001]. Metals validation using hot block digestion, Unpublished data. Wisconsin Occupational Health Laboratory, Madison, WI.
- [2] NIOSH [1994]. Method 7300: Elements by ICP, NIOSH Manual of Analytical Methods, Fourth Edition, Issue 2, Aug. 15, 1994.
- [3] WOHL [2001]. Metals Manual 2001, WOHL Internal Document, Updated Apr. 1, 2001. Wisconsin Occupational Health Laboratory, Madison, WI.
- [4] WOHL [2001]. WOHL General Operations Procedures Manual, WOHL Internal Document, Updated 2001. Wisconsin Occupational Health Laboratory, Madison, WI.
- [5] Thermal Jarrell Ash [1991]. ICAP 61E Plasma Spectrometer Operator's Manual, Thermal Jarrell Ash Corp., Part No. 128832-01, Feb., 1991.
- [6] Thermal Jarrell Ash [1997]. IRIS Plasma Spectrometer User's Guide, Thermal Jarrell Ash Corp., Part No. 135811-0, Feb. 4, 1997.

METHOD WRITTEN BY:

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TABLE 1: ANALYTE INFORMATION FOR VALID ELEMENTS AND COMPOUNDS

Analyte	Properties		LOD (µg/mL)	LOQ (µg/mL)	Estimated LOQ (µg/sample)*	Minimum** air vol. (L)	Maximum*** air vol. (L)
	MW	MP (°C)					
Al	26.98	660	0.111	0.37	9.25	2	10,000
As	74.92	817	0.009	0.03	0.075	8	5,000,000
Au	196.97	10.63	0.015	0.05	1.25	1	3,300
B	10.81	2177	0.0094	0.0283	0.71	1	3,300
Ba	137.34	3.51	0.0018	0.006	0.15	1	100,000
Be	9.01	2178	0.00075	0.0025	0.062	35	25,000,00
Bi	208.98	271	0.025	0.085	2.12	1	10,000
Ca	40.08	842	0.099	0.33	8.25	2	10,000
CaO	56.08	2927	0.139	0.462	11.6	3	10,000
Cd	112.4	321	0.0037	0.012	0.30	3	500,000
Co	58.93	1495	0.003	0.011	0.27	3	500,000
Cr	52.00	1890	0.009	0.03	0.75	8	500,000
Cu	63.54	1083	0.020	0.060	1.50	15	500,000
Fe	55.85	1535	0.070	0.20	5.00	1	5,000
Fe ₂ O ₃ (as Fe)	159.69	1462	0.070	0.20	5.00	1	5,000
Ga	69.72	29.75	0.03	0.09	2.25	1	3,300
In	114.82	156.3	0.015	0.05	1.25	15	500,000
Mg	24.31	651	0.047	0.14	3.50	1	10,000
MgO	40.32	2825	0.078	0.23	5.75	5	33,000
Mn	54.94	1244	0.0012	0.004	0.10	0.05	10,000
Mo	95.94	651	0.0072	0.024	0.60	0.5	10,000
Nd	92.906	2477	0.01	0.03	0.75	0.1	3,300
Ni	58.71	1453	0.012	0.039	0.98	1	50,000
P	30.97	44	0.3	1.0	25	250	500,000
Pb	207.19	328	0.023	0.07	1.75	35	100,000
Pd	106.4	1550	0.009	0.03	0.75	0.1	3,300
Pt	195.09	1769	0.0045	0.015	0.38	200	25,000,000
Sb	121.75	630.5	0.018	0.06	1.50	3	100,000
Se	78.96	217	0.021	0.064	1.60	8	250,000
Sn	118.69	232	0.015	0.05	1.25	1	25,000
Sr	87.62	769	0.002	0.006	0.15	300	100,000,000
Te	127.60	450	0.15	0.5	12.5	125	500,000
Ti	47.90	1675	0.005	0.016	0.40	0.1	10,000
Tl	204.37	304	0.044	0.133	3.32	35	500,000
V	50.94	1890	0.003	0.01	0.25	2.5	500,000
Y	88.91	1495	0.001	0.003	0.075	0.1	50,000
Zn	65.37	419	0.022	0.066	1.65	0.5	10,000
ZnO	81.37	1970	0.027	0.082	2.05	0.5	10,000

* Value based on a 25-mL sample volume.

** The minimum sampling volume needed to obtain the OSHA PEL at the LOQ for the element/compound at a sample digestion volume of 25 mL.

*** The maximum sampling volume for a given sample, calculated by taking 50,000 µg as the limit for the element/compound per sample.

NOTE: The LOD and LOQ values are dependent on the particular analytical instrument used. Also, LOD and LOQ values may vary for a particular element due to certain interelement interferences.

TABLE 2. EXPOSURE LIMITS, CAS #, RTECS

Element (Symbol)	CAS #	RTECS	Exposure Limits, mg/m ³ (Ca = carcinogen)		
			OSHA	NIOSH	ACGIH
Silver (Ag)	7440-22-4	VW3500000	0.01 (dust, fume, metal)	0.01 (metal, soluble)	0.1 (metal) 0.01 (soluble)
Aluminum (Al)	7429-90-5	BD0330000	15 (total dust) 5 (respirable)	10 (total dust) 5 (respirable fume) 2 (salts, alkyls)	10 (dust) 5 (powders, fume) 2 (salts, alkyls)
Arsenic (As)	7440-38-2	CG0525000	varies	C 0.002, Ca	0.01, Ca
Barium (Ba)	7440-39-3	CQ8370000	0.5	0.5	0.5
Beryllium (Be)	7440-41-7	DS1750000	0.002, C 0.005	0.0005, Ca	0.002, Ca
Calcium (Ca)	7440-70-2	--	varies	varies	varies
Cadmium (Cd)	7440-43-9	EU9800000	0.005	lowest feasible, Ca	0.01 (total), Ca 0.002 (respir.), Ca
Cobalt (Co)	7440-48-4	GF8750000	0.1	0.05 (dust, fume)	0.02 (dust, fume)
Chromium (Cr)	7440-47-3	GB4200000	0.5	0.5	0.5
Copper (Cu)	7440-50-8	GL5325000	1 (dust, mists) 0.1 (fume)	1 (dust) 0.1 (fume)	1 (dust, mists) 0.2 (fume)
Iron (Fe)	7439-89-6	NO4565500	10 (dust, fume)	5 (dust, fume)	5 (fume)
Potassium (K)	7440-09-7	TS6460000	--	--	--
Lanthanum	7439-91-0	--	--	--	--
Lithium (Li)	7439-93-2	--	--	--	--
Magnesium (Mg)	7439-95-4	OM2100000	15 (dust) as oxide 5 (respirable)	10 (fume) as oxide	10 (fume) as oxide
Manganese (Mn)	7439-96-5	OO9275000	C 5	1; STEL 3	5 (dust) 1; STEL 3 (fume)
Molybdenum (Mo)	7439-98-7	QA4680000	5 (soluble) 15 (total insoluble)	5 (soluble) 10 (insoluble)	5 (soluble) 10 (insoluble)
Nickel (Ni)	7440-02-0	QR5950000	1	0.015, Ca	0.1 (soluble) 1 (insoluble, metal)
Phosphorus (P)	7723-14-0	TH3500000	0.1	0.1	0.1
Lead (Pb)	7439-92-1	OF7525000	0.05	0.05	0.05
Antimony (Sb)	7440-36-0	CC4025000	0.5	0.5	0.5
Selenium (Se)	7782-49-2	VS7700000	0.2	0.2	0.2
Tin (Sn)	7440-31-5	XP7320000	2	2	2
Strontium (Sr)	7440-24-6	--	--	--	--
Tellurium (Te)	13494-80-9	WY2625000	0.1	0.1	0.1
Titanium (Ti)	7440-32-6	XR1700000	--	--	--
Thallium (Tl)	7440-28-0	XG3425000	0.1 (skin) (soluble)	0.1 (skin) (soluble)	0.1 (skin)
Vanadium (V)	7440-62-2	YW2400000	--	C 0.05	--
Tungsten	7440-33-7	--	5	5 10 (STEL)	5 10 (STEL)
Yttrium (Y)	7440-65-5	ZG2980000	1	N/A	1
Zinc (Zn)	7440-66-6	ZG8600000	--	--	--
Zirconium (Zr)	7440-67-7	ZH7070000	5	5, STEL 10	5, STEL 10

TABLE 3: VALIDATION SUMMARY

Analyte	Status ¹	Analyte	Status	Analyte	Status
Ag	Not Valid	CuO	Valid	S	Not Valid
Al	Valid	Fe	Valid	Sb	Partially Valid ⁴
Al ₂ O ₃	Not Valid	Fe ₂ O ₃	Valid	Sb ₂ O ₃	Partially Valid ⁵
As	Valid	Ga	Valid	Se	Valid
Au	Valid	In	Valid	Si	Not Valid
B	Valid	KCl	Pending	Sn	Partially Valid ⁶
Ba	Pending	Mg	Valid	SnO	Pending
BaO	Pending	MgO	Valid	SnO ₂	Pending
BaO ₂	Pending	Mn	Valid	Sr	Valid
BaCl ₂	Valid	MnO	Valid	SrCrO ₄	Valid (by Cr)
BaSO ₄	Pending	Mo	Valid	Te	Valid
Be	Valid	NaCl	Pending	Ti	Valid
Bi	Partially Valid ²	Nd	Valid	Tl	Valid
Ca	Valid	Ni	Valid	V	Valid
CaCO ₃	Valid	P	Valid	V ₂ O ₅	Valid
CaO	Valid	Pb	Partially Valid ³	Y	Valid
Cd	Valid	PbCrO ₄	Valid (by Cr)	Zn	Valid
Co	Valid	PbO	Valid	ZnO	Valid
Cr	Valid	Pd	Valid	Zr	Not Valid
Cu	Valid	Pt	Valid	ZrO	Not Valid

¹**Status definitions**

Valid: The method is suitable for samples up to at least 0.0500 g bulk material with recoveries of between 90 and 110 percent. This weight exceeds most expected levels encountered in work environments.

Partially Valid: The method is suitable with bulk-material recoveries of between 90 and 110 percent under certain conditions (as footnoted above).

Not Valid: The method procedure is not suitable for samples at any weight with recoveries of between 90 and 110 percent. An alternative method should be used.

²

Valid up to 10,000 µg/sample and within 7 days of sample digestion.

³

Valid up to 50,000 µg/sample and at least 24 hours after sample digestion; Valid up to 15,000 µg/sample within 24 hours of sample digestion.

⁴

Valid up to 25,000 µg/sample and within 7 days of sample digestion.

⁵

Valid up to 25,000 µg/sample and within 7 days of sample digestion.

⁶

Valid up to 30,000 µg/sample and within 7 days of sample digestion.

NOTE: The upper limits of the method can be extended by serial dilution of the samples at the time of analyses.

ATTACHMENT 2

SUPERFUND X-RAY FLUORESCENCE FIELD OPERATIONS GUIDE

(23 Pages)

**Region 4 – Superfund Division
U.S. Environmental Protection Agency
Atlanta, Georgia**

GUIDANCE

Title: Superfund X-Ray Fluorescence Field Operations Guide

Effective Date: July 19, 2017

DCN: SFDGUID-001-R0

Author

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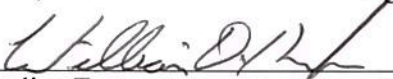
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Revision History

This table shows changes to this controlled document over time. The most recent version is presented in the top row of the table. Previous versions of this document are maintained by the Region 4 Superfund Division Document Control Coordinator.

History	Effective Date
SFDGUID-001-R0, Superfund X-Ray Fluorescence Field Operations Guide , Original Issue	July 19, 2017

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1. General Information

1.1 Purpose

The intent of this FOG is to provide Region 4 On-Scene Coordinators (OSCs) and Remedial Project Managers (RPMs) with a methodology to collect defensible XRF data for lead and arsenic (approach may apply to other metals) in soil samples.

1.2 Scope/Application

The procedures contained in this document provides the methods to measure concentrations of contaminants in soil in a practical, cost-effective, and timely manner. The steps below outline the XRF FOG for lead and arsenic. By following the steps outlined, SSS has confidence XRF data collected can be defined as definitive data (See Appendix C: Case Studies). Mention of trade names or commercial products in this operating procedure does not constitute endorsement or recommendation for use.

1.3 Documentation/Verification

This procedure was prepared by persons deemed technically competent by Superfund management, based on their knowledge, skills and abilities and has been tested in practice and was peer reviewed. The official copy of this procedure will be scanned in to EPA's Superfund Enterprise Management System (SEMS) and published on EPA's internet. The Document Control Coordinator (DCC) is responsible for ensuring the most recent version of the procedure is placed in SEMS and for maintaining records of review conducted prior to its issuance.

1.4 Authors and Peer Reviewers

This document was prepared by Sydney Chan, Tim Frederick, Kevin Koporec, and Glenn Adams of EPA Region 4 Superfund Scientific Support Section (SSS).

SSS would like to acknowledge and thank our peers that took time to review and comment on the draft versions of this document. This document was peer reviewed by Greg Harper, Region 4; Cathy Amoroso, Region 4; Terry Tanner, Region 4; M Crowe, SEDS, Region 4; Mike Neill, SEDS, Region 4; Mike Beringer, Region 7; Duane Newell, ERT; Deana Crumbling, OSRTI; Michele Burgess, OSTRI; John Wheeler, ATSDR; Bryan Vasser, Tetra Tech; Quinn Kelley, Tetra Tech; Russell Henderson, OTIE; and Elizabeth Roddy, OTIE.

1.5 Executive Summary

The EPA Region 4 Superfund Scientific Support Section (SSS) has prepared this X-Ray Fluorescence (XRF) Field Operation Guide (FOG) for consideration by Region 4 On-Scene Coordinators (OSCs) and Remedial Project Managers (RPMs). The intent of this FOG is to provide OSCs/RPMs with a methodology to collect defensible XRF data for lead and arsenic (approach may apply to other metals) in soil samples. This FOG also provides the methods to measure concentrations of contaminants in soil in a practical, cost-effective, and timely manner. The previous methodology generally required the OSC/RPM to make decisions based on a single XRF reading and/or laboratory analysis from a five-point composite or a grab sample within a grid. EPA Office of Superfund Remediation and Technology Innovation (OSRTI) states statistically valid data can be collected when using the XRF by increasing the number of XRF readings on a soil sample and calculating an upper confidence level (UCL) and/or lower confidence level (LCL) on the sample bag. SSS field tests have concluded the recommended OSRTI approach to using the XRF is a viable option that OSCs and RPMs may consider for obtaining lead and arsenic concentrations in soil for decision making purposes. The steps below outline the XRF FOG for lead and arsenic. By following the steps outlined, SSS has confidence XRF data collected can be defined as definitive data (See Appendix C: Case Studies).

The Region 4 Science and Ecosystem Support Division (SESD) Operating Procedure: Field X-Ray Fluorescence Measurement (SESDPROC=107-R3) should be acknowledged in any Sampling and Analysis Plan/Quality Assurance Project Plan (SAP/QAPP) utilizing XRF. This XRF FOG does not specifically follow the process outlined in Section 4, Study Design, of SESD's protocol, but it does address the intent of the protocol. A percentage of samples should be determined in the QAPP to be analyzed by the XRF FOG process and a laboratory. The comparison of the XRF FOG data with the laboratory can be used as recommended in the SESD protocol to confirm the quality of data. However, the data quality objectives of a particular project should be determined by the RPM/OSC on a site specific basis. (EPA, 1993; EPA, 2006)

Before starting, it is important to establish a lead and/or arsenic decision point value {i.e. Regional Removal Management Level (RML), Regional Screening Level (RSL), site-specific clean-up levels, etc.}. This value is extremely important in making site-specific decisions for further analysis and/or clean-up. Please note that concentration data for total arsenic in soil collected using the XRF FOG may be higher at some sites than data reported by extraction-based analysis at a fixed laboratory (See Lessons Learned). If this happens at a site, it is recommended that the RPM and/or OSC consult with their Regional risk assessor and the laboratory to work through site-specific issue before making a final decision.

Spreadsheets developed by OSRTI are central to using the XRF FOG. The spreadsheets are periodically updated and modified with the latest applicable information. Please contact SSS for the latest versions of all spreadsheets prior to beginning field work. Example spreadsheets are included in Appendix B.

2. Quick Start Guide

Field Procedure for use of XRF in Lead and Arsenic Soil Sampling are summarized below:

- a) Collect soil samples according to SAP/QAPP. Mix and disaggregate soil sample in bowl or appropriate container, per the QAPP.
- b) Samples may need to be sieved per OLEM Guidance which recommends using soils passing a No. 100 screen size or particles less than 150 μm .
- c) Measure the soil sample's moisture content. If moisture is $\geq 10\%$, then sample should be dried to less than 10%.
- d) Determine the duration time needed for XRF reading. Typically, the Niton® XRF requires a minimum of 30 seconds to analyze lead and arsenic and the Innov-X XRF requires 45 seconds.
- e) Control outside variables with the XRF by confirming with a systems check, field calibration check, and a Bag Test. Consult equipment manual for instrument specific systems check directions. SSS has spreadsheets to assist with these instrument checks and Bag Test. Please contact SSS for the latest version of the spreadsheets. Perform systems check and field calibration check at the beginning of sample readings and every subsequent 5 hours.
- f) Take 4 XRF readings at different locations of each bagged soil sample through the plastic bag. Record the results in Data Spreadsheet and field logbook.
- g) Evaluate the data to determine whether additional readings are needed. If after 4 XRF readings, the relative standard deviation (RSD) $< 35\%$ then, no additional XRF readings are needed. The 95% upper confidence limit (UCL) value should be compared to the decision point.

3. X-Ray Fluorescence Field Operation Guide Procedures

When conducting a field XRF soil sample study to produce statistically defensible results, the steps below should be followed after the sample has been collected.

3.1. Sieve:

OLEM Directive 9200.1-128 recommends sieving soil samples during all lead Superfund and Resource Conservation and Recovery Act (RCRA) site investigations. When starting a soil sampling project, SSS recommends comparing sieved and non-sieved XRF results of a representative subsample. If the results are generally comparable or a ratio of un-sieved to sieved data can be determined, then sieving the remaining soil samples may not be necessary. The data quality objectives should specify the number of sieve samples and the level of comparability needed on a site-specific basis. If sieved and non-sieved XRF soil sample results are not comparable or a ratio cannot be determined, it is recommended that the remaining soil samples be sieved per the OLEM Directive. Sieving to particle fractions < 150 µm would probably require a controlled environment (i.e., mobile lab) to be conducted correctly with the set of sieves stacked from coarsest to finest to prevent packing of the soil sample. To prevent cross-contamination, the set of sieves should be decontaminated between samples and field quality control samples or equipment blanks are recommended. The decontamination procedures should be defined. Also, if XRF result values are close to the decision point or if sieved and non-sieved results are not in agreement, it is suggested that the soil sample be sieved.

3.2. Moisture Percentage:

Moisture at greater than or equal to 10% may dilute and bias the XRF results low, and Lead Technical Review Workgroup (TRW) recommendations for sampling lead sites, soil moisture be less than 10% (EPA, 2006; EPA, 2000). Therefore, the sample moisture percentage needs to be measured. This can be accomplished by using a soil moisture meter to test in the bagged soil sample. The moisture meter must have the ability to read in percentage to single digits (See Figure 1). The following guidance should be considered regarding moisture content. Please note that the moisture meter should be properly decontaminated between reading each soil sample.

- If moisture is less than 10%, the sample does not require drying and XRF results are acceptable.
- If moisture is greater than or equal to 10% and XRF result is greater than the decision point, the result may be acceptable because the sample already exceeds the decision point.
- If moisture is greater than or equal to 10% and XRF result is less than the decision point, the sample requires drying and then should be reanalyzed. This can be accomplished through solar drying methods or a portable drying apparatus. See Appendix E for example drying options.



Figure 1: Obtaining a moisture reading using General Tools DSMM500 Precision Digital Soil Moisture Meter.

3.3. Time Needed for XRF Reading:

The SSS study (Harper, 2017) revealed shorter measurement times (30 to 60 seconds) are acceptable for precision and accuracy requirements. When analyzing with a particular XRF, there was minimal or no change in result when analyzing a soil sample containing lead and arsenic for 30 seconds instead of 60 seconds. The SSS study regarding analysis time is further supported by investigations from the State of Washington Ecology Department. Its findings reveal that longer reading times allow the XRF to obtain lower detection limits (Furl, 2012). The time used should be appropriate for the instrument to ensure the detection limit is below the decision point to the analyte.

3.4. Control outside variables by confirming systems check, calibration, and by performing bag test:

QA/QC check	Frequency	Standards used	Comparison for approval
Bag Check	Each lot number	NIST 2709a, RCRA 180-661, CCRMP TILL	Spreadsheet determines effect of bag and approval for use
Standard Check	At the beginning of work day and every 5 hours of analysis time	NIST 2709a, RCRA 180-661, Silica/Sand Blank	The mean of the 4 readings should be within 20% of the known value of the standard
Duplicate Reading	Every 20 sample bags	Current sample	2 of 3 readings should be within 95% confidence limit based on reported instrument error

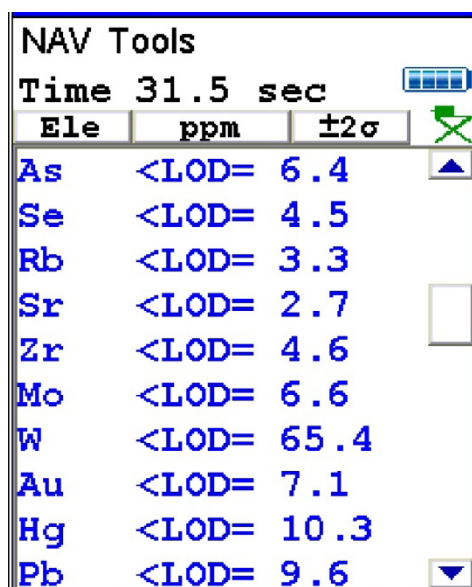
Each XRF should come with a sheet reflecting the certified values of the accompanying standards and silica blanks that are used to check the calibration of the XRF. The manufacturer's technical support can also provide certified values for standards.

a) Calibration Check

- Blank Standards: Take 4 XRF readings (reported in parts per million (ppm) unless otherwise noted) for established duration time with silica or sand blank standard provided with the instrument to ensure it is reading less than the instrument's detection limit (DL). If result reads '<LOD' (Limit of Detection), scroll down on the screen to get the numeric result (see Figure 2). Record results in Standard Spreadsheet. Ensure the average results are below DL. The mean or average are calculated in the Standards Spreadsheet (see Appendix B).
- Quantitative standards: Also known as standard reference material (SRM). We recommend NIST-certified SRMs that have certified values as close to the decision point as possible: NIST 2709a (low), RCRA 180-661 (high), CCRMP TILL (medium)

SESD suggests reconfirming calibration when the temperature has changed by more than 10 degrees F since the last confirmation. An additional Quality Assurance (QA) calibration confirmation can be conducted when sampling activities are complete. Consider checking calibrations after the XRF has been off for an extended period of time or if the battery has been changed. Standards and silica/sand blanks should be considered properly calibrated when the average readings are within 20% of known values provided with each XRF.

It is recommended that the QAPP should establish a minimum cleaning frequency of the XRF reading window. Cleaning may also be necessary when a "blank" has concentrations above the LOD. Figure 2 shows an example of readings from a silica blank.



Ele	ppm	±2σ
As	<LOD= 6.4	
Se	<LOD= 4.5	
Rb	<LOD= 3.3	
Sr	<LOD= 2.7	
Zr	<LOD= 4.6	
Mo	<LOD= 6.6	
W	<LOD= 65.4	
Au	<LOD= 7.1	
Hg	<LOD= 10.3	
Pb	<LOD= 9.6	

Figure 2: XRF screen after scrolling down when reading silica blanks or if results are less than the limit of detection (<LOD).

Any items, including clear, plastic bags located between the instrument and the sample may interfere with the XRF reading. Therefore, plastic bags need to be tested, as seen in Figures 3 and 4, to ensure they do not interfere with the analytical results (Crumbing). Each lot of plastic bags should be tested because the manufacturing process may differ slightly with each lot. SSS found that colored or tinted bags have a tendency to cause interference. The Bag Test Spreadsheet (Figure 5) will calculate the degree to which the bag interferes with the results. If the spreadsheet shows the plastic bag lot is within acceptable limits, all bags with that manufacturer's lot number can be used. The manufacturer lot number is typically found on the box (Figure 6). If the degree of interference (use the Bag Test Spreadsheet tool) from the bag is determined to be outside of acceptable limits, all bags with that lot number should not be used.



Figure 3: Reading standard **without** bag.



Figure 4: Reading standard **with** bag.

It is recommended using a manufacturer-supplied stand (see Appendix E) when possible and to maintain a ¼" thickness of soil to avoid interference from outside sources.

- b) Bag Test: To ensure the plastic bags do not interfere with the XRF soil sample results, take 4 XRF readings for established duration time with the low, medium, and high soil standard inside the plastic bag (Figure 4). Record results in Bag Test Spreadsheet. Readings from the calibration check should be used in the bag test spreadsheets for the "without bag" column. After results are entered in Bag Test Spreadsheet, the Excel calculator program will recommend whether or not the lot of plastic bags is acceptable for collecting and analyzing samples (see Figure 5).

*Note: If the bag fails at levels not applicable for the contaminant, the bag may still be used. For example, if the bag test fails at the low standard (i.e. 20 ppm) for lead but passes the medium and high standard, the bag can still be used. See Appendix D: Lessons Learned for more information.

- c) Evaluate outside variables to determine if there are calibration or bag issues that need to be addressed according to the spreadsheets.

Medium Concentration Level									
Control sample ID: USGS Sdar-M2									
180-706pp									
*With XRF film protector									
Target Analyte: As (click in box for drop-down list)					Target Analyte: As (click in box for drop-down list)				
WITHOUT Plastic Layer					WITHOUT Plastic Layer				
XRF reading #	Conc	XRF reading #	Conc		XRF reading #	Conc	XRF reading #	Conc	
1	90	1	72		1	87	1	67	
2	79	2	66		2	99	2	45	
3	80	3	54		3	71	3	80	
4	74	4	74		4	78	4	77	
5		5			5		5		
6		6			6		6		
7		7			7		7		
8		8			8		8		
SUMMARY STATISTICS					SUMMARY STATISTICS				
n =	4	n =	4		n =	4	n =	4	
mean =	80.8	mean =	66.5		mean =	83.8	mean =	67.3	
SD =	6.7	SD =	9.0		SD =	12.1	SD =	15.8	
2-sided 95% t-UCL =	91.4	2-sided 95% t-UCL =	80.8		2-sided 95% t-UCL =	103.0	2-sided 95% t-UCL =	92.5	
2-sided 95% t-LCL =	70.1	2-sided 95% t-LCL =	52.2		2-sided 95% t-LCL =	64.5	2-sided 95% t-LCL =	42.0	
confidence interval (CI) width =	21.3	CI width =	28.6		CI width =	38.5	interval width =	50.4	
Absolute difference between the 2 concentration means = 14.3 ppm					Absolute difference between the 2 concentration means = 16.5 ppm				
Difference between the 2 concentration means = 19.4 %					Difference between the 2 concentration means = 21.9 %				
2-sample t-Test for a difference between concentration means					2-sample t-Test for a difference between value means				
Variances are equal (2) or unequal (3) 2 t-Test result: 0.0441					Variances are equal (2) or unequal (3) 2 t-Test result: 0.1488				
Does the 2-sample t-Test find a difference between the means? yes					Does the 2-sample t-Test find a difference between the means? no				
Initial conclusion: This bag reduces the X-ray signal; this lot of bags should NOT be used.					Initial conclusion: This bag lot is ok to use.				
Mitigating factors for Pb and As: conc >1300? no abs(diff)<100? yes %diff<8? no					Mitigating factors for Pb and As: conc >1300? no abs(diff)<100? yes %diff<8? no				
Is the concentration very high and the amount of difference relatively small? FALSE					Is the concentration very high and the amount of difference relatively small? FALSE				
Final conclusion: Don't use this bag lot unless these concentrations are not relevant for decision-making.					Final conclusion: This bag lot is ok to use.				

Figure 5: Bag Test Spreadsheet.



Figure 6: Lot number on upper right corner of plastic bags box.

3.5. Taking XRF Readings for Soil Samples:

Examine bag to ensure the fines and coarse particles are still homogenized. If segregation has occurred, remix the bag by rotating the bag vertically so that the particles tumble together. Take 4 XRF readings of each bagged soil sample through the plastic bag by taking an XRF reading from the left and then one from the right side of the bag, then flip bag over and take a reading from the left and then one from the right side of the bag. Record the results in Data Spreadsheet and field logbook. (see Figure 7).

One XRF reading per soil sample is insufficient to make a statistically valid measurement. A minimum of 4 XRF readings taken in different locations of the sample are needed (Crumbling). Therefore, at least 2 readings from each side of the soil sample bag are recommended. This process should provide a statistically representative result for the sample. When the readings are entered into the Data Spreadsheet, the 1-sided t and 1-sided Chebyshev 95% UCLs are calculated. The appropriate UCL and individual XRF results can then be compared to the decision point to inform risk management decisions.

- a) If after 4 XRF readings, the relative standard deviation (RSD) <35% (ITRC, 2012) then, no additional XRF readings are needed. The 95% upper confidence limit (UCL) value should be compared to the decision point.
- b) If after 4 XRF readings, the %RSD is greater than 35%, continue flipping the bag and shooting until the %RSD is below 35% or 10 readings are taken. Typically, the 1-sided t UCL should be used for decision making. If readings are highly variable, see Appendix B for more information on using 1 sided Chebyshev UCL for decision making.
- c) If individual results are both above and below the decision point and the RSD is >35% after 10 readings, consider additional risk factors. To help make risk management decisions, additional information can be obtained by collecting additional samples and/or analyzing subsamples collected from the same bag by a laboratory. Consult SSS for further assistance.

The spreadsheet will calculate a variety of statistics. The 95% UCL for the sample that should be used to represent the sample concentration is typically the one-sided t-test calculation (See Figure 7).

DU or Bag ID: CV-0675A-AsR-A2		Element: As		% Moisture: 10.7	
Replicate Bag Readings	Date & Time	Run Time (sec)	Instrument Result (ppm)	Instrument Error (as 1 Std Dev)	Note?
Replicate reading 1	1546	30	35.0	7	
2	1547	30	25.0	5.0	
3	1548	30	32.0	6	
4	1548	30	25.0	7.0	
5 (optional)	0	0			
6 (optional)	0	0			
7 (optional)	0	0			
8 (optional)	0	#REF!			
9 (optional)	0	#REF!			
10 (optional)	0	#REF!			
		Mean	29.3		
		SD	5.06	Ttl %RSD	17.29
		n =	4		
		ProUCL distribution =		(optional)	
	2-sided	Sample 95% t-LCL =	21		
	2-sided	Sample 95% t-UCL =	37		
	1-sided	Sample 95% t-LCL =	23		
	1-sided	Sample 95% t-UCL =	35		
	1-sided Smple 95% Chebyshev LCL =		18		
	1-sided Smple 95% Chebyshev UCL =		40		
		instrument error =	21.55	as %RSD	

Figure 7: Selecting the 95% UCL from the Data Spreadsheet.

3.6. Duplicate XRF Readings:

Regular quality control checks with the XRF are recommended. Low battery, foreign material on XRF reading window, and slight movements while the XRF operator is analyzing the sample may cause variability in results. A duplicate reading should be collected every 20 soil samples. Duplicate XRF readings are performed by

collecting multiple readings in the same location on the soil sample bag without moving the placement of the bag or XRF analyzer.

Without moving the XRF, read the soil sample twice, and record results in Duplicate Spreadsheet (see Figure 8). If the two results are within the 95% confidence interval, the process is complete. If the duplicate results taken with the XRF in the same location are not within the 95% confidence interval, follow these steps:

- Confirm the correct Error Type is being used from the instrument (i.e. 1 SD or 2 SD)
- Conduct the duplicate procedure with a known certified value standard.
- If standard is within the 95% confidence interval, then repeat duplicate procedure with different area on the soil sample.
- If standard is outside the 95% confidence interval, troubleshoot XRF. Check battery level, cross-contamination, operator technique, etc. Once problem is corrected, confirm XRF calibration with the XRF standards.
- After calibration is confirmed, repeat duplicate procedure with the soil sample. If duplicates are frequently out of range, it is likely due to operator error or the XRF may need to be replaced and serviced by the manufacturer.

Project information:	Southside Chatt Phase II							
Operator:	SRC							
Date:	1/17/2017		Element:	Pb		Read Time (sec):	30 sec per filter	
Sample ID	1st Result of Duplicate Pair	Error as Reported by the XRF	Error Type (1 - 1 SD; 2 - 2 SD) (Notes 5 & 6)	Lower Bound of 95% Confidence Interval		Upper Bound of 95% Confidence Interval	2nd Result of Duplicate Pair	Do the duplicates agree: (Is the duplicate result within the statistical Confidence Interval?)
RH035-FY	315	11	2	304	—	326	307	yes
SG111-EY	246	10	2	236	—	256	243	yes
AP319-EY	126	7	2	119	—	133	130	yes
AP290-EY	213	9	2	204	—	222	219	yes
CH001-16	141	8	2	133	—	149	137	yes

Figure 8: Duplicate Spreadsheet for quality control checks with XRF's readings. Results are in red box.

4. Summary and Conclusions

The EPA Region 4 SSS prepared this XRF FOG for consideration by Region 4 OSCs and RPMs. The intent of this XRF FOG is to provide the OSC/RPM with a XRF methodology to collect quality XRF data for lead and arsenic in ex-situ soil samples (approach may apply to other metals). This XRF FOG is meant to add another "tool in the toolbox" for OSCs and RPMs. This XRF FOG has been field tested, but every possible field situation has not been addressed. SSS believes if this FOG is followed, the OSC/RPM should have quality data to make risk management decisions.

Disclaimer: This document is not designed to promote or endorse any brand names. If a brand name is mentioned it should be considered an example used during the field testing of this XRF FOG only.

5. References

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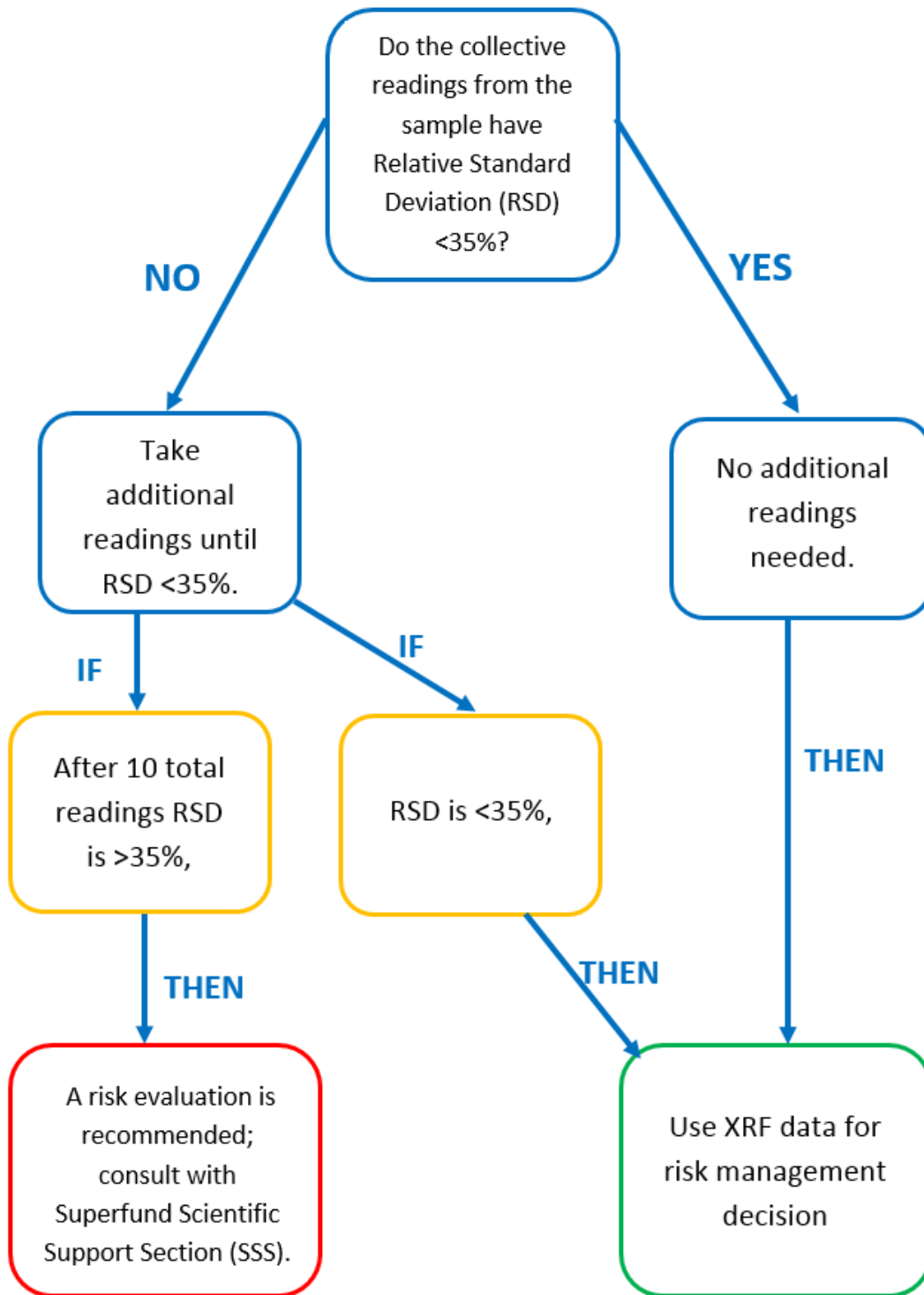
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Appendix A: Example XRF Decision Matrix



Appendix B: Spreadsheets

1	XRF Instrument Duplicate QC Calculator					sheet protection PW = dup				
2										
3										
4	This spreadsheet performs a statistical evaluation of duplicate agreement based on the counting "error" reported by the instrument.									
5										
6	Project information:									
7	Operator:		DMC							
8	Date:		6/5/2015		Element:		Pb		Read Time (sec): 30 sec per filter	
9										
10										
11	Sample ID	1st Result of Duplicate Pair	Error as Reported by the XRF	Error Type (1 - 1 SD; 2 - 2 SD) (Notes 5 & 6)	Lower Bound of 95% Confidence Interval		Upper Bound of 95% Confidence Interval	2nd Result of Duplicate Pair	Do the duplicates agree? (Is the duplicate result within the statistical Confidence Interval?)	Time
12	SW 15	1192	13	1	1167	—	1217	1218	NO	8:27 AM
13	SW 15	1192	13	1	1167	—	1217	1194	yes	8:28 AM
14	SW 24	14.78	2.16	1	11	—	19	15.45	yes	12:23 PM
15	SW 24	14.78	2.16	1	11	—	19	17.78	yes	12:23 PM
16	SW 35	470	8.4	1	454	—	486	488.3	NO	2:31 PM
17	SW 35	498	8.6	1	481	—	515	492.1	yes	2:38 PM
18	SW 35	498	8.6	1	481	—	515	505.8	yes	2:39 PM
19	SW 45	155	4.9	1	145	—	165	170	NO	4:45 PM
20	SW 45	155	4.9	1	145	—	165	130	NO	4:46 PM
21				1	#NUM!	—	#NUM!			
22				1	#NUM!	—	#NUM!			
23				1	#NUM!	—	#NUM!			
24				1	#NUM!	—	#NUM!			
25				1	#NUM!	—	#NUM!			
26										
27	Example Discussion: This example shows Pb results									

Example Duplicate QC Spreadsheet

1-Sided or 2-Sided Confidence Interval:

A 1-sided confidence interval should be used when a decision needs to be made by comparing a sample concentration to the decision point (Crumbling, 2014). This comparison is focused on whether the sample concentration is either above or below the decision point, but not both. Therefore, only one side of the confidence interval is needed; the upper or lower side. The 1-sided confidence interval is usually the value most appropriate for decision making purposes in the removal program.

A 2-sided confidence interval should be used when a decision needs to be made regarding the concentration's potential range in relation to the decision point (Crumbling, 2014). This comparison is focused on the chances of the sample concentration being both above and below the decision point. Therefore, the upper and lower sides of the confidence interval are needed. This is not the case with most removal activities.

Southside Chattanooga Background Standards and Blank Readings				Morning			
Date: 1/20/17				Standards, Blank and System Check			
Recorded By: Sydney Chan							
Equipment: Thermo Scientific Niton XL3t GOLDD+ #83540							
Blank:	SiO2 99.995% PP 180-647			Blank:	SiO2 99.995% PP 180-647		
Time:	0825			Time:	0825		
Reading	Time	Arsenic Result (ppm)	Standard Deviation	Reading	Time	Lead Result (ppm)	Standard Deviation
1	0826	<LOD = 2.9		1	0826	<LOD = 3.6	
2	0828	<LOD = 2.9		2	0828	<LOD = 3.6	
3	0829	<LOD = 2.9		3	0829	<LOD = 3.7	
4	0831	<LOD = 2.9		4	0831	<LOD = 3.7	
Average = #DIV/0!				Average =			
* Run time 30 seconds per beam				* Run time 30 seconds per beam			
Blank:	SiO2 99.995% PP 180-647			Blank:	SiO2 99.995% PP 180-647		
Time:	0825			Time:	0825		
Reading	Time	Copper Result (ppm)	Standard Deviation	Reading	Time	Nickel Result (ppm)	Standard Deviation
1	0826	<LOD = 11.4		1	0826	31	14
2	0828	<LOD = 11.6		2	0828	<LOD = 20	
3	0829	<LOD = 11.6		3	0829	27	13
4	0831	<LOD = 11.1		4	0831	<LOD = 19.3	
Average = #DIV/0!				Average = *did not p			
SiO2 RCRApp NIST							

Example Standards Check Spreadsheet conducted with blank, high, and low SRMs.

Project:					
Property ID:					
Particle Size Fraction in Bag:	S100				
Operator:					
Date:					
DU or Bag ID:	Element: As				
Bag Readings	Time	Run Time (sec)	Instrument Result (ppm)	Instrument Error (as 2 Std Dev)	Note?
1		30			
2		30			
3		30			
4		30			
5 (optional)					
6 (optional)					
7 (optional)					
8 (optional)		#REF!			
9 (optional)		#REF!			
10 (optional)		#REF!			
		Mean	NA		
		SD	NA	Ttl %RSD	#VALUE!
		n =	0		
		ProUCL distribution =		(optional)	
	2-sided	Sample 95% t-LCL =	#VALUE!		
	2-sided	Sample 95% t-UCL =	#VALUE!		
	1-sided	Sample 95% t-LCL =	#VALUE!		
	1-sided	Sample 95% t-UCL =	#VALUE!		
		1-sided Smple 95% Chebyshev LCL =	#VALUE!		
		1-sided Smple 95% Chebyshev UCL =	#VALUE!		
		instrument error =	#DIV/0!	as %RSD	

Example Excel Data Spreadsheet

XRF Bag Entry

Project ID	<input type="text"/>	Operator	<input type="text"/>
Property ID	<input type="text"/>		
Bag ID	<input type="text"/>	Sample Nomenclature:	JH019-SF-EY
Particle Size Fraction in Bag	Raw		
Date and Time	<input type="text"/>	Readings Run time	30
% Moisture	0		
Reading 1 Time	0		
Reading 1 Arsenic Result	0	Reading 1 Arsenic SD	<input type="text"/>
Reading 1 Lead Result	0	Reading 1 Lead SD	<input type="text"/>
Reading 2 Time	0		
Reading 2 Arsenic Result	0	Reading 2 Arsenic SD	<input type="text"/>
Reading 2 Lead Result	0	Reading 2 Lead SD	<input type="text"/>
Reading 3 Time	0		
Reading 3 Arsenic Result	0	Reading 3 Arsenic SD	<input type="text"/>
Reading 3 Lead Result	0	Reading 3 Lead SD	<input type="text"/>
Reading 4 Time	0		
Reading 4 Arsenic Result	0	Reading 4 Arsenic SD	<input type="text"/>
Reading 4 Lead Result	0	Reading 4 Lead SD	<input type="text"/>
Arsenic Mean	0	Arsenic 95% UCL	0
Arsenic St Dev	0	Arsenic %RSD	#Num!
Lead Mean	0	Lead 95% UCL	0

Example Microsoft Access Data Form

Appendix C: Case Studies

Study of the Effectiveness of the X-Ray Fluorescence (XRF) Analyzers on Arsenic Contaminated Soils

The *Study of the Effectiveness of the X-Ray Fluorescence (XRF) Analyzers on Arsenic Contaminated Soils* was based on the collection of 30 discrete soil samples with arsenic levels ranging from 5 ppm arsenic to 335 ppm arsenic (un-sieved *ex situ* XRF readings). The soil samples were collected from an actual arsenic-contaminated CERCLA site. Multiple laboratory analyses and *ex situ* XRF readings were conducted on the 30 discrete soil samples. A statistical comparison of the XRF readings to the laboratory analytical results was completed for each soil sample. The statistical analysis was used to determine the precision, accuracy, and statistical reliability of XRF field screening procedures.

The means of the un-sieved and sieved XRF readings were compared to the mean un-sieved ICP-MS results and a correlation was calculated. The R-squared for the un-sieved XRF/un-sieved ICP-MS data was 0.83. The R-squared for the sieved XRF/un-sieved ICP-MS data was 0.93. These findings show that the XRF data, especially sieved soils, correlate well with laboratory data and can be assumed to reflect accurate results.

The means of the un-sieved and sieved XRF readings were compared to the mean un-sieved ICP-AES results and a correlation was calculated. The R-squared for the un-sieved XRF/un-sieved ICP-AES data was 0.84. The R-squared for the sieved XRF/un-sieved ICP-AES data was 0.91. These findings show that the XRF data, especially sieved soils, correlate well with laboratory data and can be assumed to reflect accurate results.

The statistical analysis was used to determine the precision, accuracy, and statistical reliability of XRF field screening procedures. The statistical analysis presented in the study showed the XRF data collected during this study was both accurate and precise. The study showed when the XRF is used to evaluate arsenic contaminated soils while using the XRF Field Screening Procedure and statistical spreadsheets developed by Office of Superfund Remediation and Technology Innovation (OSRTI), the XRF results can be as accurate as laboratory analysis.

Appendix D: Lessons Learned

Please note during calibrations, SSS suggests measuring the time shown on the XRF versus “real time”, the time on your watch. For example, real time is 40 seconds versus XRF “nominal” time of 30 seconds. If there is a significant difference, the XRF may need to be sent to the manufacturer for calibration.

When running calibration checks with SRMs, Nickel always comes back above LOD when running the silica SRM. Nickel should read <10, but generally averages around 30. Because any decision point pertaining to Nickel should be higher than 30, the LOD should not affect the decision making process.

It should be noted, that concentration data for total arsenic in soil collected using the XRF FOG may be higher at some sites than data reported by extraction-based analysis at a fixed laboratory. It is important to clarify that this does not necessarily reflect a bias or error in either the XRF or the fixed laboratory data. The XRF could be reporting total arsenic which is higher than the total inorganic arsenic digested in the laboratory and/or the XRF data could be a result of an interference like high lead concentrations can sometimes cause. Either way, if this happens at a site, it is recommended that the RPM and/or OSC consult with their Regional risk assessor and the laboratory to work thru site specific issues before making a final decision.

SESD recommends the use of a manufacturer-supplied test-stand when using “cupped” samples. It allows the operator to more consistently align the sample cup under the instrument prior to measurement, and gives a consistent “back-stop” for the analysis. A consistent (non-metal) back-stop should also be used for the bagged samples, since whatever is under the bag could impact the measurement.

SSS recommends having a designated data management collector along with a customized spreadsheet. Currently, SSS uses Microsoft Access to keep all completed soil sample spreadsheets in one, uniform database. With multiple persons containing individual spreadsheets on their respective computers, the transfer of data to a combined location can cause some files to be missed or older versions transferred.

If it is not practical to sufficiently dry samples in the field, SSS recommends drying samples overnight. SSS has successfully used inexpensive electric smokers for this purpose (See Appendix E).

Using stainless sieves may be difficult and time consuming in the field. SSS has successfully used disposable, polyester sieve mesh to reduce decontamination time. Also, sieving contaminated soils may require the use of Personal Protective Equipment (PPE) including respiratory protection and a portable fume hood to minimize exposure.

The Bag Check procedure can be a very time consuming process. SSS recommends bag checking prior to the start of the project to ensure bags for the project have been approved. SSS has found that colored or tinted bags have a tendency to interfere with the X-ray and generally does not pass the bag check.

This is intended to be a living document, if you encounter issues or make improvements to the method, please share with SSS.

Appendix E: Pictures



XRF stand connected to the computer with XRF screen replicated.



XRF stand with XRF attached.



Drying ovens with soil samples inside (above)



Soil samples being dried alternatively by Florida's sunshine.



Soil samples being sieved under a fume hood.



Stacked disposable sieves capturing the fraction



Sieved soil samples properly labeled and waiting XRF coarse readings.



Subsamples taken from the parent fines soil sample.



Decontamination of surface soil samplers.



Surface soil samples drying after decontamination process.

ATTACHMENT 3

**NIST CERTIFICATE OF ANALYSIS,
STANDARD REFERENCE MATERIAL 2709A**

(Seven Pages)



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 2709a

San Joaquin Soil

Baseline Trace Element Concentrations

This Standard Reference Material (SRM) is intended primarily for use in the analysis of soils, sediments, or other materials of a similar matrix. A unit of SRM 2709a consists of 50 g of dried, powdered, agricultural soil.

Certified Values: The certified concentrations of elements, expressed as mass fractions [1] on a dry-mass basis, are provided in Table 1. Certified values are based on results obtained from critically evaluated independent analytical techniques. 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 taken into account [2]. The measurands are the total concentrations of the elements reported in Table 1. Metrological traceability is to the SI unit of mass expressed as the derived unit of mass fraction.

Reference Values: The reference values for elements, expressed as mass fractions on a dry-mass basis, are provided in Table 2. The reference values are based on results obtained from a single NIST analytical method. Reference values are non-certified values that are the best estimate of the true value; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty [2]. The measurands are the total concentrations of the elements reported in Table 2. Metrological traceability is to the SI unit of mass expressed as the derived unit of mass fraction.

Information Values: Information values for elements based on results obtained from one NIST method, are provided in Table 3. Particle size measurements are provided in Figure 1. An information value is considered to be a value that will be of use to the SRM user, but insufficient information is available to assess the uncertainty associated with the value or only a limited number of analyses were performed [2]. Information values cannot be used to establish metrological traceability.

Expiration of Certification: The certification of **SRM 2709a** is valid, within the measurement uncertainties specified, until **01 November 2028**, provided the SRM is handled in accordance with the instructions given in this certificate (see "Instructions for Use"). This certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

E.A. Mackey and R.R. Greenberg, formerly of the NIST Analytical Chemistry Division, and S.E. Long of the NIST Chemical Sciences Division were responsible for coordination of the technical measurements.

Statistical analyses were performed by J.H. Yen of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Steven J. Choquette, Director
Office of Reference Materials

INSTRUCTIONS FOR USE

Sampling: The SRM should be thoroughly mixed by repeatedly inverting and rotating the bottle horizontally before removing a test portion for analysis. A minimum mass of 250 mg (dry mass - see *Drying*) should be used for analytical determinations to be related to the mass fraction values in this Certificate of Analysis.

To obtain the certified values, sample preparation procedures should be designed to effect complete dissolution. If volatile elements (i.e., arsenic, mercury, selenium) are to be determined, precautions should be taken in the dissolution of SRM 2709a to avoid volatilization losses.

Drying: To relate measurements to the certified, reference, and information values that are expressed on a dry-mass basis, users should determine a drying correction at the time of each analysis. The recommended drying procedure is oven drying for 2 h at 110 °C. Note that analytical determination of volatile elements (i.e., arsenic, mercury, selenium) should be determined on samples as received; separate samples should be dried as previously described to obtain a correction factor for moisture. Correction for moisture is to be made to the data for volatile elements before comparing them to the certified values. This procedure ensures that these elements are not lost during drying. The mass loss on drying for this material as bottled was approximately 3 %, but this value may change once the bottle is opened and the soil is exposed to air.

SOURCE, PREPARATION, AND ANALYSIS

Source and Preparation of Material⁽¹⁾: The U.S. Geological Survey (USGS), under contract to NIST, collected and processed the soil for SRM 2709a with assistance from the U.S. Bureau of Reclamation's Sacramento CA office. The agricultural soil used to produce SRM 2709a was collected from a fallow field, in the central California San Joaquin Valley. Three separate collection sites were used to obtain the necessary amount of material. Each collection site covered an area of approximately 4 m². Prior to sample collection the area was scraped clean of surface vegetation. Collected material was transferred to 20 plastic-lined five-gallon plastic buckets and shipped to the USGS laboratory for processing. At USGS, the SRM 2709a soil was dried at room temperature, disaggregated, and sieved to remove coarse material (≥ 2 mm). The resulting soil was ball-milled in 50 kg portions, and then the entire batch of soil was transferred to a cross-flow V-blender for mixing. The blended soil was radiation sterilized prior to bottling. In the final preparation step the blended material was split into containers using a custom-designed spinning riffler, which was used to divide the material into smaller batches, and then used to apportion approximately 50 g into each pre-cleaned bottle.

Every 100th bottle was set aside for chemical analyses designed to assess material homogeneity using X-ray fluorescence spectrometry (XRF), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) at the USGS. Homogeneity assessments were performed at NIST as well, and results indicated that additional processing was needed to achieve optimum homogeneity. The material from all bottles was combined, and then ground in batches between stainless steel plates for a time sufficient to produce a powder of which ≥ 95 %, by mass, passed through a 200 mesh (74 μ m) sieve. The resulting powder was blended, and 50 g portions were dispensed into bottles using the spinning riffler. Results from additional analyses indicated material homogeneity was acceptable (see below).

Homogeneity Testing: The homogeneity was assessed for elements in the bottled material using X-ray fluorescence spectrometry and instrumental neutron activation analysis. In a few cases, statistically significant differences were observed, and the variance due to material inhomogeneity is included in the expanded uncertainties of the certified values. The estimated relative standard deviation for material inhomogeneity for most elements is ≤ 1 %, for calcium it is approximately 2 %, and for chromium it is approximately 3 %. Significant material heterogeneity was observed for mercury, for which a reference value with a prediction interval is provided; see Table 2.

Analysis: Analyses of this material were performed at NIST and at the USGS (Denver, CO). Results from NIST were used to provide the certified, reference, and information values shown in Tables 1, 2, and 3 respectively. Results from the USGS were used to confirm those values. The analytical techniques used for each element are listed in Table 4; the analysts are listed in Tables 5 and 6.

Particle Size Measurements: Particle size measurements for SRM 2709a were made using a Malvern Mastersizer 3000 laser-based light scattering system and the particle size distribution is shown in Figure 1.

⁽¹⁾ Certain commercial equipment, instruments, or materials are identified in this certificate in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1. Certified Values^(a) (Dry-Mass Basis) for Elements in SRM 2709a

Element	Mass Fraction (%)		Coverage Factor, <i>k</i>	Element	Mass Fraction (mg/kg)		Coverage Factor, <i>k</i>
Aluminum (Al)	7.37	± 0.16	2.04	Antimony (Sb)	1.55	± 0.06	2.36
Calcium (Ca)	1.91	± 0.09	2.05	Barium (Ba)	979	± 28	2.57
Iron (Fe)	3.36	± 0.07	2.23	Cadmium (Cd)	0.371	± 0.002	2
Magnesium (Mg)	1.46	± 0.02	2.02	Chromium (Cr)	130	± 9	2.05
Phosphorus (P)	0.0688	± 0.0013	2.12	Cobalt (Co)	12.8	± 0.2	2.45
Potassium (K)	2.11	± 0.06	2.45	Lead (Pb)	17.3	± 0.1	2
Silicon (Si)	30.3	± 0.4	2.57	Manganese (Mn)	529	± 18	2.16
Sodium (Na)	1.22	± 0.03	2.02	Strontium (Sr)	239	± 6	2.26
Titanium (Ti)	0.336	± 0.007	2.26	Vanadium (V)	110	± 11	2.10
				Zirconium (Zr)	195	± 46	2.10

^(a) Certified values for all elements except cadmium and lead are the equally weighted means of results from two or three analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean. 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 effect of between-method and within-method components of uncertainty, following the ISO/JCGM Guide [3,4]. A component for material heterogeneity is incorporated into the uncertainties of aluminum, calcium, chromium, manganese, and sodium. The coverage factor (k) is determined from the Student's t -distribution corresponding to the appropriate associated degrees of freedom and approximately 95 % confidence for each analyte. The certified values for cadmium and lead are each results from a single NIST method (isotope dilution (ID)-ICP-MS, see Table 4) for which a complete evaluation of all sources of uncertainty has been performed. The uncertainty provided is an expanded uncertainty about the mean to cover the measurand with approximately 95 % confidence, consistent with the ISO/JCGM Guide [4]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is the combined uncertainty that incorporates within-method uncertainty and Type B uncertainty components related to the analysis, and k is the coverage factor corresponding to approximately 95 % confidence for each analyte.

Table 2. Reference Values^(a) (Dry-Mass Basis) for Elements in SRM 2709a

Element	Mass Fraction (mg/kg)		
Arsenic (As)	10.5	±	0.3
Cerium (Ce)	42	±	1
Cesium (Cs)	5.0	±	0.1
Copper (Cu)	33.9	±	0.5
Europium (Eu)	0.83	±	0.02
Gadolinium (Gd)	3.0	±	0.1
Lanthanum (La)	21.7	±	0.4
Mercury (Hg) ^(b)	0.9	±	0.2
Nickel (Ni)	85	±	2
Rubidium (Rb)	99	±	3
Scandium (Sc)	11.1	±	0.1
Thallium (Tl)	0.58	±	0.01
Thorium (Th)	10.9	±	0.2
Uranium (U)	3.15	±	0.05
Zinc (Zn)	103	±	4

^(a) Reference values for all elements are based on results from one analytical method at NIST. Uncertainty values represent the expanded uncertainties about the mean to cover the measurand with approximately 95 % confidence, consistent with the ISO/JCGM Guide [4]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is the combined uncertainty that incorporates within-method uncertainty and type B uncertainty components related to the analysis, and k is the coverage factor ($k = 2$) corresponding to approximately 95 % confidence for each analyte.

^(b) The reference value for mercury represents the average value from analysis of portions from six bottles using ID-cold vapor (CV)-ICP-MS. Results indicate significant material heterogeneity; values ranged from 0.8 mg/kg to 1.1 mg/kg. The uncertainty for this reference value is in the form of a prediction interval.

Table 3. Information Values^(a) (Dry Mass Basis) for Elements in SRM 2709a

Element	Mass Fraction (mg/kg)
Boron (B)	74
Dysprosium (Dy)	3
Hafnium (Hf)	4
Lutetium (Lu)	0.3
Neodymium (Nd)	17
Samarium (Sm)	4
Selenium (Se)	1.5
Tantalum (Ta)	0.7
Terbium (Tb)	0.5
Ytterbium (Yb)	2

^(a) Information values are based on results from one analytical method at NIST.

SUPPLEMENTAL INFORMATION FOR SRM 2709a

Particle Size Measurements: Particle size measurements for SRM 2709a were made using a Malvern Mastersizer 3000 laser-based light scattering system. Approximately 0.5 g of SRM 2709a material was measured using water as the dispersant (refractive index: 1.330). Sample was introduced into the measurement cell before ten individual measurements were made at an obscuration of 14 % – 18 % of the laser beam. The information values calculated 10th ($D_v(10)$), 50th ($D_v(50)$) and 90th ($D_v(90)$) percentile particle sizes are $D_v(10) = 2.62 \mu\text{m}$, $D_v(50) = 12.6 \mu\text{m}$, and $D_v(90) = 71.7 \mu\text{m}$. The volume fraction of material smaller than $10.1 \mu\text{m}$ in diameter is approximately 44 %. The particle size distribution is shown in Figure 1.

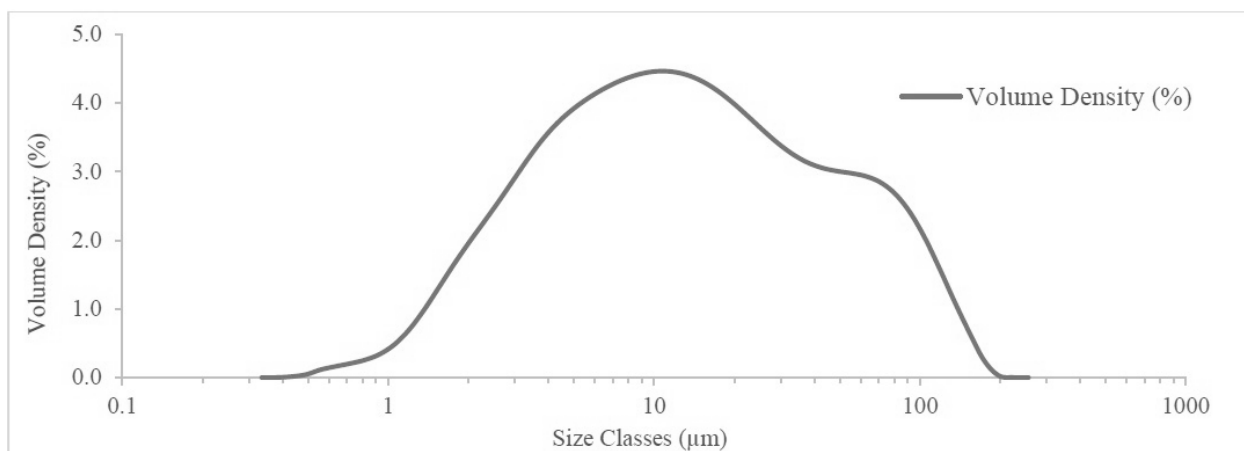


Figure 1. Particle size distribution in SRM 2709a

Table 4. Methods^(a,b) Used for the Analysis of SRM 2709a

Element	Methods	Element	Methods
Al	INAA; XRF	Na	NAA; XRF
As	INAA	Nd	INAA
B	PGAA	Ni	ICP-MS
Ba	ICP-OES; INAA; XRF	P	ICP-OES; XRF
Ca	INAA; XRF	Pb	ID-ICP-MS
Cd	ID-ICP-MS; PGAA	Rb	INAA
Ce	INAA	Sb	INAA; ICP-MS
Co	INAA; ICP-OES	Sc	INAA
Cr	INAA; XRF	Se	CCT-ICP-MS
Cs	INAA	Si	PGAA; XRF
Cu	ICP-MS	Sm	INAA
Dy	INAA	Sr	INAA; ICP-OES; XRF
Eu	INAA	Ta	INAA
Fe	INAA; PGAA; XRF	Tb	INAA
Gd	PGAA	Th	INAA
Hf	INAA	Ti	INAA; PGAA; XRF
Hg	CV-ID-ICP-MS	Tl	ICP-MS
K	INAA; PGAA; XRF	U	ICP-MS
La	INAA	V	INAA; XRF
Lu	INAA	Yb	INAA
Mg	INAA; XRF	Zn	INAA
Mn	INAA; PGAA; XRF	Zr	INAA; XRF

^(a) NIST Methods of Analysis:

CCT-ICP-MS	Collision Cell Inductively Coupled Plasma Mass Spectrometry
CV ID-ICP-MS	Cold Vapor Isotope Dilution Inductively Coupled Plasma Mass Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ID-ICP-MS	Isotope Dilution Inductively Coupled Plasma Mass Spectrometry
INAA	Instrumental Neutron Activation Analysis
PGAA	Prompt Gamma-Ray Activation Analysis
XRF	X-ray Fluorescence Spectrometry

^(b) USGS Methods of Analysis (used to confirm results from certification methods).

WD-XRF	Wavelength Dispersive X-ray Fluorescence Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry

Table 5. Participating NIST Analysts:

S.J. Christopher	A.F. Marlow	S.A. Rabb	B.E. Tomlin
D.L. Ellisor	K.E. Murphy	J.R. Sieber	L.J. Wood
R.M. Lindstrom	J.M. Ness	R.O. Spatz	L.L. Yu
S.E. Long	R.L. Paul	R.S. Popelka-Filcoff	R. Zeisler
E.A. Mackey			

Table 6. Participating USGS Laboratory and Analysts

Laboratory	Analysts
U.S. Geological Survey Branch of Geochemistry (Denver, CO)	M.G. Adams; Z.A. Brown; P.L. Lamothe; J.E. Taggart; S.A. Wilson

REFERENCES

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Certificate Revision History: 02 November 2018 (Updated uncertainty calculation information; added particle size distribution; change of expiration date; editorial changes); 07 April 2009 (Original certificate date).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at <https://www.nist.gov/srm>.

Appendix A

Leachable Concentrations Determined Using USEPA Methods 200.7 and 3050B

The mass fraction values contained in the NIST Certificate of Analysis for SRM 2709a represent the total element content of the material. The measurement results used to provide the certified, reference, or information values are obtained from methods that require complete sample decomposition, or from nondestructive analytical methods such as instrumental neutron activation analysis or prompt gamma-ray activation analysis. Where complete sample decomposition is required, it can be accomplished by digestion with mixed acids or by fusion. For mixed-acid decomposition, hydrofluoric acid must be included in the acid mixture used to totally decompose siliceous materials such as soils and sediments.

In its monitoring programs, the U.S. Environmental Protection Agency (USEPA) has established a number of leach methods for the preparation of soil samples for the determination of extractable elements. Eight laboratories participated, seven of which used USEPA Method 200.7; the remaining laboratory used USEPA SW-846 Method 3050B for preparation of soil samples. All elements were determined in leachates by inductively coupled plasma optical emission spectrometry. Six of the eight laboratories provided individual results from duplicate portions, and these results were averaged together to provide one result for each element from each participating laboratory. Results rejected as outliers by the USEPA Contract Laboratory Program (CLP) officials were not included. Results are summarized in Table A1. The ranges of mass fraction values, median values (to two significant figures), and the number of results included for each are given for 23 elements. The percent recovery values based on the ratios of the median values to the total element content (from the certified, reference, or information values in the Certificate of Analysis) are listed in the last column of Table A1. **Note that the certified values provided as total mass fractions in the Certificate of Analysis are the best estimate of the true mass fraction values for this material.**

This USEPA CLP Study was coordinated by Clifton Jones, Quality Assurance and Technical Support Program, Shaw Environmental & Infrastructure Group (Las Vegas, NV) under the direction of J. Nebelsick, USEPA, Analytical Services Branch. The participating laboratories are listed below the table.

Table A1. Results from Laboratories Participating in the EPA Contract Laboratory Program Study.

Element	n	Range (mg/kg)		Median (mg/kg)	Recovery (%)
Aluminum	7	13000	– 17000	16000	22
Antimony	2	1.2	– 1.5	1.4	88
Arsenic	8	6.4	– 10	7.8	74
Barium	8	350	– 400	380	39
Beryllium	7	0.50	– 0.72	0.61	—
Cadmium	5	0.33	– 0.66	0.40	110
Calcium	8	12000	– 14000	12000	65
Chromium	8	46	– 67	53	41
Cobalt	8	8.2	– 13	10	81
Copper	7	24	– 28	27	81
Iron	8	22000	– 26000	24000	70
Lead	7	8.1	– 11	9.2	53
Magnesium	7	9700	– 11000	10000	71
Manganese	8	380	– 450	420.0	79
Mercury	8	0.79	– 0.92	0.87	97
Nickel	8	59	– 71	66	77
Potassium	8	2600	– 4000	2900	14
Selenium	5	0.69	– 1.9	0.95	63
Silver	4	0.14	– 4.1	0.64	—
Sodium	7	460	– 610	500	4
Thallium	2	0.74	– 1.6	1.2	200
Vanadium	8	43	– 71	48	44
Zinc	8	69	– 87	79	77

List of CLP and non-CLP Participating Laboratories: A4 Scientific, Inc.; Bonner Analytical Testing Co.; Chem Tech Consulting Group; Datachem Laboratories, Inc.; Liberty Analytical Corporation; MSE Laboratory Services; Shealy Environmental; SVL Analytical Inc.

ATTACHMENT 4

**NIST CERTIFICATE OF ANALYSIS,
STANDARD REFERENCE MATERIAL 2710A**

(Eight Pages)



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 2710a

Montana I Soil

Highly Elevated Trace Element Concentrations

This Standard Reference Material (SRM) is intended primarily for use in the analysis of soils, sediments, or other materials of a similar matrix. A unit of SRM 2710a consists of 50 g of the dried, powdered soil, blended with lead oxide.

Certified Values: The certified concentrations of elements, expressed as mass fractions [1] on a dry-mass basis, are provided in Table 1. Certified values are based on results obtained from critically evaluated independent analytical techniques. 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 taken into account [2]. The measurands are the total concentrations of the elements reported in Table 1. Metrological traceability is to the SI unit of mass expressed as the derived unit of mass fraction.

Reference Values: The reference values for elements, expressed as mass fractions on a dry-mass basis, are provided in Table 2. Ten reference values are based on results obtained from a single NIST analytical method, and three are based on results from two NIST analytical methods. Reference values are non-certified values that are the best estimate of the true value; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty [2]. The measurands are the total concentrations of the elements reported in Table 2. Metrological traceability is to the SI unit of mass expressed as the derived unit of mass fraction.

Information Values: Information values for elements based on results obtained from one NIST method, are provided in Table 3. Particle size measurements are provided in Figure 1. An information value is considered to be a value that will be of use to the SRM user, but insufficient information is available to assess the uncertainty associated with the value or only a limited number of analyses were performed [2]. Information values cannot be used to establish metrological traceability.

Expiration of Certification: The certification of **SRM 2710a** is valid, within the measurement uncertainties specified, until **01 January 2029**, provided the SRM is handled in accordance with the instructions given in this certificate (see "Instructions for Use"). This certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

E.A. Mackey and R.R. Greenberg, formerly of the NIST Analytical Chemistry Division, and S.E. Long of the NIST Chemical Sciences Division, were responsible for coordination of the technical measurements.

Statistical analyses were performed by J.H. Yen of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Gaithersburg, MD 20899
Certificate Issue Date: 02 November 2018
Certificate Revision History on Page 7

Steven J. Choquette, Director
Office of Reference Materials

INSTRUCTIONS FOR USE

Sampling: The SRM should be thoroughly mixed by repeatedly inverting and rotating the bottle horizontally before removing a test portion for analysis. A minimum mass of 250 mg (dry mass - see *Drying*) should be used for analytical determinations to be related to the mass fraction values in this Certificate of Analysis.

To obtain the certified values, sample preparation procedures should be designed to effect complete dissolution. If volatile elements (i.e., arsenic, mercury, selenium) will be determined, precautions should be taken in the dissolution of SRM 2710a to avoid volatilization losses.

Drying: To relate measurements to the certified, reference, and information values that are expressed on a dry-mass basis, users should determine a drying correction at the time of each analysis. The recommended drying procedure is oven drying for 2 h at 110 °C. Note that analytical determination of volatile elements (i.e., arsenic, mercury, selenium) should be determined on samples as received; separate samples should be dried as previously described to obtain a correction factor for moisture. Correction for moisture must be made to the data for volatile elements before comparing to the certified values. This procedure ensures that these elements are not lost during drying. The mass loss on drying for this material as bottled was approximately 2 %, but this value may change once the bottle is opened and the soil is exposed to air.

SOURCE, PREPARATION, AND ANALYSIS

Source and Preparation of Material⁽¹⁾: The U.S. Geological Survey (USGS), under contract to NIST, collected and processed the material for SRM 2710a. The original collection site used for SRM 2710 was no longer available due to remediation efforts by the Montana Department of Environmental Quality. An alternative nearby site, located within the flood plain of the Silver Bow Creek, was selected. The site is approximately five miles west of Butte, Montana. Soil for SRM 2710a was placed in 22 plastic-lined five-gallon buckets using a common garden spade. The buckets were sealed and transferred to the USGS using a commercial freight carrier. At the USGS, the SRM 2710a soil was dried at room temperature, disaggregated, and sieved to remove coarse material (≥ 2 mm). The resulting soil was ball-milled in 50 kg portions together with an amount of lead oxide sufficient to achieve a mass fraction of 0.55 % lead in the final product. The entire ball-milled batch of soil was transferred to a cross-flow V-blender for mixing. The blended soil was radiation sterilized prior to bottling. In the final preparation step the blended material was split into containers using a custom-designed spinning riffler, which was used to divide the material into smaller batches, and then used to apportion approximately 50 g into each pre-cleaned bottle.

Every 100th bottle was set aside for chemical analyses designed to assess material homogeneity using X-ray fluorescence spectrometry (XRF), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) at the USGS. Homogeneity assessments were performed at NIST as well, and results indicated that additional processing was needed to achieve optimum homogeneity. The material from all bottles was combined, and then ground in batches between stainless steel plates for a time sufficient to produce a powder of which ≥ 95 %, by mass, passed through a 200 mesh (74 μm) sieve. The resulting powder was blended, and 50 g portions were dispensed into bottles using the spinning riffler. Results from additional analyses indicated material homogeneity was acceptable (see below).

Homogeneity Testing: The homogeneity was assessed for elements in the bottled material using X-ray fluorescence spectrometry and instrumental neutron activation analysis (INAA). The estimated relative standard deviation for material inhomogeneity is < 1 % and no component for inhomogeneity was included in the expanded uncertainties of the certified or reference values.

Particle Size Measurements: Particle size measurements for SRM 2710a were made using a Malvern Mastersizer 3000 laser-based light scattering system and the particle size distribution is shown in Figure 1.

⁽¹⁾ Certain commercial equipment, instruments, or materials are identified in this certificate in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

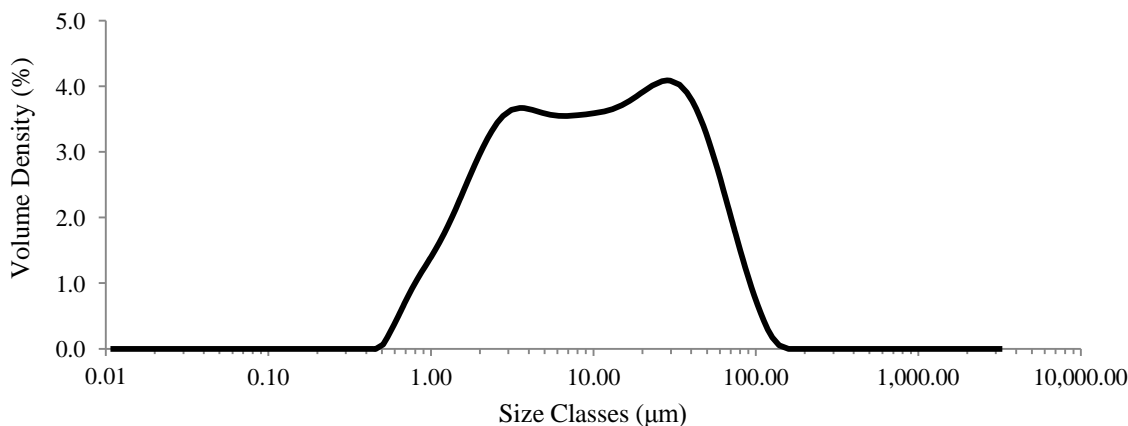


Figure 1. Particle size distribution in SRM 2710a

Analysis: Analyses of this material were performed at NIST and at the USGS (Denver, CO). Results from NIST were used to provide the certified, reference, and information values shown in Tables 1, 2, and 3 respectively. Results from the USGS were used to confirm those values. The analytical techniques used for each element are listed in Table 4; the analysts are listed in Tables 5 and 6.

Table 1. Certified Values^(a,b) (Dry-Mass Basis) for Elements in SRM 2710a

Element	Mass Fraction (%)	Coverage Factor, <i>k</i>	Element	Mass Fraction (mg/kg)	Coverage Factor, <i>k</i>
Aluminum (Al)	5.95 ± 0.05	2.05	Antimony (Sb)	52.5 ± 1.6	2.23
Arsenic (As)	0.154 ± 0.010	2.78	Barium (Ba)	792 ± 36	2.11
Calcium (Ca)	0.964 ± 0.045	2.16	Cadmium (Cd)	12.3 ± 0.3	2.10
Copper (Cu)	0.342 ± 0.005	2.12	Cobalt (Co)	5.99 ± 0.14	2.16
Iron (Fe)	4.32 ± 0.08	2.09	Lanthanum (La)	30.6 ± 1.2	2.12
Lead (Pb)	0.552 ± 0.003	2	Mercury (Hg)	9.88 ± 0.21	2
Magnesium (Mg)	0.734 ± 0.038	2.16	Strontium (Sr)	255 ± 7	2.18
Manganese (Mn)	0.214 ± 0.006	2.37	Uranium (U)	9.11 ± 0.30	2.16
Phosphorus (P)	0.105 ± 0.004	2.45			
Potassium (K)	2.17 ± 0.13	2.57			
Silicon (Si)	31.1 ± 0.4	2.11			
Sodium (Na)	0.894 ± 0.019	2.09			
Titanium (Ti)	0.311 ± 0.007	2.09			
Zinc (Zn)	0.418 ± 0.015	2.14			

^(a) Certified values for all elements except lead and mercury are the equally weighted means of results from two or three analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean. 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 effect of between-method and within-method components of uncertainty, following the ISO/JCGM Guide [3,4]. The coverage factor, k , is determined from the Student's t -distribution corresponding to the appropriate associated degrees of freedom and approximately 95 % confidence for each analyte.

^(b) The certified values for lead and mercury are each results from a single NIST method (see Table 4) for which a complete evaluation of all sources of uncertainty has been performed. The uncertainty provided is an expanded uncertainty about the mean to cover the measurand with approximately 95 % confidence, consistent with the ISO/JCGM Guide [4]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is the combined uncertainty that incorporates within-method uncertainty and Type B uncertainty components related to the analysis, and k is the coverage factor corresponding to approximately 95 % confidence for each analyte.

Table 2. Reference Values^(a,b,c) (Dry-Mass Basis) for Elements in SRM 2710a

Element	Mass Fraction (mg/kg)			Coverage Factor, <i>k</i>
Cesium (Cs)	8.25	±	0.11	2
Chromium (Cr)	23	±	6	2
Europium (Eu)	0.82	±	0.01	2
Gadolinium (Gd)	3.0	±	0.1	2
Lutetium (Lu)	0.31	±	0.01	2
Neodymium (Nd)	22	±	2	2
Nickel (Ni)	8	±	1	2
Rubidium (Rb)	117	±	3	2
Samarium (Sm)	4.0	±	0.2	2.18
Scandium (Sc)	9.9	±	0.1	2
Thallium (Tl)	1.52	±	0.02	2
Thorium (Tr)	18.1	±	0.3	2
Vanadium (V)	82	±	9	2

^(a) Reference values for all elements except chromium, nickel, samarium, and vanadium are based on results from one analytical method at NIST (see Table 4) and the uncertainty provided is an expanded uncertainty about the mean to cover the measurand with approximately 95 % confidence, consistent with the ISO/JCGM Guide [4]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is the combined uncertainty that incorporates within-method uncertainty and Type B uncertainty components related to the analysis, and k is the coverage factor corresponding to approximately 95 % confidence for each analyte.

^(b) Reference values for nickel and samarium are the equally weighted means of results from two analytical methods for nickel and two INAA experiments for samarium. The uncertainty listed with each value is an expanded uncertainty about the mean. 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 effect of between-method and within-method components of uncertainty, following the ISO Guide [3,4]. The coverage factor (k) is determined from the Student's t -distribution corresponding to the appropriate associated degrees of freedom and approximately 95 % confidence for each analyte.

^(c) Reference values for chromium and vanadium are based on a weighted mean calculated by the Dersimonian-Laird method [5], which incorporates an estimate of the between-method variance into the weights. 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 effect of between-method and within-method components of uncertainty, following the ISO Guide [3,4]. The coverage factor (k) is determined from the Student's t -distribution corresponding to the appropriate associated degrees of freedom and approximately 95 % confidence for each analyte.

Table 3. Information Values^(a) (Dry-Mass Basis) for Elements in SRM 2710a

Element	Mass Fraction (mg/kg)
Boron (B)	20
Cerium (Ce)	60
Dysprosium (Dy)	3
Gold (Au)	0.2
Hafnium (Hf)	7
Indium (In)	7
Selenium (Se)	1
Silver (Ag)	40
Tantalum (Ta)	0.9
Terbium (Tb)	0.5
Tungsten (W)	190
Ytterbium (Yb)	2
Zirconium (Zr)	200

^(a) Information values are based on results from one analytical method at NIST.

SUPPLEMENTAL INFORMATION FOR SRM 2710a

Particle Size Measurements: Particle size measurements for SRM 2710a were made using a Malvern Mastersizer 3000 laser-based light scattering system. Approximately 0.5 g of SRM 2710a material was measured using ethanol as the dispersant (refractive index: 1.36). Sample was introduced into the measurement cell and allowed to disperse for 10 s before ten individual measurements were made at an obscuration of 12.9 % of the laser beam. The calculated 10th ($D_v(10)$), 50th ($D_v(50)$) and 90th ($D_v(90)$) percentile particle sizes are $D_v(10) = 1.69 \mu\text{m}$, $D_v(50) = 9.9 \mu\text{m}$, and $D_v(90) = 49 \mu\text{m}$. The fraction of material smaller than $10.1 \mu\text{m}$ in diameter is approximately 50 %. The particle size distribution is shown in Figure 1.

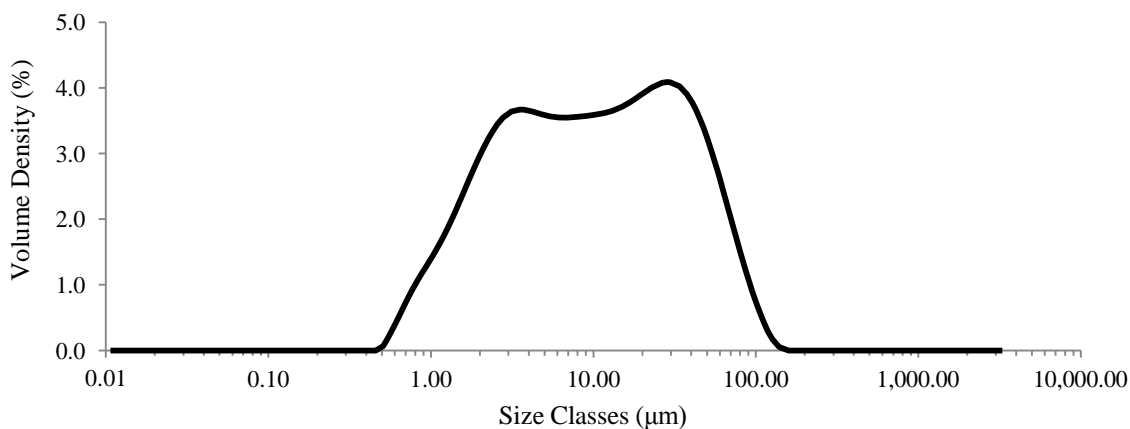


Figure 1. Particle size distribution in SRM 2710a

Table 4. NIST Methods^(a,b) Used for the Analysis of SRM 2710a

Element	Methods	Element	Methods
Ag	INAA	Na	INAA; XRF
Al	INAA; XRF	Nd	INAA
As	CCT-ICP-MS; INAA; XRF	Ni	ICP-MS; ICP-OES
Au	INAA	P	ICP-OES; XRF
B	PGAA	Pb	ID-ICP-MS
Ba	INAA; XRF	Rb	INAA
Ca	INAA; XRF	Sb	ICP-MS; INAA
Cd	ID-ICP-MS; PGAA	Sc	INAA
Ce	INAA	Se	CCT-ICP-MS
Co	INAA; ICP-OES	Si	PGAA; XRF
Cr	INAA; XRF	Sm	INAA ^(c)
Cs	INAA	Sr	ICP-OES; XRF
Cu	INAA; XRF	Ta	INAA
Dy	INAA	Tb	INAA
Eu	INAA	Th	INAA
Fe	INAA; PGAA; XRF	Ti	PGAA; XRF
Gd	PGAA	Tl	ICP-MS
Hf	INAA	U	ICP-MS; INAA
Hg	CV-ID-ICPMS	V	INAA; XRF
K	INAA; PGAA; XRF	W	INAA
La	INAA ^(c)	Yb	INAA
Lu	INAA	Zn	INAA; XRF
Mg	INAA; XRF	Zr	XRF
Mn	INAA; PGAA; XRF		

^(a) NIST Methods of Analysis:

CCT-ICP-MS	Collision Cell Inductively Coupled Plasma Mass Spectrometry
CV ID-ICP-MS	Cold Vapor Isotope Dilution Inductively Coupled Plasma Mass Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ID-ICP-MS	Isotope Dilution Inductively Coupled Plasma Mass Spectrometry
INAA	Instrumental Neutron Activation Analysis
PGAA	Prompt Gamma-Ray Activation Analysis
XRF	X-ray Fluorescence Spectrometry

^(b) USGS Methods of Analysis (used to confirm results from certification methods):

WD-XRF	Wavelength Dispersive X-ray Fluorescence Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry

^(c) Two different INAA experiments, performed using different sub-samples and different analytical conditions, were used to provide certified and reference values for lanthanum and samarium, respectively.

Table 5. Participating NIST Analysts:

S.J. Christopher	A.F. Marlow	S.A. Rabb	B.E. Tomlin
R.D. Day	K.E. Murphy	J.R. Sieber	L.J. Wood
S.E. Long	J.M. Ness	R.O. Spatz	L.L. Yu
E.A. Mackey	R.L. Paul	R.S. Popelka-Filcoff	R. Zeisler

Table 6. Participating USGS Laboratory and Analysts

Laboratory	Analysts
U.S. Geological Survey Branch of Geochemistry (Denver, CO)	M.G. Adams; Z.A. Brown; P.L. Lamothe; J.E. Taggart; S.A. Wilson

REFERENCES

- [1] Thompson, A.; Taylor, B.N.; *Guide for the Use of the International System of Units (SI)*, NIST Special Publication 811 (2008); available at <https://www.nist.gov/pml/special-publication-811> (accessed Nov 2018).
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Certificate Revision History: 02 November 2018 (Updated uncertainty calculation information; added particle size distribution; change of expiration date; editorial changes); 07 April 2009 (Original certificate date).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at <https://www.nist.gov/srm>.

Appendix A

Leachable Concentrations Determined Using USEPA Methods 200.7 and 3050B

The mass fraction values contained in the NIST Certificate of Analysis for SRM 2710a represent the total element content of the material. The measurement results used to provide the certified, reference or information values are obtained from methods that require complete sample decomposition, or from nondestructive analytical methods such as instrumental neutron activation analysis or prompt gamma-ray activation analysis. Where complete sample decomposition is required, it can be accomplished by digestion with mixed acids or by fusion. For mixed-acid decomposition, hydrofluoric acid must be included in the acid mixture used to totally decompose siliceous materials such as soils and sediments.

In its monitoring programs, the U.S. Environmental Protection Agency (USEPA) has established a number of leach methods for the preparation of soil samples for the determination of extractable elements. Six laboratories participated, five of which used USEPA Method 200.7; the remaining laboratory used USEPA SW-846 Method 3050B for preparation of soil samples. All elements were determined in leachates by inductively coupled plasma optical emission spectrometry. All laboratories provided individual results from duplicate portions, and these results were averaged together to provide one result for each element from each participating laboratory. Results rejected as outliers by the USEPA Contract Laboratory Program (CLP) officials were not included. Results are summarized in Table A1. The ranges of mass fraction values, median values (to two significant figures), and the number of results included for each are given for 23 elements. The percent recovery values based on the ratios of the median values to the total element content (from the certified, reference, or information values in the Certificate of Analysis) are listed in the last column of Table A1. **Note that the certified values provided as total mass fractions in the Certificate of Analysis are the best estimate of the true mass fraction values for this material.**

This USEPA CLP Study was coordinated by Clifton Jones, Quality Assurance and Technical Support Program (QATS), Shaw Environmental & Infrastructure Group, Las Vegas, NV, under the direction of J. Nebelsick, USEPA, Analytical Services Branch. The participating laboratories are listed below this table.

Table A1. Results from Laboratories Participating in the EPA Contract Laboratory Program Study.

Element	n	Range (mg/kg)			Median (mg/kg)	Recovery (%)
Aluminum	6	8200	–	12000	10000	17
Antimony	6	5.0	–	12	9.6	18
Arsenic	6	1300	–	1600	1400	92
Barium	6	490	–	540	510	65
Beryllium	6	0.24	–	0.51	0.48	--
Cadmium	5	9.6	–	12	11	86
Calcium	6	1700	–	2000	1800	19
Chromium	6	9.2	–	11	10	41
Cobalt	6	2.8	–	5.2	3.8	64
Copper	6	3100	–	3500	3300	95
Iron	6	30000	–	36000	34000	79
Lead	6	4700	–	5800	5100	93
Magnesium	6	3200	–	3600	3500	48
Manganese	6	1500	–	1800	1700	77
Mercury	6	9.3	–	11.7	10	104
Nickel	5	4.8	–	6.1	5.5	69
Potassium	6	3800	–	4700	4100	19
Selenium	2	1.5	–	2.6	2.0	200
Silver	6	31	–	39	36	91
Sodium	6	550	–	650	590	7
Thallium	3	1.3	–	3.6	3.2	213
Vanadium	6	35	–	43	38	48
Zinc	6	3300	–	4400	3800	90

List of CLP and non-CLP Participating Laboratories: A4 Scientific, Inc.; Bonner Analytical Testing Co.; Chem Tech Consulting Group; Datachem Laboratories, Inc.; Liberty Analytical Corporation; MSE Laboratory Services; Shealy Environmental; SVL Analytical Inc.

ATTACHMENT 5

**NIST CERTIFICATE OF ANALYSIS,
STANDARD REFERENCE MATERIAL 2711A**

(Seven Pages)



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2711a

Montana II Soil

Moderately Elevated Trace Element Concentrations

This Standard Reference Material (SRM) is intended primarily for use in the analysis of soils, sediments, or other materials of a similar matrix. One unit of SRM 2711a consists of 50 g of the dried, powdered soil.

Certified Values: The certified concentrations of elements, expressed as mass fractions [1] on a dry-mass basis, are provided in Table 1. Certified values are based on results obtained from critically evaluated independent analytical techniques. 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 taken into account [2]. The measurands are the total concentrations of the elements reported in Table 1. Metrological traceability is to the SI unit of mass expressed as the derived unit of mass fraction.

Reference Values: The reference values for elements, expressed as mass fractions on a dry-mass basis, are provided in Table 2. The reference values are based on results obtained from a single NIST analytical method. Reference values are non-certified values that are the best estimate of the true value; however, the values do not meet NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty [2]. The measurands are the total concentrations of the elements reported in Table 2. Metrological traceability is to the SI unit of mass, expressed as the derived unit of mass fraction.

Information Values: Information values for elements obtained from one NIST method, are provided in Table 3. Particle size measurements are provided in Figure 1. An information value is considered to be a value that will be of use to the SRM user, but insufficient information is available to assess the uncertainty associated with the value or only a limited number of analyses were performed [2]. Information values cannot be used to establish metrological traceability.

Expiration of Certification: The certification of SRM 2711a is valid, within the measurement uncertainty specified, until **01 January 2029**, provided the SRM is handled in accordance with the instructions given in this certificate (see "Instructions for Use"). This certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

E.A. Mackey and R.R. Greenberg, formerly of the NIST Analytical Chemistry Division, and S.E. Long of the NIST Chemical Sciences Division, were responsible for coordination of the technical measurements.

Statistical analyses were performed by J.H. Yen of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Steven J. Choquette, Director
Office of Reference Materials

Gaithersburg, MD 20899
Certificate Issue Date: 29 October 2018
Certificate Revision History on Page 6

INSTRUCTIONS FOR USE

Sampling: The SRM should be thoroughly mixed by repeatedly inverting and rotating the bottle horizontally before removing a test portion for analysis. A minimum mass of 250 mg (dry mass - see *Drying*) should be used for analytical determinations to be related to the mass fraction values in this Certificate of Analysis.

To obtain the certified values, sample preparation procedures should be designed to effect complete dissolution. If volatile elements (i.e., arsenic, mercury, selenium) will be determined, precautions should be taken in the dissolution of SRM 2711a to avoid volatilization losses.

Drying: To relate measurements to the certified, reference, and information values that are expressed on a dry-mass basis, users should determine a drying correction at the time of each analysis. The recommended drying procedure is oven drying for 2 h at 110 °C. Note that analytical determination of volatile elements (i.e., arsenic, mercury, selenium) should be determined on samples as received; separate samples should be dried as previously described to obtain a correction factor for moisture. Correction for moisture must be made to the data for volatile elements before comparing to the certified values. This procedure ensures that these elements are not lost during drying. The mass loss on drying for this material as bottled was approximately 2 %, but this value may change once the bottle is opened and the soil is exposed to air.

SOURCE, PREPARATION, AND ANALYSIS

Source and Preparation of Material⁽¹⁾: The U.S. Geological Survey (USGS), under contract to NIST, collected and processed the material for SRM 2711a. Soil was collected from the top 10 cm to 12 cm of an agricultural field located near a site formerly used by a smelting plant, in east Helena, Montana. Collection was performed using a common garden spade, and the material was stored in 20 plastic-lined five-gallon buckets with snap-on lids. At the USGS, the SRM 2711a soil was dried at room temperature, disaggregated, and sieved to remove coarse material (≥ 2 mm). The resulting soil was ball-milled in 50 kg portions. The entire ball-milled batch of soil was transferred to a cross-flow V-blender for mixing. The blended soil was radiation sterilized prior to bottling. In the final preparation step the blended material was split into containers using a custom-designed spinning riffler, which was used to divide the material into smaller batches, and then used to apportion approximately 50 g into each pre-cleaned bottle.

Every 100th bottle was set aside for chemical analyses designed to assess material homogeneity using X-ray fluorescence spectrometry (XRF), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) at the USGS. Homogeneity assessment and sieving tests performed at NIST indicated that additional processing was needed to achieve optimum homogeneity. The material from all bottles was combined, and then ground in batches between stainless steel plates for a time sufficient to produce a powder of which ≥ 95 %, by mass, passed through a 200 mesh (74 μ m) sieve. The resulting powder was blended, and 50 g portions were dispensed into bottles using the spinning riffler. Results from analyses at NIST indicated that material homogeneity was acceptable (see below).

Homogeneity Testing: The homogeneity was assessed for elements in the bottled material using instrumental neutron activation analysis (INAA). The estimated relative standard deviation for material inhomogeneity is ≤ 1 % for most elements evaluated. For antimony, magnesium, and zinc, a component for material heterogeneity (of 1 %, relative, at the 1s level) was included in the expanded uncertainties of the certified values.

Particle Size Measurements: Particle size measurements for SRM 2711a were made using a Malvern Mastersizer 3000 laser-based light scattering system and the particle size distribution is shown in Figure 1.

Analysis: Analyses of this material were performed at NIST and at the USGS (Denver, CO). Results from NIST were used to provide the certified, reference, and information values shown in Tables 1, 2, and 3, respectively. Results from the USGS were used to confirm those values. The analytical techniques used for each element are listed in Table 4; the analysts are listed in Tables 5 and 6.

⁽¹⁾ Certain commercial equipment, instruments, or materials are identified in this certificate in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1. Certified Values^(a,b) (Dry-Mass Basis) for Elements in SRM 2711a

Element	Mass Fraction (%)		Coverage Factor, <i>k</i>	Element	Mass Fraction (mg/kg)		Coverage Factor, <i>k</i>
Aluminum (Al)	6.72	± 0.06	2.10	Antimony (Sb)	23.8	± 1.4	2.06
Calcium (Ca)	2.42	± 0.06	2.10	Arsenic (As)	107	± 5	2.18
Iron (Fe)	2.82	± 0.04	2.36	Barium (Ba)	730	± 15	2.26
Lead (Pb)	0.140	± 0.001	2	Cadmium (Cd)	54.1	± 0.5	2
Magnesium (Mg)	1.07	± 0.06	2.23	Chromium (Cr)	52.3	± 2.9	2.31
Potassium (K)	2.53	± 0.10	2.36	Cobalt (Co)	9.89	± 0.18	2.07
Silicon (Si)	31.4	± 0.7	2.57	Copper (Cu)	140	± 2	2.09
Sodium (Na)	1.20	± 0.01	2.07	Manganese (Mn)	675	± 18	2.06
Titanium (Ti)	0.317	± 0.008	2.26	Mercury (Hg)	7.42	± 0.18	2
				Nickel (Ni)	21.7	± 0.7	2.16
				Phosphorus (P)	842	± 11	2.09
				Samarium (Sm)	5.93	± 0.28	2.78
				Strontium (Sr)	242	± 10	2.45
				Uranium (U)	3.01	± 0.12	2.10
				Vanadium (V)	80.7	± 5.7	2.18
				Zinc (Zn)	414	± 11	2.05

^(a) Certified values for all elements except cadmium, lead, and mercury are the equally weighted means of results from two or three analytical methods. The uncertainty listed with each value is an expanded uncertainty about the mean. 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 effect of between-method and within-method components of uncertainty, following the ISO/JCGM Guide [3,4]. A component for material heterogeneity is incorporated into the uncertainties for antimony, manganese, and zinc. The coverage factor, k is determined from the Student's t -distribution corresponding to the appropriate associated degrees of freedom and approximately 95 % confidence for each analyte.

^(b) The certified values for cadmium, lead, and mercury are each results from a single NIST method (see Table 4) for which a complete evaluation of all sources of uncertainty has been performed. The uncertainty provided is an expanded uncertainty about the mean to cover the measurand with approximately 95 % confidence, consistent with the ISO/JCGM Guide [4]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is the combined uncertainty that incorporates within-method uncertainty and Type B uncertainty components related to the analysis, and k is the coverage factor corresponding to approximately 95 % confidence for each analyte.

Table 2. Reference Values^(a) (Dry-Mass Basis) for Elements in SRM 2711a

Element	Mass Fraction (mg/kg)	
Cesium (Cs)	6.7	± 0.2
Europium (Eu)	1.1	± 0.2
Hafnium (Hf)	9.2	± 0.2
Lanthanum (La)	38	± 1
Neodymium (Nd)	29	± 2
Rubidium (Rb)	120	± 3
Scandium (Sc)	8.5	± 0.1
Thorium (Th)	15	± 1

^(a) Reference values are based on results from one analytical method at NIST (see Table 4). Uncertainty values represent the expanded uncertainties about the mean to cover the measurand with approximately 95 % confidence, consistent with the ISO/JCGM Guide [4]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is the combined uncertainty that incorporates within-method uncertainty and type B uncertainty components related to the analysis, and k is the coverage factor ($k = 2$) corresponding to approximately 95 % confidence for each analyte.

Table 3. Information Values^(a) (Dry-Mass Basis) for Elements in SRM 2711a

Element	Mass Fraction (mg/kg)
Boron (B)	50
Cerium (Ce)	70
Dysprosium (Dy)	5
Gadolinium (Gd)	5
Indium (In)	1
Lutetium (Lu)	0.5
Selenium (Se)	2
Silver (Ag)	6
Tantalum (Ta)	1
Terbium (Te)	0.8
Thallium (Tl)	3
Ytterbium (Yb)	3

^(a) Information values are based on results from one analytical method at NIST.

SUPPLEMENTAL INFORMATION FOR SRM 2711a

Particle Size Measurements: Particle size measurements for SRM 2711a were made using a Malvern Mastersizer 3000 laser-based light scattering system. Approximately 0.5 g of SRM 2711a material was measured using water as the dispersant (refractive index 1.330). Sample was introduced into the measurement cell before ten individual measurements were made at an obscuration of 20 % – 21 % of the laser beam. The calculated 10th ($D_v(10)$), 50th ($D_v(50)$) and 90th ($D_v(90)$) percentile particle sizes are $D_v(10) = 2.26 \mu\text{m}$, $D_v(50) = 15.5 \mu\text{m}$, and $D_v(90) = 58.6 \mu\text{m}$. The volume fraction of material smaller than $10.1 \mu\text{m}$ in diameter is approximately 41 %. The particle size distribution is shown in Figure 1.

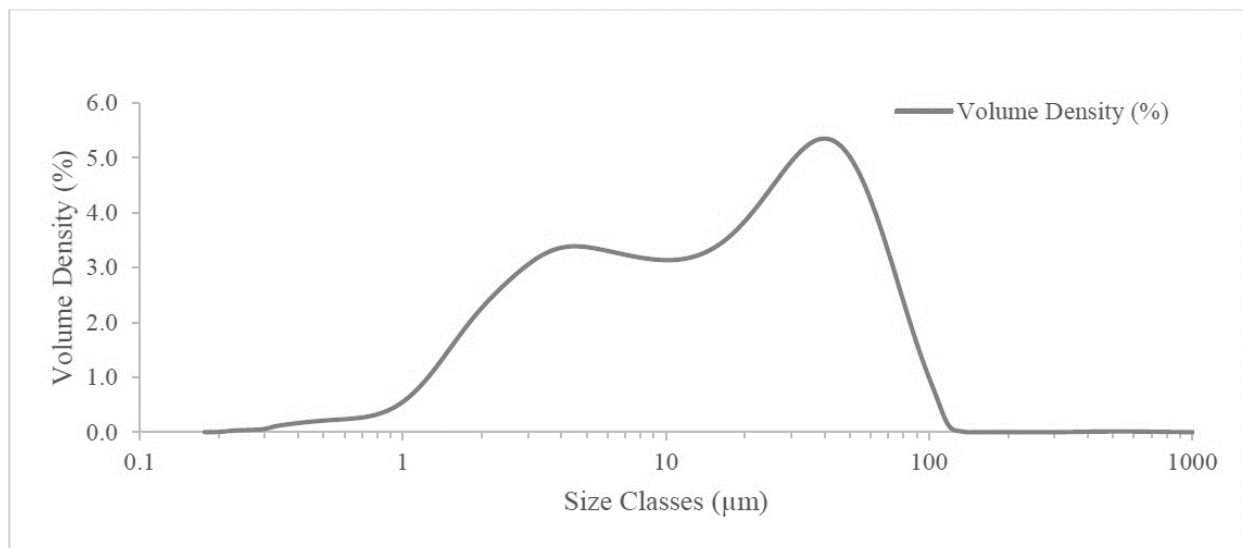


Figure 1. Particle size distribution in SRM 2711a

Table 4. NIST Methods^(a,b) Used for the Analysis of SRM 2711a

Element	Methods	Element	Methods
Ag	INAA	Mn	INAA; XRF
Al	INAA; XRF	Na	INAA; XRF
As	INAA; XRF	Nd	INAA
B	PGAA	Ni	ICP-MS; ICP-OES
Ba	ICP-OES; INAA; XRF	P	ICP-OES; XRF
Ca	INAA; XRF	Pb	ID-ICP-MS
Cd	ID-ICP-MS	Rb	INAA
Ce	INAA	Sb	ICP-MS; INAA
Co	INAA; ICP-OES	Sc	INAA
Cr	INAA; XRF	Se	CCT-ICP-MS
Cs	INAA	Si	PGAA; XRF
Cu	ICP-OES; ICP-MS	Sm	INAA ^(c) ; PGAA
Dy	INAA	Sr	ICP-OES; INAA; XRF
Eu	INAA	Ta	INAA
Fe	INAA; PGAA; XRF	Tb	INAA
Gd	PGAA	Th	INAA
Hf	INAA	Ti	INAA; PGAA; XRF
Hg	CV-ID-ICPMS	Tl	ICP-MS
In	INAA	U	ICP-MS; INAA
K	INAA; PGAA; XRF	V	INAA; XRF
La	INAA ^(c)	Yb	INAA
Lu	INAA	Zn	INAA; XRF
Mg	INAA; XRF		

^(a) NIST Methods of Analysis:

CCT-ICP-MS	Collision Cell Inductively Coupled Plasma Mass Spectrometry
CV ID-ICP-MS	Cold Vapor Isotope Dilution Inductively Coupled Plasma Mass Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ID-ICP-MS	Isotope Dilution Inductively Coupled Plasma Mass Spectrometry
INAA	Instrumental Neutron Activation Analysis
PGAA	Prompt Gamma-Ray Activation Analysis
XRF	X-ray Fluorescence Spectrometry

^(b) USGS Methods of Analysis (used to confirm results from certification methods).

WD-XRF	Wavelength Dispersive X-ray Fluorescence Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry

^(c) Two different INAA experiments, performed using different sub-samples and different analytical conditions, were used to provide certified and reference values for lanthanum and samarium, respectively.

Table 5. Participating NIST Analysts:

S.J. Christopher	J.L. Molloy	S.A. Rabb	B.E. Tomlin
R.D. Day	K.E. Murphy	J.R. Sieber	L.J. Wood
S.E. Long	J.M. Ness	R.O. Spatz	L.L. Yu
E.A. Mackey	R.L. Paul	R.S. Popelka-Filcoff	R. Zeisler
A.F. Marlow			

Table 6. Participating USGS Laboratory and Analysts

Laboratory	Analysts
U.S. Geological Survey Branch of Geochemistry (Denver, CO)	M.G. Adams; Z.A. Brown; P.L. Lamothe; J.E. Taggart; S.A. Wilson

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Certificate Revision History: 29 October 2018 (Updated uncertainty calculation information; added particle size distribution; change of expiration date; editorial changes); 22 May 2009 (Original certificate date).
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Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at <https://www.nist.gov/srm>.

Appendix A

Leachable Concentrations Determined Using USEPA Methods 200.7 and 3050B NIST Methods of Analysis

The mass fraction values contained in the NIST Certificate of Analysis for SRM 2711a represent the total element content of the material. The measurement results used to provide the certified, reference or information values are obtained from methods that require complete sample decomposition, or from nondestructive analytical methods such as instrumental neutron activation analysis or prompt gamma-ray activation analysis. Where complete sample decomposition is required, it can be accomplished by digestion with mixed acids or by fusion. For mixed-acid decomposition, hydrofluoric acid must be included in the acid mixture used to totally decompose siliceous materials such as soils and sediments.

In its monitoring programs, the U.S. Environmental Protection Agency (USEPA) has established a number of leach methods for the preparation of soils samples for the determination of extractable elements. Six laboratories participated, five of which used USEPA Method 200.7; the remaining laboratory used USEPA SW-846 Method 3050B for preparation of soil samples. All elements were determined in leachates by inductively coupled plasma optical emission spectrometry. All laboratories provided individual results from duplicate portions, and these results were averaged together to provide one result for each element from each participating laboratory. Results rejected as outliers by the USEPA Contract Laboratory Program (CLP) officials were not included. Results are summarized in Table A1. The ranges of mass fraction values, median values (to two significant figures), and the number of results included for each are given for 23 elements. The percent recovery values based on the ratios of the median values to the total element content (from the certified, reference, or information values in the Certificate of Analysis) are listed in the last column of Table A1. **Note that the certified values provided as total mass fractions in the Certificate of Analysis are the best estimate of the true mass fraction values for this material.**

This USEPA CLP Study was coordinated by C. Jones, Quality Assurance and Technical Support Program (QATS), Shaw Environmental & Infrastructure Group, Las Vegas, NV, under the direction of J. Nebelsick, USEPA, Analytical Services Branch. The participating laboratories are listed below the table.

Table A1. Results from Laboratories Participating in the EPA Contract Laboratory Program Study.

Element	n	Range (mg/kg)			Median (mg/kg)	Recovery (%)
Aluminum	6	9800	–	15000	13200	19
Antimony	6	2.8	–	7.2	4.9	21
Arsenic	6	81	–	110	89	85
Barium	6	170	–	200	190	25
Beryllium	6	0.73	–	1.1	0.93	--
Cadmium	6	43	–	56	47	90
Calcium	6	14000	–	17000	14000	61
Chromium	6	12	–	18	15	29
Cobalt	6	5.5	–	9.0	7.5	75
Copper	6	120	–	160	130	95
Iron	6	14000	–	18000	15000	54
Lead	6	1100	–	1400	1300	91
Magnesium	6	5000	–	6600	5700	54
Manganese	6	450	–	580	460	71
Mercury	6	6.3	–	8.3	7.4	100
Nickel	6	13	–	18	15	72
Potassium	6	3300	–	4600	3900	16
Selenium	5	1.4	–	1.9	1.7	85
Silver	6	4.0	–	6.1	5.5	89
Sodium	5	140	–	210	180	1.5
Thallium	5	0.71	–	3.1	2.1	68
Vanadium	6	24	–	34	28	36
Zinc	6	310	–	380	350	85

List of CLP and non-CLP Participating Laboratories: A4 Scientific, Inc.; Bonner Analytical Testing Co.; Chem Tech Consulting Group; Datachem Laboratories, Inc.; Liberty Analytical Corporation; MSE Laboratory Services; Shealy Environmental; SVL Analytical Inc.