SAMPLING AND ANALYSIS PLAN/QUALITY ASSURANCE PROJECT PLAN
FOR
GOLD KING MINE ER
EPA REGION 9 OPERATIONS
FARMINGTON, SAN JUAN COUNTY, NEW MEXICO

Prepared for

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Region 9

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SAP/QAPP Revision Log

Project: Gold King Mine ER Region 9 Operations
Task Monitors: Robert Wise
Technical Direction Document (TDD): 0002/1302-T2-R9-15-08-0001

Date	Revision Number	Reason for Change of Scope/Procedures	SAP Section Superseded

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LIST OF APPENDICES

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LIST OF ACRONYMS

µg/L	microgram per liter
°C	degrees Celsius
%D	percent difference
%R	percent recovery
%RSD	percent relative standard deviation
AES	Atomic Emission Spectrometry
ASTM	American Society for Testing and Materials
B	bias
CA	Corrective Action
CB	calibration blank
CCB	continuing calibration blank
CCV	continuing calibration verification
CDPHE	Colorado Department of Public Health and Environment
CLP	Contract Laboratory Program
CO	Contracting Officer
COC	Chain-of-Custody
COR	Contracting Officer Representative
CRL	Central Regional Laboratory
CVAA	Cold Vapor Atomic Absorption
DAO	Delegated Approval Officer
DQI	Data Quality Indicator
DQO	Data Quality Objective
EDD	electronic data deliverable
EPA	United States Environmental Protection Agency
GKM	Gold King Mine
gpm	gallons per minute
GPS	Global Positioning System
HASP	Health and Safety Plan
ICB	initial calibration blank
ICP	inductively coupled plasma
IDW	investigation-derived waste
ISTD	Instrument Standard
LCS	laboratory control sample
LOD	limit of detection
LOQ	limit of quantitation
MDL	method detection limit
mg/kg	milligram per kilogram
MPC	Measurement Performance Criteria
MS	matrix spike
MSD	matrix spike duplicate
NA	not applicable
NRCS	Natural Resource Conservation Service
NRWQC	National Recommended Water Quality Criteria
OSC	On-Scene Coordinator
P.E.	Professional Engineer
POC	Point of Contact
PPE	Personal Protective Equipment
PQL	Project Quantitation Limit
PQO	Project Quality Objectives

LIST OF ACRONYMS

PTL	Project Team Lead
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
RCRA	Resource Conservation and Recovery Act
RL	reporting limit
RPD	relative percent difference
RSD	relative standard deviation
RSL	Recreational Screening Level
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure
SRM	Standard Reference Material
START	Superfund Technical Assessment and Response Team
SVOC	Semi-volatile Organic Compounds
TAL	target analyte list
TBD	to-be-determined
TDD	Technical Direction Document
TDS	total dissolved solids
TSA	Technical Systems Audit
TSS	total suspended solids
UFP-QAPP	Uniform Federal Policy–Quality Assurance Project Plan
USACE	United States Army Corps of Engineers
USDA	United States Department of Agriculture
USGS	United States Department of the Interior Geologic Survey
VOC	Volatile Organic Compounds
WAM	Work Assignment Manager
WESTON	Weston Solutions, Inc.

EXECUTIVE SUMMARY

PROBLEM STATEMENT

The Gold King Mine site consists of a mine adit and waste rock piles in the Cement Creek watershed. The mine historically discharged low pH, metals-laden water at a flow rate of approximately 500 gallons per minute (gpm). The water flows through a concrete channel, through a Parshall flume, through a plastic conduit, over a steep waste rock pile, and either into the subsurface (low flow), or toward North Fork Cement Creek. A pond was constructed at the base of the waste rock pile to collect water during 2014 site activities. North Fork Cement Creek flows into Cement Creek, which discharges to the Animas River in Silverton, Colorado.

On August 5, 2015, approximately 3 million gallons of acidic metals-laden water was unexpectedly released from the Gold King Mine. The mine water flowed across the site and to Cement Creek and then to the Animas River in Silverton, Colorado. The Animas River connects with the San Juan River near the town of Farmington, New Mexico. The San Juan River flows west northwest through the Navajo Nation, intersecting the Colorado River in Lake Powell, about 30 miles northeast of Page, Arizona.

PROJECT GOAL - The goal of the study is to determine the impact of the release on downstream waters and water users in the jurisdiction of the U.S. Environmental Protection Agency Region 9, specifically, the Navajo Nation (including portions of New Mexico, Colorado, Utah and Arizona), as well as potentially non-Navajo lands in Arizona and California.

PROJECT AREA - The study area includes the San Juan and Colorado Rivers from the confluence of the Animas River near Farmington, New Mexico to the confluence of the San Juan River and Lake Powell near Page, Arizona.

PROJECT TASKS - EPA has requested that Superfund Technical Assessment and Response Team (START) perform the following tasks:

a. Collect samples from areas potentially affected by the release, including surface water, sediment, groundwater, and/or soil;

b. Have the samples analyzed for contaminants of concern by a subcontracted laboratory;

c. Perform data validation of analytical data packages received;

d. Provide global positioning system (GPS) data for sampling locations; and

e. Provide georeferenced site photo documentation.

Introduction

This Sampling and Analysis Plan (SAP)/Quality Assurance Project Plan (QAPP) identifies the data collection activities and associated quality assurance/quality control (QA/QC) measures specific to the mine water release that occurred on August 5, 2015, from the Gold King Mine site (the Site) located near Silverton, San Juan County, Colorado. This QAPP/SAP is specific to activities being performed by the Weston Solutions, Inc. (WESTON®) Superfund Technical Assessment and Response Team (START) contractor for EPA Region 9.

Sampling for this emergency response will consist of surface water and sediment sampling at specific locations downstream from the Site on the San Juan and Colorado rivers. Worksheets 17 through 23 in this QAPP address sampling procedures. This SAP/QAPP has been prepared as part of the emergency response activities for the site(s). Any deviations or modifications to the approved SAP/QAPP will be documented using the Revision Log.

This SAP/QAPP is produced in accordance with the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP). A QAPP is a formal document describing in comprehensive detail the necessary QA, QC, and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria. A QAPP presents the steps that should be taken to ensure that environmental data collected are of the correct type and quality required for a specific decision or use. The UFP-QAPP is a consensus document prepared by the Intergovernmental Data Quality Task Force (IDQTF).

Addendums to this document will be issued if needed to address any new procedures required.

Project Organization and Team

Refer to the QAPP Worksheet 3 & 5, and 4, 7, & 8 for the program organizational chart, communication pathways, personnel responsibilities and qualifications, and special personnel training requirements. Project-specific information is provided below.

The following are key individuals identified for this project:

Name	Title/Role	Organization	Receive Copy of SAP?
Robert Wise	OSC	EPA	Y
Maggie Walden	OSC	EPA	Y
Brett Moxley	OSC	EPA	Y
Randy Nattis	OSC	EPA	Y
Jon Colomb	Project Manager/Project Team Lead	START	Y
Patricia Beckley	Field Team Manager	START	Y
Rick Mehl	Resource Manager	START	Y
Niel Ellis	Health and Safety	START	Y
Lisa Graczyk	Program QA Manager	START	Y
Ian Bruce	IT Manager	START	Y

The approved SAP/QAPP will be kept on file at WESTON. The project team lead (PTL) will distribute the most current copy of the project QA documents via electronic or hard copy, as directed by the on-scene coordinator (OSC). Files for this project will be kept in accordance with Section H.20 of Contract No.: EP-S5-13-05, stating a length of 10 years from close of the project or end of litigation.

The following summarizes the relationship of the UFP-QAPP worksheets to the QA/G5 guidance.

Crosswalk: UFP-QAPP Workbook to 2106-G-05 QAPP

Optimized UFP-QAPP Worksheets		2106-G-05 QAPP Guidance Section	
A. Project Management and Objectives			
1 & 2	Title and Approval Page	2.2.1	Title, Version, and Approval/Sign-Off
3 & 5	Project Organization and QAPP Distribution	2.2.3	Distribution List
		2.2.4	Project Organization and Schedule
4, 7, & 8	Personnel Qualifications and Sign-Off Sheet	2.2.1	Title, Version, and Approval/Sign-Off
		2.2.7	Special Training Requirements and Certifications
6	Communication Pathways	2.2.4	Project Organization and Schedule
9	Project Planning Session Summary	2.2.5	Project Background, Overview, and Intended Use of Data
10	Conceptual Site Model	2.2.5	Project Background, Overview, and Intended Use of Data
11	Project/Data Quality Objectives	2.2.6	Data/Project Quality Objectives and Measurement Performance Criteria
12	Measurement Performance Criteria	2.2.6	Data/Project Quality Objectives and Measurement Performance Criteria
13	Secondary Data Uses and Limitations	Chapter 3	QAPP ELEMENTS FOR EVALUATING EXISTING DATA
14 & 16	Project Tasks & Schedule	2.2.4	Project Organization and Schedule
15	Project Action Limits and Laboratory-Specific Detection/Quantitation Limits	2.2.6	Data/Project Quality Objectives and Measurement Performance Criteria
B. Measurement/Data Acquisition			
17	Sampling Design and Rationale	2.3.1	Sample Collection Procedure, Experimental Design, and Sampling Tasks
18	Sampling Locations and Methods	2.3.1	Sample Collection Procedure, Experimental Design, and Sampling Tasks
		2.3.2	Sampling Procedures and Requirements
19 & 30	Sample Containers, Preservation, and Hold Times	2.3.2	Sampling Procedures and Requirements
20	Field Quality Control (QC)	2.3.5	QC Requirements
21	Field Standard Operating Procedures (SOPs)	2.3.2	Sampling Procedures and Requirements

Optimized UFP-QAPP Worksheets		2106-G-05 QAPP Guidance Section	
22	Field Equipment Calibration, Maintenance, Testing, and Inspection	2.3.6	Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables
23	Analytical SOPs	2.3.4	Analytical Methods Requirements and Task Description
24	Analytical Instrument Calibration	2.3.6	Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables
25	Analytical Instrument and Equipment Maintenance, Testing, and Inspection	2.3.6	Instrument/Equipment Testing, Calibration and Maintenance Requirements, Supplies and Consumables
26 & 27	Sample Handling, Custody, and Disposal	2.3.3	Sample Handling, Custody Procedures, and Documentation
28	Analytical QC and Corrective Action	2.3.5	QC Requirements
29	Project Documents and Records	2.2.8	Document and Records Requirements
C. Assessment/Oversight			
31, 32, & 33	Assessments and Corrective Action	2.4	ASSESSMENTS AND DATA REVIEW (CHECK)
		2.5.5	Reports to Management
D. Data Review			
34	Data Verification and Validation Inputs	2.5.1	Data Verification and Validation Targets and Methods
35	Data Verification Procedures	2.5.1	Data Verification and Validation Targets and Methods
36	Data Validation Procedure	2.5.1	Data Verification and Validation Targets and Methods
37	Data Usability Assessment	2.5.2	Quantitative and Qualitative Evaluations of Usability
		2.5.3	Potential Limitations on Data Interpretation
		2.5.4	Reconciliation with Project Requirements

Worksheet 1 & 2 — Title and Approval Page

(UFP-QAPP Manual Section 2.1)
(EPA 2106-G-05 Section 2.2.1)

1. Project Identifying Information

a) Site Name/Project Name: Gold King Mine Emergency Response (ER)

b) Site Location/Number: Silverton, San Juan County, Colorado

c) Contract/Work Assignment Number: EP-S5-13-01/TDD # 0002/1302-T2-R9-15-08-0001

2) List Plans and reports from previous investigation relevant to this project.
Not applicable

Lead Investigative Organization's Program Manager:

Joe DeFao/WESTON
Printed Name/Title

Joe DeFao ***8/31/2015***
Signature/Date

Lead Investigative Organization's Project Manager:

Jon Colomb/WESTON
Printed Name/Title

Joe DeFao for Jon Colomb 8/31/2015
Signature/Date

Lead Investigative Organization's Delegated Quality Assurance Manager:

Lisa Graczyk/CSS-Dynamac
Printed Name/Title

Lisa Graczyk ***8/31/2015***
Signature/Date

Federal Regulatory Agency Contracting Officer's Representative:

Phillip Ingram/EPA
Printed Name/Title

Signature/Date

Federal Regulatory Agency Work Assignment Manager:

Robert Wise/EPA
Printed Name/Title

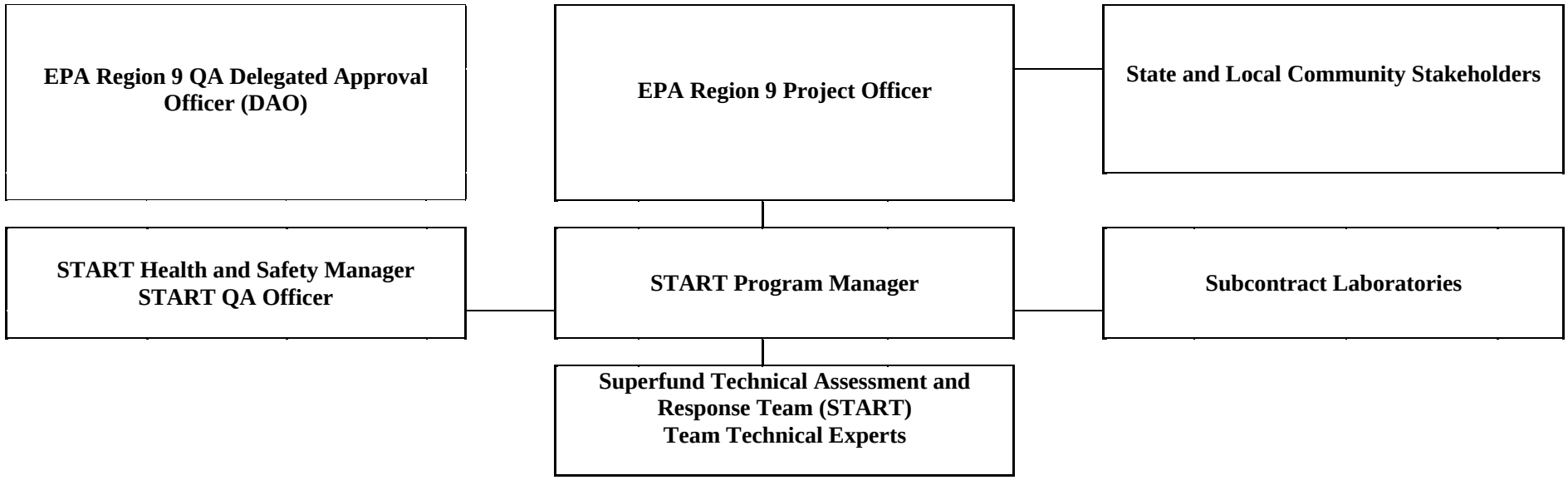
Signature/Date

Document Control Numbering System: 0066-08-AAGP

Worksheet 3 & 5 — Project Organization and QAPP Distribution

(UFP-QAPP Manual Section 2.3 and 2.4)
(EPA 2106-G-05 Section 2.2.3 and 2.2.4)

The most current and approved copy of the QAPP will be delivered to recipients using email or a web-based system in use by EPA and START at the time of submittal.



Worksheet 4, 7 & 8 — Personnel Qualifications

(UFP-QAPP Manual Sections 2.3.2 - 2.3.4)
(EPA 2106-G-05 Section 2.2.1 and 2.2.7)

Name	**Project Title / Role**	**Education / Experience**	**Specialized Training / Certifications[1]**	**Training Provider[2]**
Joe DeFao	Program Manager / Point of contact (POC) with EPA Contracting Officer (CO), Contracting Officer Representative (COR), and Team Leader. Ensures adherence to contract and project requirements/deliverables.	B.S., Environmental Science, 17 years of diversified technical and program management experience on EPA Superfund contracts.	FEMA IS Levels 100, 200, 700, and 800, and EPA Hazard Ranking System, Documentation Record, Preliminary Assessment, Site Inspection, Air Monitoring, Emergency Response, Level A Team, and Multi-Media Sampling	WESTON, Registered Training Organization – Various
Jon Colomb	Project Manager	B.S., Geology, 5 years' experience Region 5 START contract, two years' experience Region 9 START contract.	FEMA IS Levels 100, 200, 300, 400, 700, and 800; 32-Hour Advanced Radiation Training; Response Readiness Training; Biological Response Training; Nuclear, Biological, and Chemical Emergency Responders Training; 40-Hour OSHA Hazardous Waste Site Worker Training; 8-Hour OSHA Refresher Training; First Aid and CPR	WESTON, Registered Training Organization – Various

Name	Project Title / Role	Education / Experience	Specialized Training / Certifications[1]	Training Provider[2]
Lisa Graczyk	QA Officer / Delegated authority for quality systems implementation and management, review and approval of quality documents, review and approval of contract deliverables, and performing quality assessments and quality systems audits. Maintains authority over implementation of quality systems management.	B.S. Chemistry, over 20 years' experience working on EPA Technical Assistance Team contract (precursor to START) and START contracts; 18 years' experience performing data validation and preparing QAPPs	FEMA IS Levels 100, 200, 300, 400, 700, and 800; 32-Hour Advanced Radiation Training; Response Readiness Training; Biological Response Training; Nuclear, Biological, and Chemical Emergency Responders Training; 40-Hour OSHA Hazardous Waste Site Worker Training; 8-Hour OSHA Refresher Training; First Aid and CPR	CSS-Dynamac, WESTON, Registered Training Organization – Various
Niel Ellis	PTL / Supervises field sampling and coordinates all field activities. Ensures all training/certifications are satisfied for field team personnel.	B.S. Geographic Resources and Environmental Studies; 9 years' experience	40-Hour OSHA Hazardous Waste Site Worker Training; 8-Hour OSHA Refresher Training; First Aid and CPR	Registered Training Organization – Various
Ian Bruce	Field Support / Assist with field sampling activities.	B.S. Biology with GIS Minor, M.S. Multidisciplinary Studies; 10 years' experience	40-Hour OSHA Hazardous Waste Site Worker Training; 8-Hour OSHA Refresher Training; First Aid and CPR	Registered Training Organization – Various
Other field Technicians, Geologists, Environmental Scientists, Engineers as needed	To be determined (TBD)	TBD	40-Hour OSHA Hazardous Waste Site Worker Training; 8-Hour OSHA Refresher Training; First Aid and CPR	Registered Training Organization – Various

[1] Training records and/or certificates are on file at the Weston Solutions, Inc., West Chester, Pennsylvania office and are available upon request.

[2] Training provider and date of training will vary from person to person due to individual scheduling of training.

Worksheet 6 — Communication Pathways

(UFP-QAPP Manual Section 2.4.2)
(EPA 2106-G-05 Section 2.2.4)

Communication Drivers	Organization	Name	Contact Information	Procedures (Timing, Pathways, Documentation, etc.)
Regulatory Agency Interface	EPA CO	Ramon Albizu	415-972-3091	Maintain lines of communication between EPA CO and WESTON Program Manager.
Approves Site-Specific QA Documents	EPA OSC/Task Monitor	Robert Wise	562-889-2572	Approves site-specific SAPs and/or QAPPs in accordance with EPA guidance documents and policy. Provides guidance or instruction for site-specific QA documents.
POC with EPA CO	WESTON Program Manager	Joe DeFao	925-948-2677	Maintain lines of communication between EPA CO, Work Assignment Manager (WAM), COR and Team Leader.
Manage all Project Phases	WESTON Project Manager	Jon Colomb	773-947-4064	Manage day to day operations of the project. Reports to Program Manager and EPA WAM/COR issues with cost, schedule, etc.
Health and Safety Monitoring/Reporting	WESTON Health and Safety Manager	Niel Ellis	510-333-7274	Communicates with PTL and project manager regarding safety issues/reporting on a daily basis, when required.
QAPP Changes Prior to Field Work and Field and Analytical Corrective Actions	WESTON Delegated QA Manager	Ben Castellana	818-371-5388	Communicates changes to Removal Action and Emergency Response QAPP to QA Officer and site-specific SAPs and/or QAPPs to project manager and EPA WAM/COR. Communicates with PTL to determine need for field and analytical corrective actions.
QAPP Changes in the Field and Daily Field Progress Reports	WESTON PTL	Jon Colomb	773-947-4064	Communicate QAPP changes and field activities to Delegated QA Manager, EPA WAM/COR, and Project Manager on a daily basis, when required.
QAPP Amendments	WESTON QA Officer	Lisa Graczyk	312-305-6745	Major changes to the Removal Action and Emergency Response QAPP must be approved by the QA Officer and Delegated QA Manager before implementation.
Data Tracking and Management, Release of Analytical Data	WESTON Data Manager	Ian Bruce	509-845-5547	The need for corrective actions will be determined by the Delegated QA Manager upon review of the data. No analytical data will be released prior to validation and all releases must be approved by the Delegated QA Manager and EPA WAM/COR.

Worksheet 6 — Communication Pathways (Continued)

(UFP-QAPP Manual Section 2.4.2)
(EPA 2106-G-05 Section 2.2.4)

Communication Drivers	Organization	Name	Contact Information	Procedures (Timing, Pathways, Documentation, etc.)
Lab Data Quality Issues	Laboratory Project Manager – TestAmerica Laboratories	Sheila Hoffman	912-354-7858, ext. 3004	The laboratory project manager will report any issues with project samples to the QA Officer within 2 business days.

Worksheet 9 — Project Planning Session Summary

(UFP-QAPP Manual Section 2.5.1 and Figures 9-12)
(EPA 2106-G-05 Section 2.2.5)

Date: 8/7/15

Location: Email – OSC Joyce Ackerman to START Program Manager Scott Butterfield

Purpose: Identification of sampling needs for Gold King Mine release assessment

Notes/Comments: OSC Joyce Ackerman sent email to START that identified needs for sampling based on public meeting that OSC Pete Stevenson attended. START followed up with brief phone call with OSC Stevenson confirming that START will prepare the SAP. The following are the anticipated sampling needs:

- Water quality samples with field parameters and at drinking water intakes
- Residential wells along the river on request
- Water in irrigation ditches that were impacted
- River sediments
- Sediment in irrigation ditches
- Soil samples from irrigated land
- Consider long term monitoring methods

Consensus Decisions Made:

- START Region 8 to prepare SAP

Date: 8/16/15

Location: Email – OSC Robert Wise to START Region 9 Deputy Response Coordinator, Ben Castellana

Purpose: Preparation of Region 8 QAPP-SAP and incorporation of information into a similar document for Region 9

Notes/Comments: OSC Robert Wise sent email to START indicating that Region 9 should revise the Region 8 QAPP-SAP to address Region 9-specific Data Quality Objectives (DQOs).

Consensus Decisions Made:

- START to prepare SAP

Action Items:

Action	Responsible Party	Due Date
Prepare site-specific SAP	START	8/28/15

Worksheet 10 — Conceptual Site Model

(UFP-QAPP Manual Section 2.5.2)
(EPA 2106-G-05 Section 2.2.5)

- **Problem Definition**

The Gold King Mine site consists of a mine adit and waste rock piles in the Cement Creek watershed. The mine historically discharged low pH, metals-laden water at a flow rate of approximately 500 gallons per minute (gpm). The water flows through a concrete channel, through a Parshall flume, through a plastic conduit, over a steep waste rock pile, and either into the subsurface (low flow), or toward North Fork Cement Creek. A pond was constructed at the base of the waste rock pile to collect water during 2014 site activities. North Fork Cement Creek flows into Cement Creek, which discharges to the Animas River in Silverton, Colorado. The Animas River flows into the San Juan River near Farmington, New Mexico, and the San Juan River flows into the Colorado River in Lake Powell in Utah.

On August 5, 2015, approximately 3 million gallons of acidic metals-laden water was unexpectedly released from the Gold King Mine. The mine water flowed across the site and to Cement Creek and then to the Animas River in Silverton, Colorado. The orange-red runoff from this material was observed as far south as Farmington; there is concern that water quality and sediment in the watershed downgradient are affected. The San Juan River is a primary source of drinking water, as well as crop and livestock irrigation, for the communities through which it flows, as well as much of the Navajo Nation.

Region 9 has been tasked with monitoring and sampling portions of the San Juan River and Lake Powell that are down-gradient of the initial release and that are located within the coverage area of EPA Region 9.

- **Background Information/Site History**

The Red and Bonita Mine and the Gold King Mine are in the Cement Creek watershed, which originates high in the rugged San Juan Mountains of southwestern Colorado near the San Juan County and Ouray County line on the south slopes of Red Mountain Number 3 and the north slopes of Storm Peak.

The rugged and relatively inaccessible western San Juan Mountains were first prospected in the area around Silverton in 1860. The extension of the railroad from Silverton up Cement Creek to Gladstone in 1899 encouraged the mining of low grade ores, and the establishment of a lead-zinc flotation plant in 1917 allowed for the treatment of the low grade complex ores found in the area. Over a 100-year period between 1890 and 1991, mining activities in the upper Animas River Basin, including Cement Creek, produced the waste rock and mill tailings sources from which contamination spread throughout the surface water pathway. Over 18 million tons of ore were mined from the Upper Animas River Basin area, with more than 95 percent of this being dumped directly into the Animas River and its tributaries in the form of mill waste. Older waste rock piles and stope fillings were reworked and sent to mills as technology allowed lower grade ores to be processed economically. A great deal of abandoned waste was also milled during World War II when many older mining and milling structures were cannibalized for scrap metal. The last producing mine in the area was the Sunnyside Mine, which ceased production in 1991. The closing of the Sunnyside mine

occurred after Lake Emma drained into the mine and out the American Tunnel into Cement Creek in 1978. The flood water from the Lake Emma "blow-out" was reported to have flowed down Cement Creek in a 10-foot wall of water that would have transported a large quantity of tailing and other mine waste down Cement Creek to the Animas River.

Numerous historic and now abandoned mines exist within a two-mile radius of Gladstone. They include: the Upper Gold King 7 Level, American Tunnel, Grand Mogul, Mogul, Red and Bonita, Evelyne, Henrietta, Joe and John, and Lark mines. Some of these mines have acid mine drainage that flows between 30 and 300 gpm directly or indirectly into Cement Creek and eventually into the Animas River. The confluence of Cement Creek and the Animas River is located approximately eight miles downstream of Gladstone.

The Animas River Stakeholders Group; U.S. Bureau of Land Management; Division of Reclamation, Mining and Safety; EPA; and private stakeholders have participated in various projects to manage mine waste and to reduce the flow of contaminated water in the watershed. In addition, under the terms of a consent decree with the State of Colorado, Sunnyside Gold Mine Company performed several large scale projects related to historic operations on properties associated with the company's operations. One project was plugging (installing concrete bulkheads) within the Sunnyside mine workings, including the American Tunnel, during the period from 1996 to 2002. The American Tunnel is located in Gladstone, approximately ¾ to 1 mile south of the Red and Bonita and Gold King mines. During the mine operation, the American Tunnel discharged approximately 1,700 gpm of metal laden water and was treated prior discharging to Cement Creek. Following the installation of the last of the three plugs, flow from the American Tunnel has decreased to approximately 100 gpm, the result of leakage around the concrete bulkhead. The flow from the Red and Bonita Mine, the Gold King (Level 7) Mine, and the Mogul Mine all experienced significant increases in flow following the plugging of the American Tunnel.

Contaminants found in the Red and Bonita discharge water include low pH and metals. Cadmium concentrations from the mine discharge ranged from 33.3 micrograms per liter (µg/L) to 39.3 µg/L, copper concentrations ranged from 4.5 µg/L to 50.6 µg/L, iron concentrations range from 76,700 µg/L to 97,600 µg/L, lead concentrations ranged from 34 µg/L to 71.2 µg/L, and zinc concentrations ranged from 13,600 µg/L to 17,500 µg/L.

Contaminants in the Gold King discharge water include low pH and metals. From 2009 to 2011, cadmium concentrations from the mine discharge ranged from 38 µg/L to 136 µg/L, copper concentrations ranged from 2400 µg/L to 12,000 µg/L, lead concentrations ranged from 2 µg/L to 29 µg/L, and zinc concentrations ranged from 14,500 µg/L to 44,700 µg/L.

Background Reference:

- URS Operating Services, Inc. 2010. Red and Bonita Mine Remedial Action Field Sampling Plan. October 2010.
- Weston Solutions Inc., 2014. Sampling and Analysis Plan for Red and Bonita Mine. Nov 2014.

Worksheet 11 — Project/Data Quality Objectives

(UFP-QAPP Manual Section 2.6.1)
(EPA 2106-G-05 Section 2.2.6)

Data quality objectives are based on the following seven steps.

State the Problem

On August 5, 2015, approximately 3 million gallons of acidic metals-laden water and sludge was unexpectedly released from the Gold King Mine. The mine water flowed across the site and to Cement Creek and then to the Animas River in Silverton, Colorado. The waste water from the mine flowed along the Animas River to the San Juan River, potentially affecting water quality and sediments across the Navajo Nation.

EPA has requested that START assist to:

a. Collect samples from areas potentially affected by the release, including surface water, sediment, groundwater, and/or soil;

b. Analyze the samples for contaminants of concern at a subcontracted laboratory;

c. Perform data validation of the analytical data packages;

d. Provide GPS data for sampling locations; and

e. Provide georeferenced site photo documentation.

Identify the Goals of the Study

The goals of the study are to:

- Determine the impact of the release on downstream waters including Lake Powell and potential water users.

The primary study questions are:

- What areas were affected by the release from Gold King Mine?
- What are the water quality conditions, as indicated by field and laboratory analyses, in the San Juan and Colorado Rivers and Lake Powell?
- Based on laboratory analyses, are other media such as sediment, soil or groundwater affected by the mine water release?

Identify Information Inputs

To support the above objectives, the following data will be collected:

- Validated surface water and sediment sample analytical data for metals. If needed, groundwater and soil may also be sampled.

- Field measurements of surface water and/or groundwater quality.
- Geospatial data of sampling locations.
- Field documentation and photographs of site activities.

Define the Boundaries of the Study

Spatial Boundaries: The study area includes the San Juan and Colorado Rivers between Farmington, New Mexico and Page Arizona.

Temporal Boundaries: The study will represent conditions from after the release from the Gold King Mine and ending at an as yet undetermined date. A sampling schedule and sampling plan is included in Worksheets 14, 16 and 17.

Practical constraints on data collection: Scheduling adjustments will be made if physical constraints on planned field events occur due to weather, safety considerations, or problems that may impact the technical quality of the measurements.

Develop the Analytic Approach

Samples will be collected from locations designated in the field by an EPA OSC. Surface water samples will be sent for laboratory analysis of total and dissolved target analyte list (TAL) metals plus molybdenum, pH, alkalinity, hardness, total dissolved solids (TDS) and total suspended solids (TSS). Sediment samples will be sent for laboratory analysis for TAL metals plus molybdenum,

The surface water results will be compared to several screening levels including:

- Drinking water Federal and/or State Maximum Contaminant Levels (MCLs);
- EPA Recreational Screening Levels (RSL) for surface water that are based on recreational scenarios in which an adult or child hiker/camper is exposed to surface water and sediment; criteria were arrived at through risk-based calculations
- National Recommended Water Quality Criteria (NRWQC) for Aquatic Acute and Aquatic Chronic
- Navajo Nation Surface Water Quality Standards for Agricultural Water Supply
- Navajo Nation Surface Water Quality Standards for Livestock Watering

The sediment results will be compared to the following screening levels:

- EPA RSLs for sediment that are based on recreational scenarios in which an adult or child hiker/camper is exposed to surface water and sediment; criteria were arrived at through risk-based calculations

Specify Performance or Acceptance Criteria

All data will be reviewed and verified to ensure that they are acceptable for the intended use. All data will be validated in accordance with the procedures specified in Worksheet 36. QC criteria for analytical data are listed in Worksheet 28.

Decision errors will be limited to the extent practicable by following approved EPA methods and applicable standard operating procedures (SOP) listed in Worksheet #21. Any deviation from the SAP/QAPP will be documented.

Develop the Detailed Plan for Obtaining Data

Water, sediment, and soil samples will be collected at locations designated by the EPA OSC. Worksheets 17, 18, 20, and 21 present the sampling design and procedures.

Field water quality parameters will be obtained using a Horiba (U50 or U53), YSI, or similar water quality meter. Field monitoring will be used to measure the quality of water, with emphasis on pH and turbidity measurements. Visual observations of water clarity will be recorded.

Worksheets 19, 20, 24-28 and 30 specify analytical requirements. Data from the laboratories will be delivered in a SCRIBE-formatted electronic data deliverable (EDD) and an Adobe pdf file. The data will be documented in the site activities report. A site-specific Data Management Plan is provided in Appendix B.

Worksheet 12 — Measurement Performance Criteria Tables

(UFP-QAPP Manual Section 2.6.2)
(EPA 2106-G-05 Section 2.2.6)

The following are typical examples for Inorganics for all media.

Matrix: All
Analytical Group or Method: Inorganics
Concentration Level: All

Data Quality Indicator (DQI)	QC Sample or Measurement Performance Activity	Measurement Performance Criteria (MPC)
Field Precision	Field Duplicate	1 per 10 samples Relative percent difference (RPD) ≤ 30 for water samples RPD ≤ 50 for sediment samples
Field Representativeness/ Accuracy/Bias	Equipment Rinsate Blank	1 per 20 samples/matrix or 1 per day for non-dedicated sampling equipment <Limit of Quantitation (LOQ)
Accuracy/Bias	Matrix Spike (MS)/Matrix Spike Duplicate(MSD)	1 per 20 samples per matrix Percent recovery (%R) as specified in the EPA National Functional Guidelines for Inorganic Superfund Data Review (NFG) RPD <20%
Laboratory Precision	Laboratory Duplicate	1 per 20 samples per matrix RPD <20%
Accuracy/Precision	Initial Calibration	Daily prior to sample analysis (minimum 1 standard and a blank)
Accuracy/Bias	Initial Calibration Verification	Daily after initial calibration All analytes within ±10% of expected value
Accuracy/Bias	Calibration Blank (CB) Initial Calibration Blank/Continuing Calibration Blank (ICB/CCB)	After every calibration/verification No analytes detected ≥ Limit of Detection (LOD)
Precision/Accuracy	Calibration Verification (Instrument Check Standard)	At beginning of analytical sequence, after every 10 samples and at the end of the analysis sequence All analytes within ±10% of expected value and relative standard deviation (RSD) of replicate integrations <5%
Precision	Interference Check Solution	At beginning of analytical run ± 20% of the expected value
Precision/Accuracy	Serial Dilution	Method-specific
Accuracy/Bias	Post Digestion Blank	Each digestion batch %R. Analyte-specific

Data Quality Indicator (DQI)	QC Sample or Measurement Performance Activity	Measurement Performance Criteria (MPC)
Laboratory Representativeness/ Accuracy/Bias	Method Blank	1 per batch per matrix or 1 per 20 samples, whichever is more frequent No analyte ≥ reporting limit (RL)
Laboratory Accuracy	Laboratory Control Sample (LCS)	1 per batch per matrix or 1 per 20 samples, whichever is more frequent %R as specified in NFG
Sensitivity	Determined by Method Detection Limit Study	LOQ ≤ required quantitation limits for project

Worksheet 13 — Secondary Data Uses and Limitations

(UFP-QAPP Manual Section 2.7)
(EPA 2106-G-05 Chapter 3: QAPP Elements for Evaluating Existing Data)

Sources and types of secondary data include but are not limited to the following:

Data Type	Data Source (originating organization, report title and date)	Data Uses Relative to Current Project	Factors Affecting the Reliability of Data and Limitations on Data Use
Soils	United States Department of Agriculture (USDA) Natural Resource Conservation Service (NRCS) Web Soil Survey and Soil Data Mart	Identify soil types, composition, elevation, precipitation, setting, properties and qualities, profile, land capability and farmland classification	
Geology/Hydrology	United States Department of the Interior Geologic Survey (USGS) Topographic and Geologic Maps, State Agencies/EPA My WATERS Mapper	Identify area Geology, topography, surface water bodies, hydrologic units/watersheds, water quality, etc.	
Streams/Drainages	EPA My WATERS Mapper and USGS Topographic Maps	Topography, surface water bodies, hydrologic units/watersheds, water quality, etc.	
Registered Wells	State and Tribal Databases	Identify well locations, drinking water wells, and groundwater use	
Meteorological	National Weather Service	Seasonal fluctuations in storm water runoff	
Property Boundaries	County Assessor and Plot Maps	Identify property boundaries to determine site requirements for assessment	
Environmentally Sensitive Areas	U.S. and State Fish & Wildlife Service Maps, Publications, and Databases	Identify sensitive and endangered species and environments potentially present on or in removal action/emergency response area	
Wetlands	USDA NRCS Web Soil Survey and Soil Data Mart (Hydric Soils List), and U.S. and State Fish & Wildlife Databases	Identify wetlands and associated sensitive and endangered species and environments potentially present on or in removal action/emergency response area	
Historical and Current Site Use and Investigations	Historical Records, Previous Investigations, Visual Site Reconnaissance, and Interviews	Supplemental background information on historical site use and current site conditions, and previous investigations	

The project team will carefully evaluate the quality of secondary data (in terms of precision, bias, representativeness, comparability, and completeness) to ensure they are of the type and quality necessary to support their intended uses. When evaluating the reliability of secondary data and determining limitations on their uses, the project team will consider the source of the data, the time period

Worksheet 13 — Secondary Data Uses and Limitations (Continued)

(UFP-QAPP Manual Section 2.7)
(EPA 2106-G-05 Chapter 3: QAPP Elements for Evaluating Existing Data)

during which they were collected, data collection methods, potential sources of uncertainty, the type of supporting documentation available, and the comparability of data collection methods to the currently proposed methods. With respect to secondary analytical data that will be utilized to support critical decisions, such as comparison of contaminant levels with applicable standards, a detailed review of the data will be necessary to determine the usability of the data. In addition to the qualitative rating of the data source, the project team should complete a data quality review and document the review in a data usability summary. The protocol for completing the data usability report is provided in Worksheet 37.

In accordance with EPA guidance documents *A Summary of General Assessment Factors for Evaluating the Quality of Scientific and Technical Information* (June 2003) and *Guidance for Evaluating and Documenting the Quality of Existing Scientific and Technical Information* (December 2012) (Appendix Q), the following assessment factors will be utilized to assess the quality and relevance of scientific and technical information:

1. **Soundness** – the extent to which the scientific and technical procedures, measures, methods or models employed to generate the information are reasonable for, and consistent with, the intended application.
2. **Applicability and Utility** – the extent to which the information is relevant for the Agency's intended use.
3. **Clarity and Completeness** – the degree of clarity and completeness with which the data, assumptions, methods, quality assurance, sponsoring organizations and analyses employed to generate the information are documented.
4. **Uncertainty and Variability** – the extent to which the variability and uncertainty (quantitative and qualitative) in the information or in the procedures, measures, methods or models are evaluated and characterized.
5. **Evaluation and Review** – the extent of independent verification, validation and peer review of the information or of the procedures, measures, methods or models.

The type of information, sources of information and quantity of information will be project-specific. The following table can be utilized and/or modified as appropriate in the development of the site-specific SAP and/or QAPP and site report to capture the review of the secondary data assessment factors. Assessment factors will be rated as Acceptable, Marginal, Unacceptable, Not Applicable, or Indeterminate.

Citation	Reference Type	Soundness	Applicability and Utility	Clarity and Completeness	Uncertainty and Variability	Evaluation and Review

Worksheet 14 & 16 —Project Tasks & Schedule

(UFP-QAPP Manual Section 2.8.2)
(EPA 2106-G-05 Section 2.2.4)

Activity	Responsible Party	Planned Start Date	Planned Completion Date	Deliverable(s)	Deliverable Due Date
Project Initiation	EPA/START	August 7, 2015	August 7, 2015	N/A	N/A
Develop a SAP/QAPP for Removal and Emergency Response Activities	START	August 18, 2015	August 31, 2015	SAP/QAPP	August 31, 2015
Develop Health and Safety Plan (HASP)	START	August 7, 2015	August 11, 2015	HASP	August 11, 2015
Mobilization/Demobilization	START	August 7, 2015	TBD	Field Notes	N/A
Sample Collection Tasks	START	August 8, 2015	TBD	Field Notes	TBD
Analytical Tasks	START/ Laboratory	August 8, 2015	1-3 days from receipt of samples	Field Notes/Laboratory Reports	TBD
Quality Control Tasks	START	August 8, 2015	TBD	Report of Analyses/Data Package	TBD
Stage 2A Data Validation	START	August 8, 2015	1-2 days from receipt of analytical data package	Validation Summary Report	TBD

Activity	Responsible Party	Planned Start Date	Planned Completion Date	Deliverable(s)	Deliverable Due Date
Summarize Data	START	August 8, 2015	Daily or as needed	Daily Update	TBD

Worksheet 15 — Project Action Limits and Laboratory-Specific Detection/Quantitation Limits

(UFP-QAPP Manual Sections 2.6.2.3 and Figure 15)
(EPA 2106-G-05 Section 2.2.6)

The following information provides representative benchmarks that may be useful for comparison of analytical sample results. Due to the ongoing nature of the project, multiple benchmarks may be appropriate for comparison. Benchmarks utilized for data analysis and reporting will be documented within each report. The examples below are for water samples collected from residential taps based on EPA screening levels and for surface water samples based on Colorado water quality standards. Multiple laboratories may be utilized. Quantitation and detection limits may vary between laboratories based on localized equipment.

Matrix: Water
Analytical Method: 200.7, 200.8, 245.1
Concentration level (if applicable): Low to High

Analyte	CAS.NO	Units	Drinking Water MCL[1]	EPA Camper/Recreational RSL[2]	NRWQC, Aquatic Acute[3]	NRWQC, Aquatic Chronic[3]	Navajo Nation Agricultural Water Supply[4]	Navajo Nation Livestock Watering[4]
Metals, Total and Dissolved								
Aluminum	7429-90-5	ug/L	---	170000	750	87	5000	---
Antimony	7440-36-0	ug/L	6	---	88	30	---	---
Arsenic	7440-38-2	ug/L	10	50	340	150	2000	200
Barium	7440-39-3	ug/L	2000	33000	4	---	---	---
Beryllium	7440-41-7	ug/L	4	330	1	---	---	---
Cadmium	7440-43-9	ug/L	5	83	2	0.25	50	50
Calcium	7440-70-2	ug/L	---	---	---	---	---	---
Chromium	7440-47-3	ug/L	100	210000	570	74	1000	1000
Cobalt	7440-48-4	ug/L	---	50	23	---	50	1000
Copper	7440-50-8	ug/L	1300	6700	13	9	200	500
Iron	7439-89-6	ug/L	---	120000	---	1000	---	---
Lead	7439-92-1	ug/L	15	200	65	2.5	10000	100
Magnesium	7439-95-4	ug/L	---	---	82000	---	---	---
Manganese	7439-96-5	ug/L	---	7800	120	---	---	---
Mercury	7439-97-6	ug/L	2	---	1.4	0.77	---	---
Molybdenum	7439-98-7	ug/L	---	---	73	---	1000	---
Nickel	7440-02-0	ug/L	---	3300	52	52	---	---

Analyte	CAS.NO	Units	Drinking Water MCL[1]	EPA Camper/Recreational RSL[2]	NRWQC, Aquatic Acute[3]	NRWQC, Aquatic Chronic[3]	Navajo Nation Agricultural Water Supply[4]	Navajo Nation Livestock Watering[4]
Metals, Total and Dissolved								
Potassium	9/7/7440	ug/L	---	---	53000	---	---	---
Selenium	7782-49-2	ug/L	50	830	---	5	20	50
Silver	7440-22-4	ug/L	---	---	3	---	---	
Sodium	7440-23-5	ug/L	---	---	---	---	---	---
Thallium	7440-28-0	ug/L	2	1.7	8	---	---	---
Vanadium	7440-62-2	ug/L	---	830	20	---	100	100
Zinc	7440-66-6	ug/L	---	50000	120	120	10000	25000

Notes:
[1] EPA Drinking Water Maximum Contaminating Levels (MCLs), October 29, 2014. Online Address: http://water.epa.gov/drink/contaminants/index.cfm.

[2] EPA Recreational Screening Levels for surface water that are based on recreational scenarios in which an adult or child hiker/camper is exposed to surface water and sediment; criteria were arrived at through risk-based calculations

[3] EPA National Recommended Water Quality Criteria, June 29, 2015. Online Address: http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm. Values not adjusted for hardness.

4 Navajo Nation Surface Water Quality Standards 2007. Online Address: http://water.epa.gov/scitech/swguidance/standards/wqslibrary/upload/2009_03_31_standards_wqslibrary_tribes_navajo.pdf

Matrix: Sediment
Analytical Method: 6010C, 6020A, 7471A
Concentration level (if applicable): Low to High

Analyte	CAS.NO	Units	EPA Camper/ Recreational RSL[1]
Metals			
Aluminum	7429-90-5	mg/kg	3300000
Antimony	7440-36-0	mg/kg	1300
Arsenic	7440-38-2	mg/kg	4200
Barium	7440-39-3	mg/kg	670000
Beryllium	7440-41-7	mg/kg	6700
Cadmium	7440-43-9	mg/kg	1700
Calcium	7440-70-2	mg/kg	---
Chromium	7440-47-3	mg/kg	4300000
Cobalt	7440-48-4	mg/kg	1000
Copper	7440-50-8	mg/kg	130000
Iron	7439-89-6	mg/kg	2300000
Lead	7439-92-1	mg/kg	20000
Magnesium,	7439-95-4	mg/kg	---
Manganese	7439-96-5	mg/kg	160000
Mercury	7439-97-6	mg/kg	1000
Molybdenum	7439-98-7	mg/kg	17000
Nickel	7440-02-0	mg/kg	67000
Potassium	7440-09-7	mg/kg	---
Potassium	9/7/7440	mg/kg	---
Selenium	7782-49-2	mg/kg	17000
Silver	7440-22-4	mg/kg	---
Sodium	7440-23-5	mg/kg	---
Thallium	7440-28-0	mg/kg	33
Vanadium	7440-62-2	mg/kg	17000
Zinc	7440-66-6	mg/kg	1000000

Notes:
[1] EPA Recreational Screening Levels for sediment that are based on recreational scenarios in which an adult or child hiker/camper is exposed to surface water and sediment; criteria were arrived at through risk-based calculations

mg/kg = milligram per kilogram

Worksheet 17 — Sampling Design and Rationale

(UFP-QAPP Manual Section 3.1.1)
(EPA 2106-G-05 Section 2.3.1)

START will collect surface water samples to characterize water quality and flow impacts from the Gold King Mine release. Surface water will be monitored for pH and turbidity. Other water quality parameters such as conductivity, temperature, oxygen-reduction potential and dissolved oxygen will be measured as long as the additional information is helpful in evaluating site conditions.

For streams, rivers, lakes, and other surface waters, a direct method of collection will be utilized to collect water samples from the surface directly into sample containers. At shallow stream locations the sample will be collected under the surface water while pointing the sample container upstream; the sample container will be positioned upstream of the collector. While collecting the water sample caution will be used to avoid disturbing the substrate. For lakes and other surface water bodies, samples will be collected under the surface water avoiding surface debris and the boat wake.

Additional media such as sediment, soil and/or groundwater may also be sampled, as directed by the EPA OSC.

This project involves the collection of laboratory samples and field screening data. Sample points will be located with a GPS device to be used for mapping purposes and to document sample locations selected in the field. If sampling locations become inaccessible, alternate sampling locations which provide similarly adequate or sufficient data as the original will be identified and sampled based upon the best judgment of the inspector/sampler, if necessary.

Sample Locations and Nomenclature

Sample locations will be identified in the field in coordination with the EPA OSC. In general, the sampling area extends from the confluence of the Animas River and the San Juan River, to the Colorado River and Lake Powell near Page, Arizona. The priority and importance of each sample will be determined by the OSC.

Sample nomenclature will use the location identification as listed in the table below, followed by the followed by the date (MMDDYY), and then a number to indicate the sample matrix and whether the sample is a field duplicate as follows:

- 11 – surface water
- 12 – surface water field duplicate
- 10 – sediment
- 09 – sediment field duplicate

If needed, additional identifiers to distinguish other media types may be added. These will be noted by the sampler in the field logbook. Identified locations that may be sampled are listed below.

Location ID	Sample Location Description	Latitude / Longitude
SJLP	San Juan River below confluence with Animas River.	36.735887 N -108.253987 W
SJFP	San Juan River Farmington area.	36.748156 N -108.412016 W
SJHB	San Juan River, Hogback area.	36.745102 N -108.537758 W
SJSR	San Juan River Ship Rock (discontinued)	36.893312 N -108.878642 W
SJDS	San Juan River below Ship Rock (discontinued)	36.781624 N -108.692784 W
SJ4C	San Juan River, near Four Corners area (New Mexico – Colorado border).	36.996216 N -109.004684 W
MECT	McElmo Creek.	37.218462 N -109.190811 W
SJME	San Juan River, below confluence with McElmo Creek.	37.216811 N -109.19615 W
SJMC	San Juan River at Montezuma Creek	37.258226 N -109.310604 W
SJBB	San Juan River, Bluff area, near Buck Creek	37.25737 N -109.618586 W
SJMH	San Juan River, Mexican Hat area	37.149993 N -109.866284 W
SJPF	San Juan River, Piute Farms Wash (discontinued)	37.252582 N -110.440532 W
SJCH	San Juan River, above Lake Powell	37.293336 N -110.399293 W
SJIN	San Juan River, above Lake Powell	37.2536 N -110.6632 W
LPCH	San Juan River, above Lake Powell	37.25567 N -110.66414 W
SJIN2	San Juan River, above Lake Powell	37.2563 N -110.67912 W
SJPL	San Juan River, above Lake Powell	37.26238 N -110.70908 W
SJPL2	San Juan River, above Lake Powell	37.25948 N -110.7110 W
LPPW	Lake Powell	37.16278 N -110.7085 W
LPRC	Lake Powell	37.13642 N -111.19226 W
LPGB	Lake Powell	37.05487 N -111.23475 W
LPPC	Lake Powell	37.06631 N -111.26525 W
LPNC	Lake Powell	36.9390 N -111.32459 W
LPDAM	Lake Powell Dam	36.94436 N -111.48691 W

For example, SJLP-080915 -11 would designate the surface water sample collected on 8/9/15 from location SJLP and its field duplicate would be labeled as SJLP-080915-12. Samples will be recorded in a logbook and GPS coordinates recorded. If site conditions warrant the modification of nomenclature, this change will be documented in the logbook.

Sampling and Field QC Procedures

Samples will be analyzed for the parameters listed on Worksheet 18. Requirements for the sample container, volume, preservation, and QC samples are presented on Worksheet 19 & 30 of the QAPP.

Sampling and analytical activities performed on site will follow all applicable SOPs outlined in Worksheet 21, including EPA ERT SOP 2001 "General Field Sampling Guidelines." Sampling is anticipated to be performed in Level D personal protective equipment (PPE).

Samples will be collected using equipment and procedures appropriate to the matrix, parameters, and sampling objectives. The volume of the sample collected will be sufficient to perform the analysis requested. Samples will be stored in the proper types of containers and preserved in a manner for the analysis to be performed per laboratory guidelines.

Field water quality parameters will be obtained using a YSI or Horiba water quality meter. Field monitoring will be used to measure the quality of water discharged from the treatment system, with emphasis on pH and turbidity measurements. Visual observations of water clarity will be recorded.

Dedicated sampling equipment, sample containers, and PPE will be maintained in a clean, segregated area. Personnel responsible for sampling will change gloves between each sample collection/handling activity. Personnel will use unpowdered nitrile gloves as some types of powder in the powdered gloves contain zinc which could potentially contaminate samples.

START personnel will collect field duplicate and MS/MSD samples and QA/QC samples as needed during the sampling activities. QA/QC samples will be collected according to the following dictates and summarized on Worksheet 20:

- Blind field duplicate water samples will be collected during sampling activities at locations selected by the START PTL. The data obtained from these samples will be used to assist in the quality assurance of the sampling procedures and laboratory analytical data by allowing an evaluation of reproducibility of results. Efforts will be made to collect duplicate samples in locations where there is visual evidence of contamination or where contamination is suspected. One duplicate sample will be collected for this sampling activity. In general blind field duplicate samples are collected at the rate of one duplicate for every 10 samples collected.
- Temperature Blanks - Each sample cooler shall contain a temperature blank. The temperature blank should be supplied by the receiving laboratory and can a plastic bottle filled with water. The purpose of the temperature blank is to document the temperature of the representative solution contained within the same transport cooler as the collected field sample.

- Equipment Rinsate Blanks - Rinsate blanks are only required for non-disposable sampling equipment. WESTON anticipates using only disposable sampling equipment for each sample collected and does not anticipate needing to collect rinsate blanks. However, if required, the equipment rinsate blank will be prepared by pouring de-ionized water over non-disposable sampling equipment after it has been decontaminated and by collecting the rinse water in sample containers for analyses. These samples will be prepared to demonstrate that the equipment decontamination procedures for the sampling equipment were performed effectively. It is anticipated that enough pre-cleaned disposable equipment will be available and that the collection of an equipment rinsate blank will not be needed during this sampling event. However if field conditions change, an equipment rinsate blank will be collected following equipment decontamination procedures.
- MS/MSD samples will be collected during sampling activities at locations selected by the START PTL. The data obtained from these samples will be used to assist in the quality assurance of the laboratory analytical procedure. Matrix spiking ensures that the laboratory is able to extract an acceptable percentage of a spiked constituent. At the direction of EPA, one MS sample may be collected for every 20 samples submitted for analysis. The matrix spiking analysis often duplicates the spiking procedure on a separate sample volume (MSD).

Additional Sampling/Long Term Considerations

Sampling beyond the initial surface water sampling may be required. Tasks that may be required and implemented at the direction of the EPA OSC include:

- Continuous water quality measurements with telemetry
- Installation of mini-sipper units at designated stations
- Repeat sampling at surface water stations
- Collection of biotic samples

In addition, START will work with EPA to provide support, as needed, to complement sampling efforts conducted by other agencies collaborating with EPA on the assessment.

Worksheet 18 — Sampling Locations and Methods

(UFP-QAPP Manual Section 3.1.1 and 3.1.2)
(EPA 2106-G-05 Sections 2.3.1 and 2.3.2)

The following information is project-specific and will be included in the site-specific SAP, and/or QAPP.

Sampling Location / ID	Matrix	Depth (units)	Type	Analyte/Analytical Group	Sampling SOP Reference	Comments
Location ID_mmddyy-11	Surface Water	TBD	Grab	Metals, Alkalinity, TDS, TSS, Hardness, Alkalinity, pH	See Worksheet 21	
Location ID-mmddyy-10	Sediment	TBD	Grab/Composite	Metals	See Worksheet 21	

Worksheet 19 & 30 — Sample Containers, Preservation, and Hold Times

(UFP-QAPP Manual Section 3.1.2.2)
(EPA 2106-G-05 Section 2.3.2)

All analyses will be conducted by a Contract Laboratory Program (CLP) laboratory, the Region 9 Central Regional Laboratory (CRL), or a WESTON-subcontracted laboratory.

Laboratory (Name, sample receipt address, POC, e-mail, and phone numbers): TestAmerica located in Savannah, GA; Irvine, CA; and Denver, CO
List Any Required Accreditations/Certifications: National Environmental Laboratory Accreditation Program (NELAP) and State Drinking Water Certifications (required only for any drinking water samples or source intakes)
Back-up Laboratory: TBD
Sample Delivery Method: FedEx

Matrix	Analyte/ Analyte Group	Method/ SOP[1]	Container(s) (number, size & type per sample)[2]	Preservation	Analytical Holding Time	Data Package Turnaround
Sediment	Metals	200.7/200.8/245.1	One 4-ounce jar	Store @ < 4°C	28 days for mercury, 180 days for all other metals	1-3 days for a QA Level II data package
Water	Total Metals (including mercury)	200.7/200.8/245.1	One 500-milliliter polyethylene bottle	HNO_3 to pH < 2 and store @ < 4°C	28 days for mercury, 180 days for all other metals	
	Dissolved Metals (including mercury)	200.7/200.8/245.1	One 500-milliliter polyethylene bottle	Field Filtered: HNO_3 to pH < 2 and store @ < 4°C If not field filtered, no preservative	28 days for mercury, 180 days for all other metals	
	Total Dissolved Solids	Standard Method (SM) 2540C	One 1-Liter polyethylene bottle	Store @ < 4°C	7 days	
	Total Suspended Solids	SM2540D	One 1-Liter polyethylene bottle	Store @ < 4°C	7 days	
	pH	SM4500H+B	One 1-Liter polyethylene bottle	Store @ < 4°C	As soon as possible	

Matrix	Analyte/ Analyte Group	Method/ SOP[1]	Container(s) (number, size & type per sample)[2]	Preservation	Analytical Holding Time	Data Package Turnaround
	Alkalinity	SM2320B	One 500 mL polyethylene bottle	Store @ < 4°C	14 days	
	Hardness	SM2340B	One 500 mL polyethylene bottle	HNO_3 to pH < 2 and store @ < 4°C	180 days	

[1] Refer to the Analytical SOP References table (Worksheet 23).

[2] The minimum sample size is based on analysis allowing for sufficient sample for reanalysis. Additional volume is needed for the laboratory MS/MSD sample analysis.

Worksheet 20 — Field Quality Control Sample Summary

(UFP-QAPP Manual Sections 3.1.1 and 3.1.2.)
(EPA 2106-G-05 Section 2.3.5)

Matrix	Analyte/Analytical Group	No. of Field Samples[1]	No. of Field Duplicates	No. of MS/MSD	No. of Equip. Blanks	No. of Trip Blanks	No. of Other	Total No. of Samples to Laboratory
Surface water	Total Metals	TBD	1 per 10	1 per 20 or 1 per day	1 per 20 if using non-disposable equipment	0	0	TBD
Surface water	Dissolved Metals	TBS	1 per 10	1 per 20 or 1 per day	1 per 20 if using non-disposable equipment	0	0	TBD
Surface water	General Chemistry Parameters	TBD	1 per 10	Not Applicable	1 per 20 if using non-disposable equipment	0	0	TBD
Sediment	Total Metals	TBD	1 per 10	1 per 20 or 1 per day	1 per 20 if using non-disposable equipment	0	0	TBD

[1] Samples that are collected at different depths at the same location, and analyzed separately, will be counted as separate field samples. Even if they are taken from the same container as the parent field sample, MS/MSDs are counted separately, because they are analyzed separately. If composite samples or incremental samples are collected, only the sample that will be analyzed will be included; subsamples and increments will not be listed separately.

[2] Total number of samples to the laboratory does not include MS/MSD samples.

Note: If EPA requests that field samples be collected from treatment system water and analyzed for total and dissolved metals, the need for a duplicate will be determined based on the rationale for sampling. The number and types of QC samples will be based on project-specific DQOs and this worksheet will be adapted, as necessary, to accommodate project-specific requirements. Project-specific QC samples may include field duplicate, field blank, equipment blank, trip blank, field split, MS/MSD, and PT samples and will be collected in accordance with the frequencies recorded on QAPP Worksheet 12. Quality Assurance Assessment and Corrective Actions are found in QAPP Worksheet #28.

Worksheet 21 — Field SOPs

(UFP-QAPP Manual Section 3.1.2)
(EPA 2106-G-05 Section 2.3.2)

SOPs may include, but are not limited to, those identified in the table below.

SOP Number or Reference	Title, Revision, Date, and URL (if available)	Originating Organization	SOP Option or Equipment Type (if SOP provides different options)	Modified for Project? Y/N	Comments
2006	Sampling Equipment Decontamination, 6/2011	EPA Environmental response Team (ERT)		N	
2007	Groundwater Well Sampling, 6/2011	EPA ERT		N	
2012	Soil Sampling, 6/2011	EPA ERT		N	
2013	Surface Water Sampling, 6/2011	EPA ERT		N	
2016	Sediment Sampling, 6/2011	EPA ERT		N	
2017	Waste Pile Sampling, 6/2011	EPA ERT		N	
2043	Water Level Measurement, 6/2011	EPA ERT		N	
2049	Investigation-Derived Waste (IDW) Management, 6/2011	EPA ERT		N	
G-12	Specifications and Guidance for Contaminant-Free Sample Containers, 12/1992	EPA, Office of Solid Waste and Emergency Response		N	
SS-5	Residential Soil Lead Sampling Guidance, 4/2000	EPA R8 Superfund Program		N	
NN2044	Monitoring Well Development, 6/2011	EPA ERT		N	
2001	General Field Sampling Guidelines, 6/2011	EPA ERT		N	
CDPHE 2010	Standard Operating Procedures for the Collection of Water Samples, 2010 https://www.colorado.gov/pacific/sites/default/files/WQ_nonpoint_source-SOP-Collection-of-Water-Chemistry-Samples-050110.pdf	Colorado Department of Public Health and Environment (CDPHE)		N	
WQCDSOP-001	Benthic Macroinvertebrate Sampling Protocols, 2010.	CDPHE		N	

START will review existing information and may conduct sampling for removal/emergency response activities.

Inclusive of the EPA Region 9 Removal and Emergency Response Program, START may conduct a wetland determination on a site-specific basis in accordance with the methods described in the *Corps of Engineers Wetlands Delineation Manual (USACE 1987*, http://www.usace.army.mil/Missions/CivilWorks/RegulatoryProgramandPermits/reg_supp.aspx*)*, regional supplemental guidance, and subsequent clarification memoranda. The wetland determination is based on a three-parameter approach that requires evidence of the following wetland indicators: dominant hydrophytic vegetation, hydric soil characteristics, and the presence of wetland hydrology. An area must meet all three wetland indicator criteria (except where noted in the USACE 1987 Supplemental Manuals) to be considered a jurisdictional wetland.

During sampling activities, IDW may be generated. IDW may consist of decontamination fluids, purge/development water, excess sampled media (e.g., soil, sediment, water, etc.), disposable sampling supplies, and PPE (e.g., Tyvek/Saranex coveralls, gloves, booties, etc.). Handling of IDW will be performed according with SOP 2049 as listed above as well as procedures described in *Management of Investigation Derived Wastes during Site Inspections (May 1991*). Waste disposal for IDW will be dependent upon classification of the waste as either Resource Conservation and Recovery Act (RCRA) hazardous or RCRA nonhazardous waste.

Worksheet 22 — Field Equipment Calibration, Maintenance, Testing, and Inspection

(UFP-QAPP Manual Section 3.1.2.4)
(EPA 2106-G-05 Section 2.3.6)

START field personnel are responsible for the calibration of EPA field equipment and field equipment provided by subcontractors. Documented and approved procedures will be used for calibrating measuring and testing equipment. Widely accepted procedures, such as those published by EPA and American Society for Testing and Materials (ASTM), or procedures provided by manufacturers in equipment manuals will be adopted. Items may include, but are not limited to those identified in the table below.

Field Equipment	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Title or Position of Responsible Person	Verification	SOP Reference[1]
Horiba U-50/YSI® 600XLM Water Quality Meters	Calibrate probes with standards per instrument instruction manual	Check batteries, clean probes, store in manufacturer recommended solution	Calibration check	Visually inspect for external damage to probe(s)	Refer to instrument SOP	Refer to instrument SOP	Refer to instrument SOP	Field personnel	WAM/COR	G-13/G-14
Water Level Indicators	Calibrate tape against calibrated steel measuring tape	Clean prior and after each use, check battery	Calibration and operational equipment check	Visually inspect for obvious defects, broken parts, or cleanliness	Prior to use	Equipment operational	Repair/ replace as needed	Field personnel	WAM/COR	Instrument-Specific
Sampling Tools (Disposable Scoops)	Not Applicable (NA)	NA	NA	Visually inspect for obvious defects or broken parts	Prior to use	NA	Replace	Field personnel	WAM/COR	NA
Disposable, inert sample mixing containers	NA	NA	NA	Visually inspect for cleanliness	Prior to use	NA	Replace	Field personnel	WAM/COR	NA
Metal sampling equipment as necessary (trowels)	NA	Clean prior and after each use	NA	Visually inspect for cleanliness	Prior to use	Should be covered from previous decontamination procedure	Perform decontamination procedure again as needed	Field personnel	NA	Metal sampling equipment as necessary (trowels)

Field Equipment	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Title or Position of Responsible Person	Verification	SOP Reference[1]
Grundfos Readiflow 2 Submersible Pump	NA	Clean prior and after each use	Operational equipment check	Visually inspect for obvious defects, broken parts, or cleanliness	Prior to use	Equipment operational	Repair/ replace as needed	Field personnel	WAM/COR	Instrument-Specific
MiniSipper	Calibrate by method with standard solutions	If poor instrument performance, replace tungsten lamp	Calibration and operational equipment check	Visually inspect for obvious defects, broken parts, or cleanliness	Prior to use	Equipment operational	Repair/ replace as needed	Field personnel	WAM/COR	Instrument-Specific
ISCO samplers	Perform volume calibration	Clean pump tubing, suction line, bottles, humidity indicator, and replace batteries	Calibration and operational equipment check	Visually inspect for obvious defects, broken parts, or cleanliness	Prior to use	Equipment operational	Repair/ replace as needed	Field personnel	WAM/COR	Instrument-Specific
Sampling Sticks	NA	NA	NA	Visually inspect for obvious defects or broken parts	Prior to use	NA	Replace	Field personnel	WAM/COR	NA

[1] Refer to Field SOPs (Worksheet 21) and Analytical SOPs (Worksheet 23).

Worksheet 23 — Analytical SOPs

(UFP-QAPP Manual Section 3.2.1)
(EPA 2106-G-05 Section 2.3.4)

Laboratory SOPs for TestAmerica (Savannah, Irvine, and Denver) are provided in Appendices B, C, and D. Items may include, but are not limited to those identified in the table below.

Lab SOP Number[1]	Title, Revision Date, and/or Number and URL (if available)	Screening or Definitive Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project? (Y/N)
Refer to Appendices B, C, and D	METHOD 200.7 DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA (ICP)-ATOMIC EMISSION SPECTROMETRY (AES), 1994, http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_07_10_methods_method_200_7.pdf	Definitive	Surface Water	ICP-AES	N
	METHOD 200.8 DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY (MS), 1994, http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_07_10_methods_method_200_8.pdf	Definitive	Surface Water	ICP-MS	N
	METHOD 245.1 Mercury (Manual Cold Vapor Technique) http://www.bucksci.com/catalogs/245_1.pdf	Definitive	Surface Water	CVAA	N
	METHOD SM 2540 D Low Level Total Suspended Solids Dried at 103-105 Deg C 20th Ed. http://www.standardmethods.org/store/ProductView.cfm?ProductID=63	Definitive	Surface Water	Gravimetric	N
	METHOD SM 2540 C Low Level Total Dissolved Solids Dried at 103-105 Deg C 20th Ed. http://www.standardmethods.org/Store/ProductList.cfm	Definitive	Surface Water	Gravimetric	N
	METHOD SM 4500H+B pH Value in Water by Potentiometry Using a Standard Hydrogen Electrode. http://standardmethods.org/	Definitive	Surface Water	pH Meter	N

Worksheet 23 — Analytical SOPs (Continued)

(UFP-QAPP Manual Section 3.2.1)
(EPA 2106-G-05 Section 2.3.4)

Lab SOP Number[1]	Title, Revision Date, and/or Number and URL (if available)	Screening or Definitive Data	Matrix/Analytical Group	SOP Option or Equipment Type	Modified for Project? (Y/N)
Refer to Appendices B, C, and D	METHOD SM2320B Alkalinity http://standardmethods.org/	Definitive	Surface Water	Titration Equipment	N
	METHOD SM2340B Hardness http://standardmethods.org/	Definitive	Surface Water	Calculation from metals results	N
	SW846 METHOD 6010C, Inductively Coupled Plasma—Atomic Emission Spectrometry, http://www.epa.gov/wastes/hazard/testmethods/sw846/online/6_series.htm	Definitive	Sediment	ICP-AES	N
	SW846 METHOD 6020B, Inductively Coupled Plasma—Mass Spectrometry, http://www.epa.gov/wastes/hazard/testmethods/sw846/online/6_series.htm	Definitive	Sediment	ICP-MS	N
	SW846 METHOD 7471A, Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique), http://www.epa.gov/wastes/hazard/testmethods/sw846/online/7_series.htm	Definitive	Sediment	CVAA	N

[1] Lab SOP numbers are lab-specific.

Worksheet 24 — Analytical Instrument Calibration

(UFP-QAPP Manual Section 3.2.2)
(EPA 2106-G-05 Section 2.3.6)

As stated in Worksheet 22, START field personnel are responsible for the calibration of EPA and sub-contractor provided analytical field equipment. Documented and approved procedures will be used for calibrating measuring and testing equipment. Widely accepted procedures, such as those published by EPA and ASTM, or procedures provided by manufacturers in equipment manuals will be adopted.

The responsibility for the calibration of laboratory equipment rests with the selected laboratories. Each type of instrumentation and each EPA-approved method have specific requirements for the calibration procedures, depending on the analytes of interest and the sample medium. The calibration procedures and frequencies of the equipment used to perform the analyses will be in accordance with requirements established by the EPA. The laboratory QA manager will be responsible for ensuring that the laboratory instrumentation is maintained in accordance with specifications. Individual laboratory SOPs will be followed for corrective actions and preventative maintenance frequencies. Laboratory quality control, calibration procedures, corrective action procedures, and instrument preventative maintenance will be included in an addendum to this QAPP once the laboratories have been selected for each of the TBA sites. Items may include, but are not limited to those identified in the table below.

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Title/Position Responsible for CA	SOP Reference[1]
CVAA	245.1/7471A	Daily initial calibration prior to sample analysis. Perform instrument re-calibration once per year minimum.	$R^2 \geq 0.995$ for linear regression	Correct problem then repeat initial calibration. If calibration fails again, re-digest the entire digestion batch.	Lab Manager/ Analyst	200.7/200.8/245.1
ICP-AES	200.7/6010C	Calibration and initial calibration verification after instrument set up, then daily; continuing calibration verifications. Upper range within 10%. New upper range limits should be determined whenever a significant change in instrument response or every six months. Low-level continuing calibration verification (LLCCV) standard with 30%.	Initial and continuing calibration verification within ± 10% of upper range true values and ± 30% LLCCV true values.	Inspect system; correct problem; re-run calibration and affected samples	Lab Manager/ Analyst	200.7/200.8/245.1

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Title/Position Responsible for CA	SOP Reference[1]
ICP/ ICP-MS	200.8/6020A	Calibration and initial calibration verification after instrument set up, then daily; continuing calibration verification 10% or every 2 hours, whichever is more frequent	Calibration r2 >0.995; initial and continuing calibration verification within ± 20% of true values	Inspect system; correct problem; re-run calibration and affected samples	Lab Manager/ Analyst	200.7/200.8/245.1

[1] Refer to the Analytical SOPs table (Worksheet 23).

Worksheet 25 — Analytical Instrument and Equipment Maintenance, Testing, and Inspection

(UFP-QAPP Manual Section 3.2.3)
(EPA 2106-G-05 Section 2.3.6)

All laboratories conducting analyses of samples collected under the contract are required to have a preventative maintenance program covering testing, inspection, and maintenance procedures and schedule for each measurement system and required support activity. The basic requirements and components of such a program include the following:

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action (CA)	Title/ Position Responsible for CA	SOP Reference[1]
CVAA	Replace disposables, flush lines, check lamp current and gas flow	Sensitivity check	Instrument performance and sensitivity	Daily or as needed	CCV pass criteria	Recalibrate	Analyst	245.1/7471A
ICP-AES	Replace disposable, flush lines, and clean autosampler	Analytical standards	Instrument performance and sensitivity	Daily or as needed	CCV pass criteria	Recalibrate	Analyst	200.7/6010C
ICP/ICP-MS	Replace pump windings and gas tanks, check standard and sample flow	Monitor instrument standard (ISTD) counts for variation	Instrument performance and sensitivity	As needed	Monitor ISTD counts for variation	Replace windings, recalibrate and reanalyze	Analyst	200.8/6020A

[1] Refer to the Analytical SOPs table (Worksheet 23). A laboratory-specific QA Manual may be referenced on a project-specific basis and will be identified in the site specific SAP, and/or QAPP.

Worksheet 26 & 27 — Sample Handling, Custody, and Disposal

(UFP-QAPP Manual Section 3.3)
(EPA 2106-G-05 Manual Section 2.3.3)

An example chain-of-custody is provided in Appendix E. A chain-of-custody form will be maintained for all samples to be submitted for analysis, from the time the sample is collected until its final deposition. Every transfer of custody must be noted and a signature affixed. Corrections on sample paperwork will be made by drawing a single line through the mistake and initialing and dating the change. The correct information will be entered above, below, or after the mistake. When samples are not under the direct control of the individual responsible for them, they must be stored in a locked container sealed with a custody seal. The chain-of-custody form must include the following:

- Sample identification numbers
- Identification of sample to be used for MS/MSD purposes
- Site name
- Sample date
- Number and volume of sample containers
- Required analyses
- Signature and name of samplers
- Signature(s) of any individual(s) with control over samples
- Airbill number
- Note(s) indicating special holding times and/or detection limits

The chain-of-custody form will be completed and sent with the samples for each laboratory and each shipment. Each sample cooler should contain a chain-of-custody form for all samples within the sample cooler.

A sample summary form will be completed for each method and each matrix of the sampling event. The sample number for all blanks, reference samples, laboratory QC samples (MS/MSDs), and duplicates will be documented on this form. This form is not sent to the laboratory. The original form will be sent to the reviewer who is validating and evaluating the data; a photocopy of the original will be made for the START project file.

Supplies and consumables can be received at a START office, EPA Warehouse or at a site. When supplies are received at a START office or EPA Warehouse, the Project Manager or PTL will sort the supplies according to vendor, check packing slips against purchase orders, and inspect the condition of all supplies before the supplies are accepted for use on a project. If the supplies do not meet the acceptance criteria, deficiencies will be noted on the packing slip and purchase order. The item will then be returned to the vendor for replacement or repair.

Procedures for receiving supplies and consumables in the field are similar to those described above. Upon receipt, items will be inspected by the START Project Manager or PTL against the acceptance criteria. Any deficiencies or problems will be noted in the field logbook, and deficient items will be returned for immediate replacement.

Worksheet 28 — Analytical Quality Control and Corrective Action

(UFP-QAPP Manual Section 3.4 and Tables 4, 5, and 6)
(EPA 2106-G-05 Section 2.3.5)

The following information is laboratory-specific. The following are typical examples for Organics and Inorganics for all media.

Matrix: All
Analytical Group: All
Analytical Method/SOP: All/All

QC Sample	Number/Frequency	Method/SOP QC Acceptance Limits[1]	Corrective Action	Title/Position of Person Responsible for Corrective Action	Project-Specific MPC
Method Blank	1/Batch (20 samples)	No Target Compounds >1/2 RL; no common lab contaminants >RL.	If sufficient sample is available, reanalyze samples. Qualify data as needed. Report results if sample results >10x blank result or sample results non-detect (U qualifier).	Analyst / Section Supervisor	No Target Compounds >1/2 RL; no common lab contaminants >RL.
LCS	1/Batch (20 samples)	Analyte-specific	If sufficient sample is available, reanalyze samples. Qualify data as needed.	Analyst / Section Supervisor	NFG %R QC Limits
MS/MSD	1/Batch (20 samples)	Analyte-specific	Determine root cause; flag MS/MSD data; discuss in narrative.	Analyst / Section Supervisor	NFG % R / RPD QC Limits
Dilution Test	One per preparatory batch	1:5 dilution must agree within ±10% of the original determination	Perform post digestion spike addition	Analyst / Section Supervisor	Only applicable for samples with concentrations > 50x LOD

Field and laboratory QC samples and measurements will be used to verify that analytical data meet project-specific MPC, which are based on Project Quality Objectives (PQOs)/DQOs. Field QC samples and measurements and laboratory QC samples will be used to assess how they influence data quality. The project-specific SAP, and/or QAPP will include the information presented in the table above for each sampling technique, analytical method/SOP, matrix, and analytical group. See Worksheet 12 and 20 for descriptions of QC samples, DQIs, and MPC.

Worksheet 29 — Project Documents and Records

(UFP-QAPP Manual Section 3.5.1)
(EPA 2106-G-05 Section 2.2.8)

All records will be generated and verified by START personnel only, stored electronically on the START server and backed up daily. All hard and electronic copies of finalized documents and technical project documents (including but not limited to the QAPP, HASP, etc.) will be retained in accordance with Contract No.: EP-S5-13-02. Other project-related files, such as contract documents, employee benefits, and other information will be retained in accordance with WESTON Policies and Procedures.

Sample Collection and Field Records			
Record	**Generation**	**Verification**	**Storage Location/Archival**
Field Logbook or Data Collection Sheets	PTL/Field Scientist	Delegated QA Manager	Project File
Chain-of-Custody (COC) Forms	PTL/Field Scientist	Delegated QA Manager	Project File
Custody Seals	PTL/Field Scientist	Delegated QA Manager	Project File
Air Bills	PTL/Field Scientist	Delegated QA Manager	Project File
Daily QC Reports	PTL	Delegated QA Manager	Project File
Deviations	PTL/Field Scientist	Delegated QA Manager	Project File
Corrective Action Reports	Delegated QA Manager	Project Manager	Project File
Correspondence	PTL	Delegated QA Manager	Project File
Field Sample Results/Measurements	PTL/Field Scientist	Delegated QA Manager	Project File
Tailgate Safety Meeting Items	PTL/Field Safety Officer	Delegated QA Manager	Project File

Project Assessments			
Record	**Generation**	**Verification**	**Storage Location/Archival**
Field Analysis Audit Checklist	Delegated QA Manager	Project Manager	Project File
Fixed Laboratory Audit Checklist	Delegated QA Manager	Project Manager	Project File
Data Verification Checklists	Delegated QA Manager	Project Manager	Project File
Data Validation Report	Delegated QA Manager	Project Manager	Project File
Data Usability Assessment Report	Delegated QA Manager	Project Manager	Project File
Corrective Action Reports	Delegated QA Manager	Project Manager	Project File
Correspondence	Delegated QA Manager	Project Manager	Project File

Worksheet 29 — Project Documents and Records (Continued)

(UFP-QAPP Manual Section 3.5.1)
(EPA 2106-G-05 Section 2.2.8)

Laboratory Records			
Record	**Generation**	**Verification**	**Storage Location/Archival**
Sample Receipt, Custody, and Checklist	Laboratory Sample Receiving	Laboratory Project Manager/Delegated QA Manager	Laboratory and Project File
Equipment Calibration Logs	Laboratory Technician	Laboratory Project Manager/Delegated QA Manager	Laboratory and Project File
Standard Traceability Logs	Laboratory Technician	Laboratory Project Manager/Delegated QA Manager	Laboratory and Project File
Sample Prep Logs	Laboratory Technician	Laboratory Project Manager/Delegated QA Manager	Laboratory and Project File
Run Logs	Laboratory Technician	Laboratory Project Manager/Delegated QA Manager	Laboratory and Project File
Equipment Maintenance, Testing, and Inspection Logs	Laboratory Technician/ Laboratory QA Manager	Laboratory Project Manager/Delegated QA Manager	Laboratory and Project File
Corrective Action Reports	Laboratory QA Manager	Laboratory Project Manager/Delegated QA Manager	Laboratory and Project File
Laboratory Analytical Results	Laboratory Technician/ Laboratory QA Manager	Laboratory Project Manager/Delegated QA Manager	Laboratory and Project File
Laboratory QC Samples, Standards, and Checks	Laboratory Technician/ Laboratory QA Manager	Laboratory Project Manager/Delegated QA Manager	Laboratory and Project File
Instrument Results (raw data) for Primary Samples, Standards, QC Checks, and QC Samples	Laboratory Technician/ Laboratory QA Manager	Laboratory Project Manager/Delegated QA Manager	Laboratory and Project File
Sample Disposal Records	Laboratory Technician	Laboratory Project Manager/Delegated QA Manager	Laboratory and Project File

Worksheet 29 — Project Documents and Records (Continued)

(UFP-QAPP Manual Section 3.5.1)
(EPA 2106-G-05 Section 2.2.8)

Laboratory Data Deliverables[1]						
Record	**VOCs**	**SVOCs**	**PCBs**	**Pesticides**	**Metals**	**Other**
Narrative						
COC						
Summary Results						
QC Results						
Chromatograms						
Tentatively Identified Compounds						

[1] The Laboratory Data Deliverables table is designed to be a checklist for use in supporting data completeness. The records and analytical groups in this table are not all inclusive of those that may be used on a specific project and should be modified and utilized by the Delegated QA Manager as applicable.

Worksheet 31, 32 & 33 — Assessments and Corrective Action

(UFP-QAPP Manual Sections 4.1.1 and 4.1.2)
(EPA 2106-G-05 Section 2.4 and 2.5.5)

All reports will be prepared by WESTON and distributed to the following to include but not be limited to the WESTON Project Manager, Program Manager and Delegated QA Manager, and the EPA COR, WAM, and DAO as applicable.

Assessment Type	Responsible Party & Organization	Number/ Frequency	Estimated Dates	Assessment Deliverable	Deliverable Due Date
Laboratory Technical System Audit (TSA)[2]	DAO/WAM/COR EPA Laboratory QA Manager TBD Delegated QA Manager WESTON	CLP, CRL, and certified sub-contract laboratories are routinely audited by accrediting authorities. The laboratory QA manager and/or WESTON Delegated QA Manager will perform audits on a project-specific basis as needed	TBD	Analytical TSA Memorandum and Checklist	TBD
Management Review	DAO/WAM/COR EPA Delegated QA Manager and Project Manager WESTON	1/year	TBD	QA Management Report	TBD
Corrective Action	DAO/WAM/COR EPA Delegated QA Manager and Project Manager WESTON	TBD	TBD	Corrective Action Reports	TBD
Data Validation	Chemist WESTON	TBD	TBD	Data Validation Report	TBD
Contract Closeout	Program Manager WESTON	1	TBD	Contract Closeout Report	TBD

[1] Field sampling TSAs may include, but are not limited to the following: sample collection records; sample handling, preservation, packaging, shipping, and custody records; equipment operation, maintenance, and calibration records.

[2] Laboratory TSAs may include, but are not limited to the following: sample log-in, identification, storage, tracking, and custody procedures; sample and standards preparation procedures; availability of analytical instruments; analytical instrument operation, maintenance, and calibration records; laboratory security procedures; qualifications of analysts; case file organization and data handling procedures.

Worksheet 34 — Data Verification and Validation Inputs

(UFP-QAPP Manual Section 5.2.1 and Table 9)
(EPA 2106-G-05 Section 2.5.1)

The following information will be used during data verification and validation. Inputs may include, but are not limited to those identified in the table below.

Item	Description	Verification (completeness)	Validation (conformance to specifications)
Planning Documents/Records			
1	Approved QAPP	X	
2	Contract	X	
3	Field SOPs	X	
4	Laboratory SOPs	X	
5	Laboratory QA Manual	X	
6	Laboratory Certifications	X	
Field Records			
7	Field Logbooks	X	X
8	Equipment Calibration Records	X	X
9	COC Forms	X	X
10	Sampling Diagrams/Surveys	X	X
11	Drilling Logs	X	X
12	Geophysics Reports	X	X
13	Relevant Correspondence	X	X
14	Change Orders/Deviations	X	X
15	Field Audit Reports	X	X
16	Field Corrective Action Reports	X	X
17	Sample Location Verification (Worksheet 18)	X	X
Analytical Data Package			
18	Cover Sheet (laboratory identifying information)	X	X
19	Case Narrative	X	X
20	Internal Laboratory COC	X	X
21	Sample Receipt Records	X	X
22	Sample Chronology (i.e. dates and times of receipt, preparation, & analysis)	X	X
23	Communication Records	X	X
24	Project-specific PT Sample Results	X	X
25	LOD/LOQ Establishment and Verification	X	X
26	Standards Traceability	X	X
27	Instrument Calibration Records	X	X
28	Definition of Laboratory Qualifiers	X	X
29	Results Reporting Forms	X	X
30	QC Sample Results	X	X
31	Corrective Action Reports	X	X
32	Raw Data	X	X
33	Electronic Data Deliverable	X	X

Worksheet 35 — Data Verification Procedures

(UFP-QAPP Manual Section 5.2.2)
(EPA 2106-G-05 Section 2.5.1)

The following information may include, but are not limited to those identified in the table below.

Records Reviewed	Required Documents	Process Description	Responsible Person, Organization
Approved QAPP	Programmatic and site-specific SAP, and/or QAPP, Contract	Verify completeness, correctness, and contractual compliance of all project QA/QC and data set against the methods, SOPs, and contract requirements conforms.	Joe DeFao, WESTON Program Manager; Cecilia H. Shappee, P.E., WESTON Lisa Graczyk, CSS-Dynamac, Inc.
Field SOPs	Programmatic and site-specific SAP, and/or QAPP, SOPs	Ensure that all field sampling SOPs were followed.	Jon Colomb, WESTON Project Manager
Analytical SOPs	Programmatic and site-specific SAP, and/or QAPP, SOPs	Ensure that all laboratory analytical SOPs were followed.	Lisa Graczyk, CSS-Dynamac Laboratory Project Manager,
Field Logbook, Field Sheets, Sample Diagrams/ Surveys	Programmatic and site-specific SAP, and/or QAPP	Verify that records are present and complete for each day of field activities. Verify that all planned samples including field QC samples were collected and that sample collection locations are documented. Verify that meteorological data were provided for each day of field activities. Verify that changes/exceptions are documented and were reported in accordance with requirements. Verify that any required field monitoring was performed and results are documented.	Jon Colomb, WESTON
Equipment Calibration Records	Programmatic and site-specific SAP, and/or QAPP, SOPs, field logbook	Ensure that all field analytical instrumentation SOPs and laboratory analytical SOPs for equipment calibration were followed.	Jon Colomb, WESTON Laboratory Project Manager, Lisa Graczyk, CSS-Dynamac

Worksheet 35 — Data Verification Procedures (Continued)

(UFP-QAPP Manual Section 5.2.2)
(EPA 2106-G-05 Section 2.5.1)

Records Reviewed	Required Documents	Process Description	Responsible Person, Organization
COC Forms	Programmatic and site-specific SAP, and/or QAPP	Verify the completeness of COC records. Examine entries for consistency with the field logbook. Check that appropriate methods and sample preservation have been recorded. Verify that the required volume of sample has been collected and that sufficient sample volume is available for QC samples (e.g., MS/MSD). Verify that all required signatures and dates are present. Check for transcription errors.	Jon Colomb, WESTON Laboratory Project Manager, Lisa Graczyk, Dynamac
Relevant reports, and correspondence	Programmatic and site-specific SAP, and/or QAPP	Verify that reports are present and complete for each day of field activities. Verify that correspondence are documented and were reported in accordance with requirements.	Jon Colomb, WESTON Lisa Graczyk, Dynamac
Laboratory Deliverable	Programmatic and site-specific SAP, and/or QAPP	Verify that the laboratory deliverable contains all records specified in the QAPP. Check sample receipt records to ensure sample condition upon receipt was noted, and any missing/broken sample containers were noted and reported according to plan. Compare the data package with COCs to verify that results were provided for all collected samples. Review the narrative to ensure all QC exceptions are described. Check for evidence that any required notifications were provided to project personnel as specified in the QAPP. Verify that necessary signatures and dates are present.	Jon Colomb, WESTON Lisa Graczyk, Dynamac
Audit Reports, Corrective Action Reports	Programmatic and site-specific SAP, and/or QAPP	Verify that all planned audits were conducted. Examine audit reports. For any deficiencies noted, verify that corrective action was implemented according to plan.	Jon Colomb, WESTON Lisa Graczyk, Dynamac Laboratory Project Manager, TBD

Worksheet 36 — Data Validation Procedures

(UFP-QAPP Manual Section 5.2.2)
(EPA 2106-G-05 Section 2.5.1)

Data Validator: WESTON START

Analytical Group/ Method	Data Deliverable Requirements	Analytical Specifications	MPC	Percent of Data Packages to be Validated	Percent of Raw Data Reviewed	Percent of Results to be Recalculated	Validation Procedure	Electronic Validation Program/ Version
Total and Dissolved Metals	Scribe Compatible EDD	QAPP Worksheet 28	Worksheets 11, 12, 19 & 30	100%	0%	0%	EPA Stage 2A	N/A

Validation will be performed on all laboratory analytical data unless a defined quantity or percentage of samples is identified by the EPA in the Technical Direction Document or during the project scoping meeting on a project-specific basis. Project validation criteria as per QAPP Worksheets 12, 15, 19 & 30, 28, and 36, and cited EPA SW-846 methodology will be used. WESTON-contracted laboratory data packages will be verified and validated using a Stage 2A validation, as described in the EPA *Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use* (January 2009) unless otherwise specified by the EPA WAM/COR during the development of the DQOs. Validation Qualifiers will be applied using the *EPA National Functional Guidelines for Inorganic Superfund Data Review* (August 2014). Methods for which no data validation guidelines exist will be validated following the guidance deemed most appropriate by the data validator.

The data validator will receive all laboratory packages and analytical results electronically. Additionally, the validator will be required to submit final validation reports via PDF format and must provide an annotated laboratory analytical result EDD with applicable data validation qualifiers identified in the NFG.

Worksheet 37 — Data Usability Assessment

(UFP-QAPP Manual Section 5.2.3 and Table 12)
(EPA 2106-G-05 Section 2.5.2, 2.5.3, and 2.5.4)

Personnel (organization and position/title) responsible for participating in the data usability assessment may include, but not be limited to:

- START Project Manager;
- START Delegated QA Manager;
- START Risk Assessor;
- START Chemist;
- START PTL;
- START Statistician.

Based on project-specific oversight responsibilities and analytical scopes, this data usability assessment worksheet outlines the approach that will be taken as the analytical scope expands on a project-specific basis. The following general steps will be followed to assure that the data usability assessment evaluates whether underlying assumptions used during systematic planning are supported, sources of uncertainty have been accounted for and are acceptable, data are representative of the population of interest, and the results can be used as intended, with the acceptable level of confidence:

- Step 1 – Review the project's objectives and sampling design;
- Step 2 – Review the data verification and data validation outputs;
- Step 3 – Verify the assumptions of the selected statistical method;
- Step 4 - Implement the statistical method;
- Step 5 – Document data usability and draw conclusions.

The data usability assessment is considered the final step in the data evaluation process; all data will be assessed for usability, regardless of the data evaluation/validation process implementation. Data usability goes beyond validation in that it evaluates the achievement of the DQOs based on the comparison of the project DQIs and individual study-specific work plans, with the obtained results. The results of the data usability assessment, and particularly any changes to the DQOs necessitated by the data not meeting usability criteria, will be reported in accordance with Worksheet 6.

Primarily, the assessment of the usability will follow procedures described in appropriate EPA guidance documents, particularly *Guidance for Data Usability in Risk Assessment* (Publication No. 9285.7-05FS, September 1992)(Appendix U), and will be conducted according to the process outlined below.

1. **Sampling and Analysis Activities Evaluation**: The first part of the data usability evaluation will include a review of the sampling and analysis activities in comparison to project-specific DQIs and study-specific work plans. Specific limitations to the data (i.e., results that are qualified as estimated [J/UJ], or rejected [R], will be determined and documented in the database).

Worksheet 37 — Data Usability Assessment (Continued)

(UFP-QAPP Manual Section 5.2.3 and Table 12)
(EPA 2106-G-05 Section 2.5.2, 2.5.3, and 2.5.4)

2. **Achievement of DQIs**: The second part of data usability pertains to the achievement of the program-specific DQIs. Each investigator will compare the performance achieved for each data quality criterion against the expected and planned performance. In general, this comparison will follow from the DQIs used to define each DQO. This comparison is the most critical component of the assessment process. Any deviation from planned performance will be documented and evaluated to determine whether corrective action is advisable. Potential corrective actions will range from re-sampling and/or reanalysis of data, to qualification or exclusion of the data for use in the data interpretation. In the event that corrective action is not possible, the limitations, if any, of the data with regard to achieving the DQOs will be noted.

   In conjunction with the DQI achievement review, the investigators will need to make decisions for the use of qualified values, which are a consequence of the formalized evaluation/validation process. Data qualifiers will be applied to individual data results. Data usability decisions will be made based on the assessment of the usability of each of these results for the intended purpose. Evaluation will describe the uncertainty (bias, imprecision, etc.) of the qualified results. Cumulative QC exceedances from the DQIs may require technical judgment to determine the overall effect on the usability of the data. Decisions about usability of qualified data for use in risk assessment will be based on the EPA document mentioned, which allows for the use of estimated values. Finally, data users may choose to determine final data usability qualifiers as a result of this overall examination and decision process.

3. **Achievement of DQOs**: The final part in the data usability process concerns achievement of the DQOs. Once the data set has been assessed to be of known quality, data limitations have been documented, and overall result applicability/usability for its intended purpose has been determined, the final data assessment can be initiated by considering the answers to the following questions:

   - Are the data adequate to determine the extent to which hazardous substances have migrated or to what extent they were expected to migrate from potential hazardous substance source areas?
   - Do the data collected adequately characterize the nature and extent of potential hazardous substance source areas at the site?
   - Are the data statistically adequate to evaluate on a per chemical and per media basis?
   - Do the data collected allow assessment of hydrogeological factors, which may influence contaminant migration/distribution?
   - Do laboratory reporting limits attain the applicable state and/or federal standards and/or screening levels?
   - Is the sample set sufficient to develop site-specific removal and disposal treatment methodologies?

Worksheet 37 — Data Usability Assessment (Continued)

(UFP-QAPP Manual Section 5.2.3 and Table 12)
(EPA 2106-G-05 Section 2.5.2, 2.5.3, and 2.5.4)

- Have sufficient data been collected to evaluate how factors including physical characteristics of the site and climate and water table fluctuations affect contaminant fate and transport?
- Have sufficient data been collected to determine the toxicity, environmental fate, and other significant characteristics of each hazardous substance present?
- Is the data set sufficient to evaluate the potential extent and risk of future releases of hazardous substances, which may remain as residual contamination at the source facility?

Principal investigators, in conjunction with the project team, will formulate solutions if data gaps are found as a result of problems, biases, trends, etc., in the analytical data, or if conditions exist that were not anticipated in the development of the DQOs. It is particularly important that each data usability evaluation specifically address any limitations on the use of the data that may result from a failure to achieve the stipulated DQO.

If the project scope changes, the DQOs will be expanded. The DQOs will address the specific action limits and measurable performance criteria, in order to make appropriate decisions on the analytical data.

DQIs, such as precision, accuracy, completeness, representativeness, and comparability measurements, aid in the evaluation process and are discussed below.

Precision

The most commonly used estimates of precision are the RPD for cases in which only two measurements are available, and the percent relative standard deviation (%RSD) when three or more measurements are available. This is especially useful in normalizing environmental measurements to determine acceptability ranges for precision because it effectively corrects for the wide variability in sample analyte concentration indigenous to samples.

Precision is represented as the RPD between measurement of an analyte in duplicate samples or in duplicate spikes. RPD is defined as follows:

$$RPD = \frac{|C_1 - C_2|}{\frac{C_1 + C_2}{2}} \times 100$$

Where:

C_1 = First measurement value
C_2 = Second measurement value

For field measurements such as pH, where the absolute variation is more appropriate, precision is often reported as the absolute range (D) of duplicate measurements:

$$\%D = m1 - m2$$

Worksheet 37 — Data Usability Assessment (Continued)

(UFP-QAPP Manual Section 5.2.3 and Table 12)
(EPA 2106-G-05 Section 2.5.2, 2.5.3, and 2.5.4)

Where:
*m*1 = First measurement value
*m*2 = Second measurement value
The % RSD is calculated by the standard deviation of the analytical results of the replicate determinations relative to the average of those results for a given analyte. This method of precision measurement can be expressed by the formula:

$$\%\,\mathrm{RSD} = \frac{\sqrt{\sum_{I-1}^{N}\left(\frac{\mathrm{RF_i} - \mathrm{RF}}{\mathrm{N}-1}\right)}}{\mathrm{RF}} \times 100$$

Where:

RF = Response factor
N = Number of measurements

Precision control limits for evaluation of sample results are established by the analysis of control samples. The control samples can be method blanks fortified with surrogates (e.g., for organics), or LCS purchased commercially or prepared at the laboratory. The LCS is typically identified as blank spikes (BS) for organic analyses. For multi-analyte methods, the LCS or BS may contain only a representative number of target analytes rather than the full list.

The RPD for duplicate investigative sample analysis provides a tool for evaluating how well the method performed for the respective matrix.

Accuracy/Bias

Accuracy control limits are established by the analysis of control samples, which are in water and/or solid/waste matrices. For organic analyses, the LCS may be a surrogate compound in the blank or a select number of target analytes in the blank spike. The LCS is subjected to all sample preparation steps. When available, a solid LCS may be analyzed to demonstrate control of the analysis for soil. The amount of each analyte recovered in an LCS analysis is recorded and entered into a database to generate statistical control limits. These empirical data are compared with available method reference criteria and available databases to establish control criteria.

The %R for spiked investigative sample analysis (e.g., matrix spike) provides a tool for evaluating how well the method worked for the respective matrix. These values are used to assess a reported result within the context of the project data quality objectives. For results that are outside control limits provided as requirements in the QAPP, corrective action appropriate to the project will be taken and the deviation will be noted in the case narrative accompanying the sample results. Percent recovery (%R) is defined as follows:

$$\%\,\mathrm{Recovery} = \frac{(A_T - A_0)}{A_F} \times 100$$

Where:

Worksheet 37 — Data Usability Assessment (Continued)

(UFP-QAPP Manual Section 5.2.3 and Table 12)
(EPA 2106-G-05 Section 2.5.2, 2.5.3, and 2.5.4)

A_T = Total amount recovered in fortified sample
A_0 = Amount recovered in unfortified sample
A_F = Amount added to sample

Accuracy for some procedures is evaluated as the degree of agreement between a new set of results and a historical database or a table of acceptable criteria for a given parameter. This is measured as percent difference (%D) from the reference value, and is primarily used by the laboratory as a means for documenting acceptability of continuing calibration.

The %D is calculated by expressing, as a percentage, the difference between the original value and new value relative to the original value. This method for precision measurement can be expressed by the formula:

$$\%\,D = \frac{C_1 - C_2}{C_1} \times 100$$

Where:
C_1 = Concentration of analyte in the initial aliquot of the sample.
C_2 = Concentration of analyte in replicate.

The laboratory will review the QC samples and surrogate recoveries for each analysis to ensure that the %R lies within the control limits listed in the UFP-QAPP. Otherwise, data will be flagged by the laboratory.

For field measurements such as pH, accuracy is often expressed in terms of bias (B) and is calculated as follows:

$$B = M - A$$

Where:
M = Measured value of Standard Reference Material (SRM)
A = Actual value of SRM

Sensitivity

Sensitivity is the ability of the analytical test method and/or instrumentation to differentiate between detector responses to varying concentrations of the target constituent. Methodology to establish sensitivity for a given analytical method or instrument includes examination of standardized blanks, instrument detection limit studies, and calibration of the QL. The findings of the usability of the data relative to sensitivity will be included in the report, including any limitations on the data set and/or individual analytical results.

The Precision, Accuracy, Representativeness, Completeness, Comparability and Sensitivity MPC are described in Worksheets 12, 15, and 28. The following steps will be performed:

Worksheet 37 — Data Usability Assessment (Continued)

(UFP-QAPP Manual Section 5.2.3 and Table 12)
(EPA 2106-G-05 Section 2.5.2, 2.5.3, and 2.5.4)

- Evaluate if the project required quantitation limits listed in Worksheet 15 were achieved for non-detected site contaminants. If no detectable results were reported and data are acceptable for the verification and validation steps, then the data are usable.
- If detectable concentrations are reported and the verification and validation steps are acceptable, the data are usable.
- If verification and validation are not acceptable, the data are qualified, estimated (J, UJ) for minor QC deviations that do not affect the data usability, or rejected for major QC deviations affecting data usability. The impact of rejected data will be evaluated and re-sampling may be necessary. Use of estimated data will be discussed in the project report.
- For statistical comparisons and mathematical manipulations, non-detect values will be represented by a concentration equal to one-half the sample-specific reporting limit. Duplicate results (original and duplicate) will not be averaged for the purpose of representing the range of concentrations. However, the average of the original and duplicate will be used to represent the concentration at that sample location.

Statistical tests will be conducted to identify potential outliers. Potential outliers will be removed if a review of the field and laboratory documentation indicates that the results are true outliers.

Method sensitivity is typically evaluated in terms of the method detection limit (MDL) and is defined as follows for many measurements:

$$MDL = {}^{t}(n - 1, 1 - \alpha = 0.99)\,(s)$$

Where:

s = Standard deviation of the replicate analyses
${}^{t}(n - 1, 1 - \alpha = 0.99)$ = Student's t-value for a one-sided 99 percent confidence level and a standard deviation estimate with n-1 degrees of freedom
n = Number of measurements
α = Statistical significance level

Representativeness

Representativeness is the degree to which sample data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, or an environmental condition. It is a qualitative parameter that depends on proper design of the sampling program.

Data representativeness for this project is accomplished by implementing approved sampling procedures and analytical methods that are appropriate for the intended data uses, and which are established within the site-specific SAP, and/or QAPP.

Field personnel will be responsible for collecting and handling samples according to the procedures in this UFP-QAPP and the site-specific SAP, and/or QAPP so that samples are representative of field conditions. Errors in sample collection, packaging, preservation, or chain-of-custody procedures may result in samples being judged non-representative and may form a basis for rejecting the data.

Worksheet 37 — Data Usability Assessment (Continued)

(UFP-QAPP Manual Section 5.2.3 and Table 12)
(EPA 2106-G-05 Section 2.5.2, 2.5.3, and 2.5.4)

Comparability

Comparability is a qualitative parameter expressing the confidence with which one data set can be compared with another, whether it was generated by a single laboratory or during inter-laboratory studies. The use of standardized field and analytical procedures ensures comparability of analytical data. Sample collection and handling procedures will adhere to EPA-approved protocols. Laboratory procedures will follow standard analytical protocols, use standard units, use standardized report formats, follow the calculations as referenced in approved analytical methods, and use a standard statistical approach for QC measurements.

Completeness

Project-specific completeness goals account for all aspects of sample handling, from collection through data reporting. The level of completeness can be affected by loss or breakage of samples during transport, as well as external problems that prohibit collection of the sample. The following calculation is used for determining the percent complete:

$$\text{Completeness} = \frac{A}{B} \text{ x} 100$$

Where:

A = Actual number of measurements judged valid (the validity of a measurement result is determined by judging its suitability for its intended use)

B = Total number of measurements planned to achieve a specified level of confidence in decision making

The formula for sampling completeness is:

$$\text{Sampling Completeness} = \frac{\text{Number of locations sampled}}{\text{Number of planned sample locations}} \text{ x} 100$$

An example formula for analytical completeness is:

$$\text{Metals Analytical Completeness} = \frac{\text{Number of Usable Data Points}}{\text{Expected Number of Usable Data Points}} \text{ x} 100$$

The ability to meet or exceed completeness objectives is dependent on the nature of samples submitted for analysis.

Graphics

Graphic figures will be generated to depict sample locations, as needed. Also, if necessary, figures will be generated to represent contaminant concentrations at each sampling location. Each figure will contain a detailed legend.

Worksheet 37 — Data Usability Assessment (Continued)

(UFP-QAPP Manual Section 5.2.3 and Table 12)
(EPA 2106-G-05 Section 2.5.2, 2.5.3, and 2.5.4)

Reconciliation

PQOs will be examined to determine if the objective was met. This examination will include a combined overall assessment of the results of each analysis pertinent to an objective. Each analysis will first be evaluated separately in terms of the major impacts observed from the data verification and validation, DQIs, and MPC assessments. Based on the results of these assessments, the quality of the data will be determined. Based on the quality determined, the usability of the data for each analysis will be determined. Based on the combined usability of the data from all analyses for an objective, it will be determined if the PQO was met and whether project action limits were exceeded. As part of the reconciliation of each objective, conclusions will be drawn, and any limitations on the usability of any of the data will be described.

APPENDIX A
SITE SPECFIC DATA MANAGEMENT PLAN

		Site-Specific Data Management Plan			
		Project Name:	Gold King Mine Release ER	**TDD Number/Site ID:**	*Pending*
		Author:	Ian Bruce	**Company:**	WESTON Solutions
		Date Initiated:	August 5, 2015	**Last Updated:**	August 9, 2015
Viewer:	https://r8.ercloud.org/GoldKing/ OR http://www.epaosc.org/site/map_list.aspx?site_id=11108 (*OSC Interface*)				

This data management plan (DMP) is intended to provide guidance for data collection by field personnel and subsequent data management activities. The data collection and management practices presented in this plan are designed to ensure data integrity and consistency for all data collection personnel and from operational period to the next. This document is intended to be used in conjunction with a Region wide data management plan and only includes the details specific to the site.

Data Processing - The following table outlines the specific requirements for various data types being collected during the project.

	Data Input (Input Device)	Data Type	Data Source	Target Database	Site Specific Data Elements	Site Specific Verification	Site Specific SOP
1	Site Information and Documents (Notebook, iPad / FileMaker)	Site Info	WESTON Field Team	Scribe, EPAOSC.org	Site Name and Site Number, Event ID	Region 9 Auditor Rules	Appendix A2, Appendix A7
2	Site Photographs (iPad / PhotosInfoPro, iPhone, Garmin GLO)	Site Info	WESTON Field Team	EPAOSC.org	Photograph each sampling location, photos must be georeferenced	Field Personnel Review	Appendix A3, Appendix A5
3	Site Spatial Data (iPad / Collector, Trimble GeoXT)	Spatial Data	WESTON Field Team	Region 9 GIS Server	Sample ID and Latitude/Longitude	Region 9 ArcSDE Data Validation	Appendix A4, Appendix A12
4	Water Quality Monitoring (Notebook, iPad / FileMaker, YSI)	Monitoring	WESTON Field Team	Scribe	Sample ID and Latitude/Longitude, Instrument, Date and Time, WQ Parameters (Temperature, Conductivity, DO, pH, ORP, Turbidity)	Region 9 Auditor Rules	Appendix A2, Appendix A7
5	Water Sampling (Notebook, iPad / Filemaker, Grab Sampler / Jars)	Water Sampling	WESTON Field Team	Scribe	Sample ID and Latitude/Longitude, Date and Time	Region 9 Auditor Rules	Appendix A2, Appendix A7
6	Water Laboratory Results (Scribe-Compatible EDD)	Water Sampling	Analytical Laboratory	Scribe	Chains-of-Custody, Analytical Results with Units	Chemist QA Review, Region 9 Auditor Rules	Appendix B5
7	Sediment Sampling (Notebook, iPad / Filemaker, Disposable Scoops / Jars)	Water Sampling	WESTON Field Team	Scribe	Sample ID and Latitude/Longitude, Date and Time	Region 9 Auditor Rules	Appendix A2, Appendix A7

	Data Input (Input Device)	Data Type	Data Source	Target Database	Site Specific Data Elements	Site Specific Verification	Site Specific SOP
8	Sediment Laboratory Results (Scribe-Compatible EDD)	Water Sampling	Analytical Laboratory	Scribe	Chains-of-Custody, Analytical Results with Units	Chemist QA Review, Region 9 Auditor Rules	Appendix B5

Data Reporting - The following table outlines the specific requirements for various data reports being distributed during the project.

	Reporting Task	Data Inputs	Data Transformation	Deliverable Format(s)	Frequency
1	Monitoring Progress	2 - 4	Publish	Scribe.NET	Daily
3	Sampling Progress	2, 3, 5 - 8	Publish	Scribe.NET	Daily
4	Online Map Viewer	2 - 8	Publish	EPAOSC.org	Daily
5	Monitoring Report	1 - 4	Compilation / Summary	Scribe Subscription, PDF Document	Project Completion
6	Analytical Report	1, 5 - 8	Compilation / Summary	Scribe Subscription, PDF Document	Project Completion
7	Photo Log	2	Upload / Export	EPAOSC.org	As Requested
8	Data Export (Backup)	1 - 8	Export / Archive	Raw Data Format	Daily
9	Calibration Log	4	Transcribe	Spreadsheet	As Requested, Project Completion
10	Project Costs	1	TimeTrack and Burn Sheets Conversion	ODC Reports, 1900-55 Forms, RCMS Database	As Requested, Weekly

APPENDIX B
TESTAMERICA, SAVANNAH, GA, SOPs

APPENDIX C
TESTAMERICA, IRVINE, CA, SOPs

Title: Metals by ICP
EPA Methods 200.7 and 6010B

Approvals (Signature/Date):

Denny Tran 3/2/15
Denny Tran Date
Department Manager

William Nash 03/02/2015
William Nash Date
Environmental Health & Safety Coordinator

3-2-2015
Marie Friedman Date
Quality Assurance Manager

3/2/2015
Ben Beauchaine Date
Interim Laboratory Director

Facility Distribution No. _____ **Distributed To: _____**

1.0 SCOPE AND APPLICATION

1.1 This method describes the simultaneous multi-elemental determination of trace metals by Inductively Coupled Plasma (ICP), atomic emission spectroscopy (AES). Methods 200.7 and 6010B are used to determine trace metals in the following matrices: water, drinking water, waste water, and for NPDES Compliance Monitoring. More information summarizing the principles of ICP can be found in EPA Methods 200.7 and 6010B.

1.2 Elements are generally measured at the following wavelengths:

1.2.1 Routinely analyzed elements:

Element	Wavelength (nm)	Element	Wavelength (nm)
Aluminum (Al)	308.215	Manganese (Mn)	257.610
Antimony (Sb)	206.833	Molybdenum (Mo)	202.030
Arsenic (As)	188.979	Nickel (Ni)	231.604
Boron (B)	249.773	Phosphorus (P)	214.914
Barium (Ba)	233.527	Potassium (K)	766.490
Beryllium (Be)	313.107	Selenium (Se)	196.026
Cadmium (Cd)	214.438	Silicon (Si)	215.611
Calcium (Ca)	315.887	Silver (Ag)	328.068
Cobalt (Co)	228.616	Sodium (Na)	589.592
Chromium (Cr)	205.552	Strontium (Sr)	421.552
Copper (Cu)	324.754	Thallium (Tl)	190.800
Iron (Fe)	238.204	Tin (Sn)	189.933
Lead (Pb)	220.353	Titanium (Ti)	334.941
Lithium (Li)	610.362	Vanadium (V)	292.402
Magnesium (Mg)	279.079	Zinc (Zn)	213.856

See Attachments 1 and 2 for nominal reporting limits.

1.2.2 Special Request elements*:

Element	Wavelength (nm)	Element	Wavelength (nm)
Bismuth (Bi)	223.061	Scandium (Sc)	357.253, 361.383, 424.683
Gallium (Ga)	294.364 & 417.206	Zirconium (Zr)	343.823
Tungsten (W)	207.912		

*Nominal reporting limits for waters are 0.1 mg/L for Bi, Ga, and Sc. 0.2 mg/L for Zr

1.3 If silver (Ag) analysis is requested, the sample must be digested in all cases. When silver concentrations exceed the concentration of the LCS (0.25 ppm) for 200.7, a dilution must be performed by re-digestion, rather than diluting the digestate at the instrument. Boron and silica digestions must be performed in quartz or Teflon beakers.

1.4 **Method 200.7 is not recommended for low-level analysis of elements such as Antimony, Arsenic, Beryllium, Cadmium, Selenium and Thallium in Drinking Waters**. For drinking waters, they must be analyzed using EPA 200.8 (ICPMS).

1.5 Drinking Water Maximum Contaminant Levels (MCL) and California Detection Limits for reporting purposes (DLR) are found below. If a sample is analyzed for drinking waters, depending on the requested analytes, the sample may have to be concentrated, analyzed by an alternative method (e.g. 200.8), or reported with J flags (down to MDL) in order to meet the DLR requirements. See attached Analysis codes for the laboratory's standard analyte list and reporting limits.

Analyte	DLR (mg/l)	MCL (mg/l)	Analyte	DLR (mg/L)	MCL (mg/l)
Aluminum	0.050	1.0	**Iron**	0.10	0.30
Antimony	0.0060	0.0060	**Lead**	0.0050	0.0
Arsenic	0.002	0.010	**Manganese**	0.020	0.050
Barium	0.10	1.0	**Nickel**	0.010	0.10
Beryllium	0.0010	0.0040	**Selenium**	0.0050	0.050
Cadmium	0.0010	0.0050	**Silver**	0.010	0.10
Chromium (total)	0.010	0.050	**Thallium**	0.0010	0.0020
Copper	0.050	1.0	**Zinc**	0.050	5.0

From Chemicals and Parameters in California Drinking Water Quality Database (12/19/07)

1.6 On occasion, clients may request modifications to this SOP. These modifications are handled following the procedures outlined in "Validation of Methods" in the Quality Assurance Manual.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using the appropriate sample preparation method (EPA 200.2, EPA 3005A, EPA 3050B or EPA 3010A). For dissolved metals, acid digestion is not necessary if the samples are filtered through a 0.45 μm membrane filter and acid preserved prior to analysis. For drinking water, if the measured turbidity is <1 NTU, digestion is not required but samples must be matrix matched to calibration standards. Yttrium internal standard is added to all samples and QC.

2.2 Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by optical photosensitive devices.

2.3 Concentrations are quantitated using a linear regression calibration curve.

3.0 DEFINITIONS

3.1 IEC--Inter-element correction

3.2 MSF--Multi-component spectral fitting

3.3 NCM—Non-Conformance Memo

There are no additional specific definitions associated with this test. See the laboratory QA manual and EPA methods 200.7 and 6010B for general definitions.

4.0 INTERFERENCES

4.1 Spectral Interferences

4.1.1 Spectral interferences are caused by background emission from stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

4.1.2 Spectral interference effects are minimized by maintaining constant plasma conditions and through the use of background corrections (IECs and/or MSF).

4.1.3 Background emission must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be as free as possible from spectral interference and must reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

4.2 Physical interferences

4.2.1 Physical interferences are effects associated with the sample nebulization and transport process.

4.2.2 Samples with high dissolved solids (TDS) or high acid concentrations can cause changes in viscosity and surface tension which, in turn, affects the sample nebulization and transport.

4.2.3 Physical interference effects can be minimized through the use of a peristaltic pump and internal standard.

4.3 Chemical interferences

4.3.1 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects.

4.3.2 These types of interferences are not normally a problem with ICP analysis. However maintaining consistent plasma conditions and the use of special procedures such as buffering the solutions, matrix matching standards or the method of standard addition (MSA) may help reduce chemical interferences.

4.4 Memory interferences

4.4.1 Memory interference result when analytes in a previous sample contribute to the signals measured in a new sample.

4.4.2 Optimizing the rinse time between samples and using a rinse solution with the proper acid strength can minimize memory effects.

4.4.3 Even using these precautions, a sample may be too high to rinse completely under normal circumstances. The analyst must be aware of this situation, and samples immediately following a high sample must be re-analyzed.

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous materials, operations, and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal, and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats, and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Personal Protective Equipment Required: safety glasses, face shield, lab coat and nitrile gloves.

The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

5.2 Primary Materials Used

The following is a list of the materials used in this method that have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 EQUIPMENT AND SUPPLIES

6.1 Instrumentation

6.1.1 Inductively coupled plasma (ICP) - OPTIMA 3000XL/4300 or equivalent
6.1.2 Autosampler - ESI SC-4DX Fast or equivalent
6.1.3 Personal computer for data acquisition, monitor, keyboard, and printer

6.2 Supplies

6.2.1 Argon gas
6.2.2 Pipettes, pipettors and tips
6.2.3 Volumetric flasks – various sizes
6.2.4 Sample tube racks
6.2.5 Graduated centrifuge tubes (15 ml)
6.2.6 Plastic containers

7.0 REAGENTS AND STANDARDS

7.1 Reagents

All purchased and prepared reagents must be made from a traceable (NIST) source material, if available, and documentation of this traceabililty must be maintained by the laboratory.

7.1.1 Yttrium standard solution (10000 ppm)
7.1.2 Concentrated Nitric Acid (HNO_3, instrument grade)
7.1.3 Reagent Grade Water (Ultrapure water)

7.2 Standards

All purchased standards must be accompanied by a Certificate of Analysis (C of A) which is kept available at the laboratory in order to demonstrate traceability of the standard to certified (NIST-traceable) source material. All prepared standards must be made from a traceable (NIST, if available) source material, if available documentation of this traceabililty must be maintained by the laboratory.

7.2.1 O2SI Metal Stock Standards (or equivalent)

7.2.2 Accutrace standard Metal Stock Standards (or equivalent)

7.2.3 Accutrace standard or Spex Spectral Interference Check Solution (SICS): 500ppm Al, Ca and Mg; 200ppm Fe

7.2.4 Sodium (1000ppm), Accutrace, Spex or equivalent standard.

7.2.5 Potassium (1000ppm), Accutrace, Spex or equivalent standard.

7.2.6 10000ppm stock standards: Al, Ca, Mg, Fe, Cr, Cu, Mn, Mo, Ni, Ti, V, Zn, Sn, Co

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Sample containers, preservation techniques, and holding times may vary and are dependent on sample matrix, EPA method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters[1,2]	Polyethylene bottles	500 ml	HNO_3 to pH<2	6 months	40 CFR Part 136.3
Soils	Glass jar/ brass sleeve	4 oz	None (Cool >0 to 6ºC if Hg needed)	6 months	SW846 Chapter 3

Footnote 1: Water samples received unpreserved must be acidified and allowed to sit for 24 hours prior to analysis.
Footnote 2: For analysis of dissolved metals, samples must be filtered and preserved in the field within 15 minutes of sampling. If samples are not preserved, sample must be acidified and allowed to sit for 24 hours prior to analysis.
Footnote 3: Samples received unpreserved for dissolved metals are filtered as soon as possible (generally within 24 hours) and acidified immediately after filtration. Samples can then be digested/analyzed immediately (i.e. they do not need to sit for 24 hours).

9.0 QUALITY CONTROL

9.1 Sample QC

The following quality control samples are prepared with each batch of samples. Each of these QC samples may be re-analyzed once if it doesn't pass, prior to sample analysis, in order to verify the failure wasn't due to a physical or mechanical problem.
NOTE: allowances for the reporting of non-detect data associated with high-biased QC (Blank and LCS) may be prohibited by specific programs or client project plans.

9.1.1 Method Blank (MB)

Prepare and analyze a method blank (MB) for each matrix and with every batch of 20 samples or less. Check that there are no analytes detected (<±RL if reporting to RL, <±MDL if reporting to MDL per specific client request)

If the method blank (MB) shows contamination for a requested metal, re-prepare and re-analyze MB once unless:

- The sample concentrations are not detected (ND). Flag the result accordingly and write an NCM.
- The sample result is > 10x the blank level. Flag the result accordingly and write an NCM

If the MB is re-analyzed, all positive samples < 10x RL must also be reanalyzed.

If the re-analyzed MB still shows contamination, re-prepare and re-digest the affected samples.

9.1.2 Laboratory Control Sample (LCS).

Prepare and analyze a primary source laboratory control sample (LCS) for every batch of 20 samples or less at following concentrations:

	All metals	**Na, K**	**Ca, Mg, Si**
EPA 200.7	0.5 ppm	5 ppm	2.5 ppm
EPA 6010B	1.0 ppm	10 ppm	5.0 ppm

The LCS recovery must be within **85-115%** for EPA 200.7 and **80-120%** for EPA 6010B and relative percent difference within ± **20%**

If the LCS is outside of the limit for a requested metal, re-prepare and re-analyze the LCS once:

- If the LCS is still below the acceptance limit, the effected samples must be re-digested and re-analyzed.
- If the LCS is above the acceptance limits and samples are ND, the results may be reported. The results must be flagged and a NCM must be submitted**.**
- If the LCS is above the acceptance limits and samples are greater than or equal to reporting limit, samples and LCS must be re-digested and/or re-analyzed.
- If the LCS is above the acceptance limits and samples are to be reported down to the MDL (J-flagging), then all samples greater than or equal to the MDL and the LCS must be re-digested and/or re-analyzed.
- All positive samples must be re-analyzed with the LCS if the LCS is re-analyzed

9.1.3 LCS Duplicate (LCSD)

Prepare and analyze in the same manner as the LCS when insufficient sample is available for the MS/MSD or when requested by the client/project/contract. The Relative Percent Difference (RPD) between corresponding analytes in the LCS/LCSD must be within the laboratory generated acceptance limits. If the RPD is outside of these limits, re-analyze once. If it is still unacceptable, perform corrective action and then re-prepare the entire batch and/or re-calibrate the system unless:

- the individual LCS and LCSD recoveries are within acceptance limits and the affected target analyte is ND in the sample. This must be flagged and documented with an NCM.
- one or both of the LCS/LCSD recoveries are above the acceptance limit and the affected target analyte is ND in the sample. This must also be flagged and documented with an NCM.

9.1.4 Matrix Spike and Matrix Spike Duplicate (MS/MSD).

The sample for MS/MSD is randomly selected, unless specifically requested by a client.
Prepare and analyze a matrix spike (MS) and a matrix spike (MSD) duplicate for each matrix and with every batch of 10 samples, or less for EPA 200.7 and every 20 samples or less for EPA 6010B. The recovery must be within **70-130%** for EPA 200.7 and **75-125%** for EPA 6010B unless the source is 4 times greater than the amount spiked. A relative percent difference within ± **20%**, unless there is matrix interference. In the case of matrix interference, flag the results accordingly and write an NCM.

9.1.5 Method Reporting Limit (MRL) for drinking water samples

Prepare and analyze an MRL for every batch of 20 samples or less.

The analyte recoveries for the MRL samples must fall within ±50% of the theoretical value for Arizona samples and must be detected for CA and Federal samples. Note: this requirement is a drinking water compliance requirement, not a method requirement.
If the MRL is outside of the limit for a requested metal, re-prepare and re-analyze once:

- If the MRL is still below the acceptance limit, the affected samples must be re-digested and re-analyzed.
- If the MRL is above the acceptance limits and samples are ND, the results may be reported. The results must be flagged and a non-conformance memo (NCM) written.
- All positive samples must be re-analyzed with the MRL if the MRL is re-analyzed

9.1.6 Dilution Test

- If the analyte concentration is sufficiently high (a factor of 10 above the RL after dilution or 50 times without dilution), an analysis of a 1:5 dilution must agree within ± 10% of the original determination.
- If the two samples differ by more than ± 10%, chemical or physical interference effect must be suspected.
- If the regular sample is reported at a dilution, then the diluted sample must be performed at 5 times that dilution (e.g., if reporting at 5X, the dilution test samples must be run at 25X)
- One dilution test must be included for each 20 samples (or less) of each batch.

9.1.7 Post Digestion Spike (for 6010B only)

If a 6010B MS and/or MSD recovery fails, a Post Digestion Spike (PDS) must be performed. A spike is added to portion of a sample or its dilution and must have a recovery of within 75 to 125 %. The spike addition must be based on the concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, a matrix effect must be suspected. Report the PDS with a flag and write and NCM.

9.2 Instrument QC

The following instrument QC samples are run with each analytical sequence. Each of these QC samples may be re-analyzed once if it does not pass in order to verify the failure wasn't due to a physical or mechanical problem. Re-analysis must be performed before the analysis of any associated batch QC or client samples.

9.2.1 Calibration Acceptance Summary

Prepare a calibration curve by plotting the response (peak area) of at least two standards and a blank against the corresponding concentrations. The resulting correlation coefficient (r) must be ≥ **0.995**. If this criterion is not met re-prepare the calibration standards and repeat the calibration. Refer to the "Calibration Curves" SOP and the "Selection of Calibration Points" SOP for more information on calibrating the instrument.

9.2.2 Internal Standard

The percent recovery of Internal Standard in all samples, batch QC and calibration checks must be within 60-140% of the true value.

- If the recovery in any calibration standard is outside acceptance limits, re-calibration is required.
- If the recovery is outside acceptance limits in any other QC sample (not including MS/MSD), re-analysis must be performed.
- If the recovery is outside acceptance limits in any other samples or MS/MSD because of matrix interference, dilute and re-analyze the samples.
- Otherwise, troubleshoot the ICP instrumentation.

9.2.3 Initial Calibration Verification (ICV)

Immediately after the initial calibration, analyze a secondary source ICV. Verify that that it meets the following criteria:

	% Recovery	%RSD
EPA 200.7	95-105	5
EPA 6010B	90-110	5

- If the recovery for any requested metal is outside the acceptance criteria, re-prepare and re-analyze the ICV once.
- If the ICV is still below the acceptance limit (<95% for 200.7 or <90% for 6010B) for the requested metal, re-calibrate and re-analyze the ICV.
- If the ICV is above the acceptance limits (105% for 200.7 or 110% for 6010) and samples are ND, the results may be reported with a flag and an appropriate NCM.
  - If the ICV is outside limits (high or low), all samples greater than or equal to RL (or MDL for samples reported to the MDL) must be re-analyzed with a new calibration and passing ICV.

9.2.4 Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB)

- Analyze the initial calibration blank (ICB) immediately after the ICV and the continuing calibration blank after every CCV. The absolute value of the blanks must not be greater

than the reporting limit (RL) for bracketed samples at concentrations above twice the RL (2xRL). For reporting samples with concentrations at or below twice the RL, the ICB/CCB must read less than half the RL or less than the MDL, whichever is greater.

- If any element exceeds the limit, check to see if it is a requested metal. If the element is not required for the analysis run, the analysis can proceed as is.

- If the element is required, re-analyze the ICB and, if it is still out of limits, re-calibrate and re-analyze ICV and ICB.
- Re-analysis is not required if the sample results are ≥ 10x the absolute value of the calibration blank or the calibration blank concentration is above the RL (or MDL for samples reported to the MDL) and samples are not detected (ND).

9.2.5 Continuing Calibration Verification (CCV)

- Analyze a CCV standard after every 10 sample aliquots (injections) or less and at the end of the analysis sequence. The recovery must be within ± 10% of the true value and its RSD must be 5% or less.

- If the CCV is outside recovery limits for the element(s) of interest, re-analyze once.

- If it is still outside the recovery limits after re-analysis, the instrument must be re-calibrated and samples not bracketed by acceptable CCVs must be re-analyzed.

- If the CCV is fails **above** the limits, any ND samples may be reported with a flag and an NCM.

- If a CCV fails during an overnight or unattended run, re-analyze all samples that need analysis of the element(s) not bracketed by acceptable CCVs.

- All samples greater than or equal to RL (or MDL for samples reported to the MDL) must be re-analyzed with a passing CCV.

9.2.6 Reporting Limit (RL) Check

- A Reporting Limit check at 1x or 2x the RL must be run before analyzing samples (and at the end of run if required by specific projects). For drinking water, it must be a 1x RL. A recovery of 50-150% must be achieved.

- If the RL check is outside recovery limits for the element(s) of interest, re-prepared and re-analyze once. If it is still out, the instrument must be recalibrated before analyzing samples.

- If the RL check fails **above** the limits, any ND samples may be reported with a flag and an appropriate NCM.

9.2.7 ICSA/ICSAB

- An ICSA is run before analyzing samples. Verify that the absolute value of any false reading is less than 2x RL of the interfered element.
- An ICSAB is run after the ICSA. Verify that the percent recovery of spiked elements is within 80-120% of the true value of the spike amount.
- If the ICSA or ICSAB are outside recovery limits for the element(s) of interest, re-analyze once.
- If the ICSA or ICSAB are still outside the recovery limits after re-analysis, IEC factor must be adjusted (see Calculation of IEC offset section) and the instrument must be re-calibrated.
- If the ICSA or ICSAB fail **above** the requirements, any ND samples may be reported with a flag and an appropriate NCM
- If required by specific projects, close the run sequence with an ICSA and ICSAB.

9.2.8 Precision (RSD%) and Response range

Sample replicates must meet the following precision:

- Results less than 2 x RL must have an RSD < 50%.
- Results equal or greater than 2 x RL must have RSD < 25% between replicates.
- Otherwise, re-analyze samples

9.2.9 Instrument Detection Limit (IDL)

- Instrument Detection Limits studies are performed by charting a minimum of 30 calibration blanks. The IDL will then be determined as the mean plus three times the standard deviation. The calculation can be performed using the TALS Control Chart module.

- The IDL of each element must be compiled every six months.

- The IDL must not be higher than Method Detection Limit of the same element.

- If the IDL for any element exceeds the MDL, instrument performance must be evaluated and any needed preventative maintenance conducted. If the IDL still exceeds the existing MDL, the higher of the two will be used as the MDL.

9.2.10 Linear dynamic range (LDR)

Every year, verify the response of each reported element by analyzing single element standards at 20 ppm or higher. The percent recovery of each element must be within 90-110% of the true value at the highest reportable range. Document the achieved linear ranges.

Sample readings must not be greater than 90% of the linear dynamic range (LDR), or the samples have to be diluted.

9.2.11 Spectral Interference Adjustments

- IEC (Interelement correction)
  - IEC is used to adjust for spectral interferences between two elements by assigning a factor that corrects the concentration of the target metal based on the concentration of the interferent metals.
  - IECs are based on the fixed spectral characteristics of each metal. For a given wavelength of the target, only specific metals will be interferents. When IECs are

established, the corrections used must be verified to ensure they are not erroneously based on other than the spectral characteristics.

- Verify and update (if necessary) every six months using the IEC factors from the analysis of 20 ppm single element standards (except Fe at 200 ppm, and Al, Ca, Mg at 500 ppm). The percent recovery of each element must be within 90-110% of the spiked value. Ensure that the standards are free of contamination and the background correction points selected for peak integration are clear of spectral interference. NOTE: verification is required only for those metals processed using IECs.
- Samples that have IEC interferents elements (Al, Ca, Fe, and Mg), at concentrations greater than or equal to 120% of the IEC check levels must be analyzed at dilutions that lower these concentration below 120% of the IEC check level.

- MSF (Multicomponent Spectral Fitting)
  - MSF uses multivariate calibration to determine the concentration of an analyte. Multivariate calibration is analogous to a mathematical filter that can distinguish between the components of a complex spectral profile. The signal contribution of three (3) components can be separated from the analyte: interference, background, and noise.
  - MSF is beneficial when:
    - it is difficult to assess background correction points, or
    - the noise contribution is significant, such as in measurements near the analyte detection limit.
  - MSF is not suitable where there is complete overlap of analyte and interferent. In that case, IEC must be used instead.

10.0 PROCEDURE

10.1 Standard Preparation

10.1.1 Acidified Reagent Grade Water:
Prepare acidified water to use in the preparation of all subsequent standards. Add the appropriate volume of HNO_3 and HCl to Reagent Grade Water to obtain a 1% (v/v) HNO_3 and 2% (v/v) HCl solution.

10.1.2 ICP rinse:
Prepare the ICP rinse solution by adding the appropriate volume of HNO_3 and HCl to Reagent Grade Water to obtain a 5% (v/v) HNO_3 and 5% (v/v) HCl solution.

10.1.3 Daily Standard:
Daily, prepare the calibration standards, S1, S2, S3, etc., by adding the appropriate volumes of Accutrace standard stock solutions to acidified Reagent Grade Water. The final concentrations are listed below.

Calibration Std	ppm (mg/L) [1]
Blank	0
S1	0.005 (Ca, Mg, K, Na at 0.05, Si at 0.025, Ag at 0.0025)
S2	0.1 (Ca, Mg, K, Na at 1, Si at 0.5, Ag at 0.05)
S3	1 (Ca, Mg, K, Na at 10, Si at 5.0, Ag at 0.5)

[1]There are metals (Ga, Bi, Sc, Zr, W, etc.) that are not routinely analyzed and the calibration concentrations are not shown above. The calibration concentrations will be shown on the instrument printout.

10.1.4 RL Check:
Prepare daily a Reporting Limit (**RL**) Check Standard at twice the RL (**at the RL for drinking water**) by using appropriate volumes of Accutrace standard stock solutions to acidified Reagent Grade Water.

10.1.5 ICB and CCB
The initial calibration blank (ICBV) and the continuing calibration blank (CCB) are prepared by acidifying Reagent Grade Water to the same concentrations of the acids found in the standards and samples.

10.1.6 ICV (2nd source):
The Initial Calibration Verification (**ICV**) standard is prepared at 2.0 ppm [20 ppm for Na, K, 10 ppm Si, 1 ppm Ag, 2.0 ppm for Ca (Spex) or 10 ppm Ca and Mg(O2Si)] from a secondary source or different lot number than that of the calibration standard.

10.1.7 CCV:
The Continuing Calibration Verification (**CCV**) – is prepared at 1ppm (10ppm for Na, K; 5 ppm for Si; 0.5 for Ag) from the same source as that used for the calibration standards.

10.1.8 ICSA:
The Interference Check Solution (**ICS**) - consists of ICSA and ICSAB portions. The ICSA solution contains 500 ppm for Al, Ca, Mg and 200 ppm for Fe. The ICSA provides a test of the correction factors. Prepare the solution with acidified Reagent Grade Water.

10.1.9 ICSAB:
The Interference Check Solution B (ICSAB) is prepared from the initial calibration standard solution at a concentration of 0.5 ppm for all target elements except: K and Na at 10 ppm; Si at 5ppm; Ag at 0.25ppm; Fe at 200 ppm; Al, Ca, and Mg at 500 ppm.

Document the preparation of all intermediate standards in the data system (LIMS) and ensure it is peer-reviewed before use. Store the solution at room temperature for up to one year.

10.2 Sample Preparation

See the appropriate laboratory SOP for sample preparation procedures.

10.2.1 Water samples to be analyzed by EPA 200.7 are to be treated per EPA 200.2.

- Pour the sample into a 15mL centrifuge tube, dilute if necessary.
- The internal standard is added using the peristaltic pump of the instrument or autosampler.

10.2.2 Water samples to be analyzed by EPA 6010 B are to be digested per EPA 3005.

- Prepare the sample in the same way as EPA 200.7.

10.2.3 Soil samples to be analyzed by EPA 6010B are to be digested per EPA 3050.

- Soil samples are diluted 5X after digestion and before analysis.
- Pipette 2.5 mL of the sample into a centrifuge tube.
- Add 10 mL of acidified Reagent Grade Water.
- The internal standard is added using the peristaltic pump of the instrument or autosampler.

10.2.4 Soil samples to be analyzed by EPA 6010B are to be digested per EPA 3050 – Special Low Level

- Soil samples are diluted 4X after digestion and before analysis.
- Pipette 3 mL of the sample into a centrifuge tube.
- Add 9 mL of acidified Reagent Grade Water.
- The internal standard is added using the peristaltic pump of the instrument or autosampler.

10.2.5 Soil samples to be analyzed by EPA 6010B are to be digested per EPA 3051.

- Soil samples are diluted 2X after digestion and before analysis.
- Pipette 6 mL of the sample into a centrifuge tube.
- Add 6 mL of acidified Reagent Grade Water.
- The internal standard is added using the peristaltic pump of the instrument or autosampler.

10.2.6 Leachates (SPLP or TCLP) are to be digested per EPA 3010.

- Pour the sample into a 12mL centrifuge tube.
- The internal standard is added using the peristaltic pump of the instrument or autosampler.

10.2.7 Leachates (STLC)

- Pipette 0.5mL of a STLC sample into a centrifuge tube.
- Add 9.5 mL of acidified Reagent Grade Water.
- The internal standard is added using the peristaltic pump of the instrument or autosampler..

10.2.8 Leachates (DI WET)

- Pour the sample into a 15mL centrifuge tube.
- The internal standard is added using the peristaltic pump of the instrument or autosampler..

10.2.9 Cation Exchange Capacity (CEC)

- Pipette 1mL of a CEC sample into a centrifuge tube.
- Add 9 mL of acidified Reagent Grade Water.
- The internal standard is added using the peristaltic pump of the instrument or autosampler.

10.3 Instrument Initialization

10.3.1 Follow the instructions provided by the instrument manufacturer for operating conditions.

10.3.2 Prior to daily calibration of the instrument, the manganese axial and radial alignment is performed using a 1ppm Mn standard. Note the highest Mn intensity. If the intensity differs by more than ±30% from the intensity measured in the most recent IEC study, then maintenance is required for the instrument.

10.3.3 Mercury (Hg) alignment is performed whenever the torch is moved, cleaned, or changed.

10.3.4 A Cu/Mn intensity ratio is not calculated.

10.3.5 Transfer all the standards and samples into their corresponding centrifuge tubes. Place the centrifuge tubes into the autosampler. Yttrium is used as the internal standard, and is added to every sample and standard.

10.4 Calibration

10.4.1 Calibrate the instrument daily using a blank, S1, S2 and S3.

10.4.2 Verify the linearity of the initial calibration and its acceptance against a secondary source ICV standard.

10.5 Sample Analysis

10.5.1 A typical daily run sequence is listed below:

		Recovery (%)	RSD (%)
1	Initial calibration		
2	ICV (6010B):	90 – 110%	5%
	ICV (200.7):	95 – 105%	5%
3	ICB	<±RL for samples ≥2x RL OR ≤ ±½ RL or MDL (whichever is greater) for samples <2x RL	
4	ICSA	≤ 2x RL	
5	ICSAB	80 – 120%	
6	RL check	50 – 150%	
7	Method Blank	< RL	
8	LCS	200.7: 85-115% RPD: 20% 6010B: 80-120% RPD: 20%	5%
9	Sample		25%*
10	MS	200.7: 70-130% RPD: 20% 6010B: 75-125% RPD: 20%	
11	MSD	Same as above	
12	5 sample aliquots		25%**
13	CCV	90 – 110%	5%
14	CCB	<±RL for samples ≥2x RL OR ≤ ±½ RL or MDL (whichever is greater) for samples <2x RL	
15	10 sample aliquots		25%*
16	CCV	90 – 110%	5%
17	CCB	<±RL for samples ≥2x RL OR ≤ ±½ RL or MDL (whichever is greater) for samples <2x RL	

ICSA/ICSAB is at the close if required by special project.

*For sample results >2X the RL, otherwise RSD must be ≤50%.
No RSD requirements for results < RL

10.6 Preventative Maintenance

10.6.1 Daily maintenance includes, but is not limited to, the inspection, cleaning, and/or replacement of the following items: peristaltic pump tubing; nebulizer assembly and torch; inert gas; and rinse solution and waste containers.

10.6.2 Document all non-routine maintenance. Document any necessary maintenance performed to bring the instrument back to control status after failing QC checks.

10.6.3 If an instrument is unusable or has limitation to its use, it must be tagged accordingly until such a time the problem has been corrected. Record the problem, solution, date, and verification of proper operation into the instrument maintenance logbook.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Accuracy

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{Observed concentration}}{\text{Known concentration}} \times 100$$

$$\text{MS \% Recovery} = \frac{\text{(Spiked sample) - (Unspiked sample)}}{\text{Spiked concentration}} \times 100$$

11.2 Precision (RPD)

$$\text{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

11.3 Concentration

11.3.1 Analytical results as measured from the instrument are referred to as initial results.

11.3.2 Initial results, and any additional dilution (in conjunction with information from the preparation bench sheet), are uploaded into the data system for final result calculation.

11.3.3 Alternatively, final results can be calculated as follows:

$$\text{fResults (ppm)} = \text{iResults} \times \text{DF} \times \frac{\text{iSample (mL or mg)}}{\text{fSample}}$$

Where:

fResults (ppm) = final results (mg/L or mg/Kg)
DF = additional Dilution Factor
iSample = initial sample volume (mL) or weight (g)
fSample = final sample digestate volume (mL

11.3.4 Results calculated from filter or wipe for air sampling (ug/m3):

$$\text{calResults (ug/m}^3\text{)} = \frac{\text{fResults (ug/filter)}}{\text{L (m}^3\text{)}}$$

Where:

calResults (ug/ m^3) = calculated results for air sampling (ug/ m^3)
fResults (ug/filter) = final results for filter or wipes (ug/filer or wipe)
L (m^3) = volume of air used in air sampling (m^3)

11.4 Calculation of IEC offset

IEC corrections factors are the ratios of the apparent concentration for each analyte to the concentration measured for the IEC reference element. The IEC table is typically done, and saved every six months by referring to instrument software manual (e.g. Winlab32 software guide).

On a daily basis, the automatically calculated and predetermined IEC factors from the table can be offset by a manual calculation, if needed, to improve the accuracy in analyzing a solution of a known concentration. For example, a reference solution of an interfering solution, 180 ppm Fe, yields an apparent concentration of -0.0123 ppm As and results in 186.6 ppm Fe. The IEC offset is calculated as:

$$\frac{-0.0123\,Asppm}{186.6\,Feppm}\times 1000 = -0.06592\ ppbAs\ /\ ppmFe$$

This result (positive or negative) is then algebraically added to the predetermined factor in the IEC table, supposedly equal to 0.19372:

$$0.19372 - 0.06592 = 0.13077$$

The newly calculated result , 0.13077, is updated in the IEC table for the interferent, Fe, and on the element, As. The IEC is saved as a new file and/or printed out for documentation.

12.0 METHOD PERFORMANCE

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure as described in laboratory's SOP, IR-QA-MDL. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains annual MDL studies and verifications for 200.7/6010B analyses. MDL analyses must also be performed before sample analysis if any major (non-routine) changes have been made to the instrumentation of a specific ICP.

12.2 Instrument Detection Limit (IDL)

The instrument detection limit (IDL) is the lowest concentration that can be detected for a given analyte on a specific instrument independent of matrix and sample preparation. It is used to determine instrument sensitivity as opposed to the method sensitivity for which the MDL is used. IDLs reflect a statistical value for instrument sensitivity and may not be achievable in actual samples. The laboratory maintains semiannual IDL studies for each instrument. These studies are compared to the MDLs and must be at or below the MDL levels.

12.3 Demonstration of Capabilities

Every analyst must perform an Initial Demonstration of Capability (IDOC) before performing analyses on any client samples. An IDOC consists of 4 consecutive LCS samples at 1 to 4 times the RL with an average recovery and RSD within laboratory acceptance limits. An On-going Demonstration of Capability (ODOC) must be performed annually. An ODOC consists of either 4 consecutive LCSs at mid-level or a passing PT.

12.4 Training Requirements

The analyst must have documented training, including reading of the SOP and source methods, conducted by the department manager, senior chemist, or other analyst with training, documentation, and a passing DOC.

13.0 POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, and preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in the "Waste Management and Pollution Prevention" section of the Corporate Environmental Health and Safety Manual (CW-E-M-001).

14.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples, and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the laboratory's Waste Disposal SOP (IR-EHS-WASTE). The following waste streams are produced when this method is carried out:

- **Metals digestates** (50 ml polytubes). Once the samples have been analyzed, they are stored on in the metal shelves for 30 - 60 days. After the 30 -60 days, analysts transfer the digestates to the main waste storage area. Sample archive technicians will store this waste on the shelves designated for metals for another 30-60 days. After this time, Sample archive technicians will bulk this waste as nitric acid waste w/RCRA metals.
- **Acid Waste** (Hydrochloric, Nitric Acid). This waste is generated by ICP /ICP-MS instruments. This waste is collected behind the instruments into 4 gal Carboy satellite container. Analysts in the metals department remove the individual Carboy satellite containers and neutralize the waste with 50% Sodium hydroxide and soda ash. The neutralized non-hazardous waste is drained to the sewer by the analysts.
- **Unused standards or reagents.** If the standard or reagent is hazardous and can not be collected with one of the waste streams generated in the method, then the analysts and technicians will take this standard or reagent and place it on the shelves labeled "hazardous waste" in the main waste storage area. The waste material must be labeled with the words "Hazardous Waste", contents and the date taken to the waste storage area. The waste material will be lab packed (example: mercury standard).
- If the waste material can be collected in the satellite waste container for one of the waste streams of the method, then pour the standard in the right satellite container, rinse the original container, and collect the rinsate in the satellite container. The original container can be placed in the regular trash. (Example, buffer solutions pH 4). Sample archive technicians will bulk this waste with the nitric acid waste w/RCRA metals.

15.0 REFERENCES / CROSS-REFERENCES

15.1 **Reference 1**: EPA Method 200.7, EMMC Version, Revision 4.4 May 1994

15.2 **Reference 2**: EPA SW-846 Final Update III, December 1996, EPA Method 6010B.

16.0 METHOD MODIFICATIONS

Item	Method	Modification
1	200.7 (9.3.1)	ICB/CCB acceptance criteria modified from 2.2 x MDL or >10% of any sample concentration, whichever is greater, to <±RL for samples ≥ 2x RL and ≤ ±½ RL (or <MDL, whichever is greater) for samples <2x RL.
2	200.7 (1.6)	Samples containing Silver are diluted only when the concentration exceeds the LCS level of 0.25 ppm rather than 0.1 ppm. Historical laboratory data (filed with SOP*) indicates that effective silver recoveries can still be attained at this level

Item	Method	Modification
3	200.7 (9.3.4)	The RSD of two replicates of the ICV has been set at 5%. The method only states the RSD be <3% if 4 or more replicates are analyzed

*****SOP support document "IR-MET-ICP_r0-Ag LCS Recoveries_12mar2009"

17.0 ATTACHMENTS

17.1 **Attachment 1a:** Analysis Information for 200.7

17.2 **Attachment 1b:** Analysis Information for 6010B - Water

17.3 **Attachment 1c:** Analysis Information for 6010B - Soil

17.4 **Attachment 2:** Data Review Checklist

17.5 **Attachment 3:** Daily ICP Standards IDs

18.0 REVISION HISTORY

This section has been added beginning with Revision 0. Only details of the last two revisions are incorporated into this SOP. Prior revisions are documented in the QA files.

18.1 Revision 4, dated 05 February 2014

- This revision superseded IR-MET-ICP, revision 3 (01/18/2013)
- Added requirement that all samples with detects (>RL) must be re-analyzed if LCS is re analyzed.
- Added MRL requirements for drinking water samples
- Added dilution test and post-digestion spike requirements, as applicable
- Revised by DD

18.2 Revision 5 dated 02 March 2015

- This revision superseded IR-MET-ICP, revision 4 (02/05/2014) as well as SOP Change Forms CF1 (01/16/2015) and CF2 (02/27/2015)
- Added LCS/LCSD RPD criteria
- Updated IDL calculation to be based on 30 blanks
- Updated criteria for manganese intensity check
- Updated data review checklist to Corporate version (icp-data-review-cklist_rev1_9jan2015_ca-q-wi-043)
- Prepared by DD

Attachment 1a
Analysis Information (200.7)

Attachment 1b
Analysis Information (6010B-Water)

Attachment 1c
Analysis Information (6010B-SOIL)

Attachment 2
Data Review Checklist, page 1 of 3

Attachment 2
Data Review Checklist, page 2 of 3

Attachment 2
Data Review Checklist, page 3 of 3

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Attachment 3
Daily ICP Standards IDs

DAILY ICP STANDARD IDs

ICP ID#:_____ **DATE:**_____

STD 0
STD 1
STD 2
STD 3

ICV
ICS A
ICS AB

CRI 2
CRI 3

CCV
CCB

ICV Failures:_____

ICS A Failures:_____

ICS AB Failures:_____

CRI Failures:_____

icpstandards_r0
rev. 12/10/2012

Title: Mercury Preparation and Analysis by Cold Vapor Atomic Absorption
EPA Method 245.1 / 7470A / 7471A

Approvals (Signature/Date):

Denny Tran — 8/11/14 — Date
Department Manager

William Nash — 08/11/2014 — Date
Environmental Health & Safety Coordinator

Maria Friedman — 8-11-2014 — Date
Quality Assurance Manager

Kirk Miltimore — 08/11/14 — Date
Laboratory Director

Facility Distribution No. _____ **Distributed To: _____**

1.0 SCOPE AND APPLICATION

EPA Methods 245.1, 7470A and 7471A are cold vapor atomic absorption (CVAA) procedures used to determine the concentration of mercury in various aqueous and solid matrices.

EPA 245.1 is used for drinking water, surface water, ground water, sea water, brackish water and industrial and domestic wastewater.

EPA Method 7470A is approved for determining the concentration of mercury in mobility-procedure extracts, aqueous waste and ground water.

EPA Method 7471A is approved for measuring total mercury (organic and inorganic) in solid wastes, soils, sediments and sludge type materials.

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in "Validation of Methods" in the Quality Assurance Manual.

See Attachment 1 for reporting limit and QC information.

2.0 SUMMARY OF METHOD

All samples are subjected to an appropriate dissolution step before analysis.

The mercury is reduced to its elemental state and aerated from solution in a closed system. The mercury vapor then passes through a cell positioned in the light path of an atomic absorption spectrophotometer.

Quantitation is based upon absorption of radiation at the 253.7 nm wavelength by mercury vapor. Absorbance (peak height) is measured as a function of mercury concentration.

3.0 DEFINITIONS

3.1 Definitions

3.1.1 IPC—Instrument Performance Check Solution. A solution containing a concentration at the mid-level calibration and analyzed immediately after the calibration to evaluate instrument performance. In this SOP, the ICV is used as the IPC.

3.1.2 QCS—Quality Control Standard. A solution containing a concentration at the mid-level calibration and analyzed immediately after the calibration to evaluate the calibration. The QCS must be prepared from a source separate from that used for the calibration standards (i.e. second source). In this SOP, the ICV is used as the QCS.

3.1.3 In order to document the preparation of calibration solutions in LIMS, the following batch sample suffixes are used (see attachment 2):

- SRM (Standard Reference Material): used for calibration standards
- CCV (Calibration standard): used for CCV
- CCB (Calibration blank): used for ICB/CCB
- MRL (MRL check): used for Reporting Limit check standard

There are no additional specific definitions associated with this test. See the laboratory QA manual and EPA methods 245.1, 7470A and 7471A for general definitions.

4.0 INTERFERENCES

Potassium permanganate is added to eliminate possible interference from sulfide.

Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 5 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (up to 5 mL). In addition, the dead air space in the test tube must be purged before adding stannous chloride.
Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents (when interference is expected) should determine if this type of interference is present.

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous.

5.1 Specific Safety Concerns or Requirements

Personal Protective Equipment Required: Safety Glasses, face shield, Labcoat, Nitrile Gloves

The use of a face shield is required when pouring large amounts of liquids or acids.

Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

Aqua regia is a mixture of concentrated hydrochloric acid and concentrated nitric acid. It has been used for centuries for dissolving noble metals (gold, platinum). Aqua regia is highly corrosive and very powerful oxidizing agent. Even without other materials present, a slow chemical reaction occurs in aqua regia and brown fumes of nitrogen peroxide are produced. The activity of Aqua Regia as a dissolving agent decreases slowly and thus, by definition, the solution is unstable. Aqua Regia should be freshly prepared, never stored in a closed vessel. Render it safe by dilution and neutralization.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

TABLE 1: PRIMARY MATERIAL HAZARDS

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury (1,000 PPM in Reagent)	Oxidizer Corrosive Poison	0.1 mg/m^3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 PPM-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 mg/m^3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 EQUIPMENT AND SUPPLIES

6.1 Instrumentation

6.1.1 Flow Injection Mercury System with Autosampler

6.1.2 Hot block

6.2 Supplies

6.2.1 150-mL beakers
6.2.2 60º stemmed funnels
6.2.3 50mL plastic centrifuge tubes with caps
6.2.4 50mL plastic digestion tubes with caps (screw type or snap cap) – Environmental Express only. NOTE: These tubes are only lot-certified for the 50mL volume. The analyst must lot-test the tubes for 20mL and 30mL volumes in accordance with the laboratory's lot testing SOP. See Attachment 4 for the lot testing verification form.
6.2.5 Filter paper (Whatman 41 grade or equivalent)
6.2.6 Top-loading balance, 0.01g sensitivity
6.2.7 Wooden tongue depressors
6.2.8 Kimwipes

7.0 REAGENTS AND STANDARDS

7.1 Reagents

All purchased and prepared reagents must be made from a traceable (NIST) source material, if available, and documentation of this traceability must be maintained by the laboratory

7.1.1 Reagent Grade Water ("Ultrapure" or "Nanopure")
7.1.2 Stannous chloride ($SnCl_2$), crystal Fisher ACS grade or equivalent
7.1.3 Sodium chloride (NaCl) Fisher ACS grade or equivalent
7.1.4 Hydroxylamine sulfate solution ($(NH_2OH)_2 \bullet H_2SO_4$)
7.1.5 Concentrated Sulfuric acid (H_2SO_4), Macron AR Select for Trace Level Analysis (or equivalent)
7.1.6 Concentrated Hydrochloric acid (HCl), Macron AR Select for Trace Level Analysis (or equivalent)
7.1.7 Potassium persulfate ($K_2S_2O_8$), 5% (**Oxidizer**) Fisher ACS grade or equivalent
7.1.8 Potassium permanganate ($KMnO_4$), 5% (**Oxidizer**) Fisher ACS grade or equivalent
7.1.9 Nitric acid (HNO_3), concentrated (**Oxidizer and Corrosive**)

7.2 Standards

All purchased standards must be accompanied by a Certificate of Analysis (C of A) which is kept available at the laboratory in order to demonstrate traceability of the standard to certified (NIST-traceable, if available) source material.
All prepared standards must be made from a traceable (NIST) source material, if available, and documentation of this traceability must be maintained by the laboratory

7.2.1 Primary stock mercury solution (Spex or equivalent), 10 mg/L
7.2.2 Secondary stock mercury solution (Ultra Scientific or equivalent), 10 mg/L

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

TABLE 2: HOLDING TIME AND PRESERVATION

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	500-mL Poly	100 mL	HNO_3 >0 to 6°C	28 Days	40 CFR Part 136.3
Soils	4 oz. Glass jar or boring rings	100 grams	Cool >0 to 6°C	28 Days	SW846, Chapter 3

9.0 QUALITY CONTROL

9.1 Sample QC

The following quality control samples are prepared with each batch of samples. Each of these QC samples may be re-analyzed once if it doesn't pass, prior to sample analysis, in order to verify the failure wasn't due to a physical or mechanical problem.

9.1.1 Method Blank (MB)

Prepare and analyze a method blank (MB) for each matrix and with every batch of 20 samples, or less. The method blank must be carried through the entire sample preparation process, including filtration if samples are also filtered. Check that there are no analytes detected at or above the reporting limit. If the method blank shows contamination, re-prepare all samples in the batch unless:

- The samples are ND (flag the result and write an NCM).
- The sample result is > 10x the blank level (flag the result and write an NCM).

9.1.2 Laboratory Control Sample (LCS).

Prepare and analyze a primary source laboratory control sample (LCS) for every batch of 20 samples or less. The LCS recovery must be within laboratory acceptance limit: **85-115% for 245.1, 80-120% for 7470A and 7471A** (see attachment 1).

If the LCS is outside of these limits, re-prepare the whole batch and/or re-calibrate the system unless the LCS recovery is above the upper limit and samples are ND. In this case, flag the result and write an NCM.

LCS Duplicate (LCSD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract. The %RSD for LCS/LCSD should be ≤ 20.

9.1.3 Matrix Spike and Matrix Spike Duplicate.

The sample for MS/MSD is randomly selected, unless specifically requested by a client.
Prepare and analyze a matrix spike (MS) and a matrix spike (MSD) duplicate for each matrix and with every batch of 20 samples, or less. The recovery and relative percent difference must be within laboratory acceptance limits of **70-130%** (see attachment 1), unless there is matrix interference. In the case of matrix interference, flag the results accordingly. The % RSD for replicate samples and MS/MSD should be ≤ 20.

9.1.4 Precision (RSD%)

Sample replicates must meet the following precision:

- Results less than 2 x RL must have an RSD ≤ 50%.
- Results equal or greater than 2 x RL must have RSD ≤ 20% between replicates.
- Sample results below the RL have no RSD acceptance criteria
- If RSD criteria are not met, re-analyze affected samples

9.2 Instrument QC

The following instrument QC samples are run with each analytical sequence. Each of these QC samples may be re-analyzed once if it does not pass, in order to verify the failure wasn't due to a physical or mechanical problem. Re-analysis must be performed before any batch QC or client samples are analyzed.

9.2.1 Initial Calibration Verification (ICV)

Prepare an ICV at 8.0 ppb from a different source as the calibration standards. Analyze an ICV at the beginning of every sequence immediately following the calibration standards. Verify that its response is within ± **5% for EPA 245.1 and** ± **10% for EPA 7470A/7471A**. The % RSD should be ≤ 10.

- If not, re-prepare the ICV standard.
- If the ICV is still out of control, re-calibrate the instrument.

Follow ICV with ICB (initial calibration blank). The ICB concentration must not be greater than or equal to the reporting limit (RL).

- If not, re-prepare the ICB
- If the ICB is still out of control, re-calibrate
- Samples <RL or >10X the ICB contamination level may be reported.

9.2.2 Reporting Limit Check Standard

Analyze the 0.2 ppm calibration standard after the ICB and at the end of the analytical run. The recovery must be ± 50% of the expected value.

- If the RL check fails, re-analyze one time.
- If the re-analysis fails, no results can be reported. Re-calibrate.

9.2.3 Continuing Calibration Verification (CCV)

Analyze a CCV standard after every 10 sample aliquots or less and at the end of the sequence. The recovery must be within **± 10% for 245.1** (**± 20% for 7470/7471**) of the true value. The % RSD should be ≤ 10. If the CCV is outside recovery limits, re-analyze once. If it is still out the instrument must be re-calibrated and samples not bracketed by acceptable CCVs be reanalyzed unless:

- The CCV is out high, any ND samples may be reported with a flag and an NCM.

Follow every CCV with a CCB (calibration blank). The CCB must not be greater than or equal to the RL. If the CCB is above the reporting limit, re-analyze once. If it is still out, the instrument must be re-calibrated and samples not bracketed by acceptable CCBs be reanalyzed however:

- Samples <RL or >10X the contamination may be reported with a flag and an NCM.

9.2.4 Calibration Acceptance Summary

Prepare a calibration curve by plotting the response (peak area) of at least 3 standards and a blank against the corresponding concentrations. Use a linear regression algorithm NOT forced through zero. The resulting correlation coefficient (r) must be > 0.995. If this criterion is not met:

- Re-evaluate the curve without the highest calibration standard or
- Re-prepare the calibration standards and repeat the calibration.

Refer to the "Calibration Curves" SOP and the "Selection of Calibration Points" SOP for more information on calibrating the instrument.

10.0 PROCEDURE

10.1 Standard Preparation

10.1.1 Prepare a working standard solution weekly. Prepare the working standard solution at a concentration of 1.0 ppm from the purchased 1,000 ppm Primary stock solution. Maintain the acidity of the working standard by using 0.15% Nitric acid as the diluent.

10.1.2 Prepare an ICV standard stock solution weekly at a concentration of 1.0 ppm from the Secondary 1,000 ppm stock solution. Maintain the acidity of the working standard by using 0.15% Nitric acid as the diluent.

10.1.3 Enter the standards information into LIMS and have it peer-reviewed Store the solutions in the refrigerator at >0 to 6°C.

10.2 Reagent Preparation

- For all reagents listed below, volumes other than those listed can be prepared provided the same ratio is maintained.
- Enter the reagent information into the reagent logbook or LIMS. Assign a unique identification code and note this on the mercury digestion logsheet for each reagent used.
- Source traceability records must be retained if available.

10.2.1 Prepare the aqua regia solution fresh daily by combining 3 parts HCl and 1 part HNO_3. Nominally, add 250mL concentrated nitric acid to a flask containing 750mL of concentrated hydrochloric acid.

10.2.2 Prepare the sodium chloride-hydroxylamine sulfate solution by dissolving 120 g of sodium chloride and 120 g of hydroxylamine sulfate in reagent grade water, and bring to a final volume of 1L. Shelf life of approximately 6 months. Store at room temperature.

10.2.3 Prepare the 5.0% potassium persulfate solution by dissolving 50 g of potassium persulfate in reagent grade water, and bring to a final volume of 1L. Shelf life is approximately 6 months. Store at room temperature.

10.2.4 Prepare the 5.0% potassium permanganate solution by dissolving 50 g of potassium permanganate in reagent grade water, and bring to a final volume of 1L. Shelf life is approximately 3 months. Store at room temperature.

10.2.5 Prepare the 3.0% HCl solution by adding 30 mL of concentrated HCl to reagent grade water, and bring to a final volume of 1L. Prepared daily.

10.2.6 Prepare the 1.1% stannous chloride solution by dissolving 11 grams of $SnCl_2$ and 30 mL of concentrated HCL in reagent grade water, and bring to a final volume of 1L. Prepared daily.

10.3 Calibration and Verification

10.3.1 Initial Calibration

- Prepare a calibration blank with reagent grade water. The calibration blank must contain all reagents in the same concentrations and in the same volume as used in preparing the calibration solutions.

- The calibration curve and verification standards are digested and prepared for analysis in the same manner as samples. However, only one calibration curve need be analyzed per day (the curve is NOT batch-specific). Provided the standards and samples are not reduced by the addition of sodium chloride-hydroxylamine sulfate, analysis need not be performed immediately.

- Prepare 5 calibration standards at 0.2 ppb, 1.0 ppb, 5.0 ppb, 10.0 ppb, and 15.0 ppb by pipetting the listed volumes of the Primary standard working solution (1.0 ppm) into 20 mL (waters) or 10 mL (soils) of reagent grade water.

- Prepare the calibration standards following the matrix-specific digestion procedures described below under “analysis procedure.”

- 50mL plastic digestion vessels are used to digest both soils and waters.

TABLE 3: CALIBRATION CURVE

SOIL SAMPLES		WATER SAMPLES	
Calibration Std.	µl of 1.0ppm Std.	Calibration Std.	µl of 1.0ppm Std.
0 ppb	0 µl	0 ppb	0 µl
0.2 ppb	10 µl	0.2 ppb	4 µl
1.0 ppb	50 µl	1.0 ppb	20 µl
5.0 ppb	250 µl	5.0 ppb	100 µl
10.0 ppb	500 µl	10.0 ppb	200 µl
15.0 ppb	750 µl	15.0 ppb	300 µl

- For water calibration samples, after digestion, analyze as is with no dilution. Filter if necessary.

- For soil calibration samples, after digestion, bring a final volume of 50 mL. Cover and invert tube to mix. The calibration standards are ready for analysis.

- Begin analyzing the calibration standards by following the same steps outlined in “analysis procedure” for samples.

- Prepare the calibration curve by plotting peak absorbance of the known standards versus concentration.

- All calibrations are processed using a linear curve that is not forced through zero

10.3.2 Continuing Calibration

- For soil samples
  - Prepare the ICV solution at 8 ppb by pipetting 400µl of the 1.0 ppm secondary source standard solution into 10 mL of reagent grade water.
  - Prepare the CCV Solution at 4 ppb solution by pipetting 200 µL of the 1.0 ppm primary source working standard solution into 10mL of reagent grade water.
  - Prepare the LCS Solution at 8 ppb by pipetting 400 µL of the 1.0 ppm primary source working standard solution into 10 mL of reagent grade water.
  - Add the remaining reagents in the same amounts as samples.

- For water samples
  - Prepare the ICV at 8 ppb by pipetting 160 µL of the 1.0 ppm secondary source standard solution into 20 mL of reagent grade water.
  - Prepare the CCV at 4 ppb by pipetting 80 µL of the 1.0 ppm primary source standard solution into 20mL of reagent grade water.
  - Prepare the LCS at 8 ppb by pipetting 160 µL of the primary source 1.0 ppm standard solution into 20mL of reagent grade water.
  - Add the remaining reagents in the same amounts as samples.

- Enter the standard information for the LCS into ELMNT. Enter the standard information for the ICV and CCV into the daily standard logbook. Store the solution in the refrigerator.

- Analyze an ICV (8ppb) at the beginning of a sequence. Analyze a CCV (4ppb) after every 10 readings or less. For an example, refer to the run sequence below. Document in the digestion logbook the digestion of all samples, QC, calibration verifications, and calibration standards.

TABLE 4: TYPICAL ANALYSIS SEQUENCE

1)	Calibration Blank
2)	Calibration Standards (minimum of 5)
3)	**ICV** (8ppb; **± 5% rec. for 245.1; 10% rec. for 7470/7471); %RSD ≤ 10**
4)	ICB < RL
5)	**RL Check** Standard (0.2ppb cal std), rec. = **± 50%**
6)	Laboratory Control Sample (every 20 samples); %RSD ≤ 10
7)	Method Blank < RL
8)	Sample; %RSD ≤ 20 *
9)	Matrix Spike (every 20 samples); %RSD ≤ 20
10)	Matrix Spike Duplicate (every 20 samples)
11)	Samples
12)	**CCV** (4ppb; **± 10% rec. 245.1; ± 20% rec. 7470/7471**); **%RSD ≤ 10**
13)	CCB < RL
14)	10 samples; %RSD ≤ 20 *
15)	CCV (4ppb; ± 10% rec. 245.1; ± 20% rec. 7470/7471); %RSD ≤ 10
16)	CCB
17)	RL Check Standard (0.2ppb cal std)

***** For sample results ≤2X the RL, RSD must be ≤50%. No RSD requirements for results < RL

10.4 Digestion

Document all reagent additions, times and temperatures, as applicable, in the digestion logbook.

10.4.1 Water Samples

- Decant 20.0 mL of a water sample into labeled digestion vessel. If preparing a sample at a dilution, aliquot smaller samples volumes and bring up to 20 mL with reagent grade water.
- For leachate samples (TCLP, SPLP, STLC), use 2.0 mL of leachate diluted to 20.0 mL with reagent grade water.
- For DI WET samples, use 20mL.
- To each vessel containing a water sample, add 1.0 mL of concentrated H_2SO_4 and 0.50 mL of concentrated HNO_3. Be sure the sample and reagents are mixed.
- Add 3.0 mL of 5% Potassium Permanganate ($KMnO_4$). Add additional $KMnO_4$, if necessary until a purple color persists for at least 15 minutes; be sure to add the same amount of $KMnO_4$ to the standards and blanks.
- Additional $KMnO_4$ is required for STLC extracts. Since only 2 mL of sample is used for STLC, include the additional $KMnO_4$ volume (i.e. 3mL) when bringing sample volume up to 20 mL with reagent grade water. Be sure this same process is performed on the Method Blank and LCS.
- Allow mixture to stand for at least 15 minutes.
- Add 1.6 mL of 5% Potassium Persulfate ($K_2S_2O_8$) and mix.
- Heat mixture for 2 hours on a hot block maintained at 95° $\pm$ 3°C.
- Remove samples from the hot block and allow them to cool.

NOTE: If samples will not be analyzed until the following day, stop here.

- Add 2.0 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Swirl to mix. Do this addition under a hood, as Cl_2 could be evolved.
- Bring final volume up to 30 mL using reagent grade water. Mix.
- When necessary to remove suspended particles, filter the sample through a 60° funnel lined with filter paper into a 50 mL digestion tube. The LCS and Method blank must also be carried through the entire sample preparation process, including filtration if samples are filtered.

10.4.2 Soil Samples

- Weigh 0.5 $\pm$ 0.01 g of a well mixed soil sample into a labeled digestion vessel (ensure that the balance has been calibrated at 0.5g).

For foreign soils, all waste generated during the weighing process must be disposed of in a separate container from other soil sample waste. (This includes, spatulas, Kimwipes, gloves, etc). When finished weighing samples, wipe balance and surrounding area with a paper towel, and dispose of the paper towel in the foreign soil waste container. Wipe surrounding area with a 10% household bleach solution to disinfect the surrounding areas and dispose of wipes in the foreign soil waste container. When the container is full, notify sample archive technicians.

- Add 5 mL of reagent grade water to each test tube.

- Add 4.2 mL of the aqua regia solution.

- Heat the mixture for 2 minutes in a hot block maintained at **95°C ± 3 °C.**
- Slowly add 12.4 mL potassium permanganate solution to each vessel.
  - **Add the potassium permanganate very slowly in two separate 6.2 mL portions**. Add the first portion to all vessels, and then add the second portion.
  - This step **generates heat** and may cause the sample to **bubble out** of the tube **if permanganate is added too quickly.**

- Cool and add 5 mL of reagent grade water to each vessel.

- Heat the mixture for 30 minutes on a hot block maintained at 95° ± 3°C.

- Remove samples from the hot block and allow to cool

.

NOTE: If samples will not be analyzed until the following day, stop here.

- **Carefully** add 5.0 mL, in two separate 2.5 mL portions, of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Swirl the mixture gently. Do this addition under a hood, as Cl_2 could be evolved.

- Filter the sample through a 60° funnel lined with wetted filter paper into a 50 mL digestion tube. Bring the sample up to a final volume of 50 mL by rinsing the filter paper with reagent grade water. Note any variation from the 50mL final volume and account for this difference in the final calculations. Mix the filtrate by capping the digestion tube and inverting to mix.

10.5 Wipe Samples

- Wipes are digested in the same manner as solid samples with the following exceptions:
  - Sample amount for wipes is 1 (as in 1 wipe)
  - Wipes are analyzed intact -- DO NOT CUT AND/OR WEIGH A WIPE
  - Wipes must be batched separately from waters, soils, or wastes
  - Wipes are never reported with MS/MSD; an LCS/LCSD must be prepared with each batch to provide precision QC
  - Wipes are reported as µg/wipe

10.6 Analysis

10.6.1 Analyze the calibration standards first. If the calibration is satisfactory, analyze the samples.

10.6.2 Transfer the extracts to plastic 15 mL centrifuge tubes and load the autosampler with the calibration standards, quality control samples, samples, and wash solution. Feed the 1.1% SnCl2 and the 3% HCl through the system.

10.6.3 Dilute the sample with a reagent blank and re-analyze a sample if its result is higher than the highest calibration standard.

10.6.4 As needed, prepare additional reagent blanks to be used to make dilutions. Add reagent grade water and all reagents in the same ratios as the samples. The reagent blanks do not need to be heated.

10.6.5 Calculate the sample concentration against the calibration curve.

10.7 Instrument Initialization

10.7.1 Instrument Parameters

- Assemble the Flow Injection System - Refer to the instrument manual for detailed information. Turn on the power to the Spectrometer and the printer then the computer (the order makes a difference). Use all instrument parameters recommended by the manufacturer.

- At the beginning of each day when samples are to be prepared, turn on the hot block first so it will have sufficient time to warm up prior to sample digestion.

- Before digesting samples, preheat the hot block to 95^{o}C. Place a digestion vessel containing reagent grade water, acids, and reagents in the hot block with a thermometer. Preheat to 95^{o}C.

10.7.2 Instrument Shutdown

- Upon completion of the analysis, rinse the sample, carrier and reagent tubing with reagent grade water. Rinse the tubing for as long as necessary to remove all traces of the previous reagent.

- Swing all the pressure levers away from the pump tube magazines. Release the pump tension on all tubing.

- Empty the FIMS waste vessel as needed and clean up any spills. Dispose of waste solutions properly and observe local safety regulations when you dispose of hazardous waste.

- Switch off the instruments: Exit the AA WinLab application; switch off the computer before switching off the FIMS spectrometer and printer.

10.7.3 Instrument Conditions

- Read time: 20 seconds
- Read delay: 0 seconds

- Pump 1 speed: 100
- Pump 2 speed: 120
- Gas Flow: 100

10.8 Preventative Maintenance

10.8.1 Check the red-red tubing and both blue-yellow tubing daily and change as needed.
10.8.2 Check the filter daily and change as needed.
10.8.3 Check black-black waste tubing daily and replace as needed.
10.8.4 Check tubing which goes from the filter cover to the lamp daily and replace as needed. Be sure to keep this tubing dry. If it is wet inside the tubing, the resulting spectrophotometric peaks may be abnormally wide.
10.8.5 On a daily basis, keep the filter dry. Also, the block, which the filter sits on, should be dry before analysis. If either is wet or dirty, the resulting spectrophotometric peaks may be abnormally wide.
10.8.6 Change all other tubing when it shows signs of wear (i.e. excessive stretching and flattening).

- Record all performed maintenance in the instrument maintenance logbook.

- If an instrument is unusable or has limitation to its use, it must be tagged accordingly until such a time the problem has been corrected. Record the problem, solution and verification of proper operation into the instrument maintenance logbook.

10.9 Troubleshooting

10.9.1 If contamination is present initially and/or a blank reads a high absorbance, then perform corrective action. The corrective action may include any or all of the following:

- Change the filter and dry the plastic block.

- Change the tubing attached to the block, which goes to the lamp.

- Change the $SnCl_2$/HCl as this solution could be contaminated.

10.9.2 If contamination occurs due to a high sample and you get an error on the computer screen then rinse all tubing and sample probe with 10% HCl using the FIAS control icon. Rinse until the contamination is removed and the analysis can continue. The tubing and filter may need to be changed to make the blanks clean again.

10.9.3 If the error message “Energy too low or high” occurs at the beginning of the run:

- Make sure the tubing attached from block to lamp is dry.

- Remove the absorption cell body and remove and clean the quartz window.

- If still not operating correctly, soak the cell tube in 20% HNO_3 for 30 minutes. Thoroughly rinse the cell tube with reagent grade water and dry.

- Replace the tube and retry.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Mercury results are reported as mg/L for waters and mg/kg for soils.

11.2 Calculate the concentration of mercury in a sample by entering the absorbance value into the linear regression calibration curve and deriving the raw result concentration. Determine the final sample concentration as follows:

$$Hg(mg/L) = r \times d \div 1000$$

$$Hg(mg/kg) = \frac{r \times f}{i} \times d \div 1000$$

Where:

r = raw result in µg/L (from instrument printout)
f = final volume in mL
i = initial sample aliquot (mLs or grams)
d = dilution factor (if no dilution, *d* = 1)

11.3 Determine the % recovery for the ICV, CCV, LCS and MS/MSD as follows:

$$\% \text{ Recovery} = \frac{(Sp - S)}{Sa} \times 100$$

11.4 Determine the RPD of the MS/MSD as follows:

$$RPD = \frac{|R1-R2|}{(R1+R2)/2} \times 100$$

Where:

Sp = Spike result
S = Sample result (0 for LCS)
Sa = Spike amount
R1 = Conc. of MS
R2 = Conc. of MSD

12.0 METHOD PERFORMANCE

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure as described in laboratory's SOP, IR-QA-MDL. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains

MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capabilities

Every analyst must perform an Initial Demonstration of Capability (IDOC) before performing analyses on any client samples. An IDOC consists of 4 consecutive LCS samples at 1 to 4 times the RL with an average recovery and RSD within laboratory acceptance limits
An on-going DOC must be performed annually. An ODOC can be 4 consecutive LCSs at mid-level or a passing PT.

12.3 Training Requirements

The analyst must have documented training, including reading of the SOP and source methods, conducted by the department manager, senior chemist, or other analyst with training documentation and a passing DOC.

13.0 POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in the "Waste Management and Pollution Prevention" section of the Corporate Environmental Health and Safety Manual (CW-E-M-001).

14.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the laboratory's Waste Disposal SOP (IR-EHS-WASTE). The following waste streams are produced when this method is carried out:

Metals analysis:

- **Acid waste:** (Hydrochloric, Nitric and small amount of Sulfuric acid). This waste is generated when preparing samples and standards. This waste is collected into 2.5 L bottle located in the Metals fume hoods. The waste is bulked as nitric acid waste.
- **Acid Waste:** (Hydrochloric, Nitric and Sulfuric) generated from Mercury analyzers. This waste is collected behind the instruments into 4 gal Carboy satellite container. The waste is bulked as nitric acid waste.
- **Metals digestates:** (50 mL polytubes). Once the samples have been analyzed they are kept in the metal shelves for 30 - 60 days. After the 30 -60 days analyst transfer the digestates to the main waste storage area. Sample archive technicians will store this waste on the shelves designated for metals for 30-60 days. After this time Sample archive technicians will bulked this waste as nitric acid waste w/RCRA metals
- **Mercury digestates:** (50 mL polytubes). Same procedure as metals digestates (see above).

Analysts in the metals department remove the individual Carboy satellite containers and the 2.5 L waste bottles from the metals area to the main waste storage area twice a week. Waste generated in the metals area is bulked as nitric acid w/RCRA metals.

Metals Digestion

- **Acid waste:** (Hydrochloric, Nitric and small amounts of Sulfuric). This waste is generated when digesting mercury and metals samples. The waste is stored under the bench of the TCLP area. This waste is stored in 4 gal carboy satellite container. Waste bulked as nitric acid waste.
- **Solid Filter paper waste:** (with HNO_3) – This waste is generated when digesting solid samples for mercury and metals. The waste is collected in a red step-on container. Wastewater logbook. Sample archive technicians will collect the waste as needed. The waste is bulked as filter paper contaminated with Nitric acid.
- **Foreign soil waste:** This soil waste is generated from foreign soil samples during the weighing process. The soil waste is stored in the Step-on waste container located in the weigh out room. Sample archive technicians remove this waste from the weight out room to the main waste storage area every two weeks or as needed. This waste is bulked as RCRA foreign soils.
- **Unused standards:** If the standard is hazardous and can not be collected with one of the waste streams generated in the method, then analyst and technicians take this standard and placed it on the shelves labeled “hazardous waste” in the main waste storage area. Waste materials placed on the lab pack shelf must be labeled as “Hazardous Waste” with the contents and a date placed on the shelf. The standard will be lab packed (example: mercury standard).

  If the standard can be collected in the satellite waste container for one of the waste streams of the method, then pour the standard in the right satellite container, rinse the original container, and collect the rinsate in the satellite container. The original container can be placed in the regular trash. (Example, buffer solutions pH 4)

15.0 REFERENCES / CROSS-REFERENCES

15.1 EPA Method 245.1, Revision 3.0, May 1994

15.2 EPA Method 7470A, EPA SW-846 Update II, September 1994

15.3 EPA Method 7471A, EPA SW-846 Update II, September 1994

15.4 EPA Method 7000A, EPA SW-846 Update I, July 1992

15.5 CA-Q-S-005, Calibration Curves

15.6 CA-T-P-002, Selection Of Calibration Points

15.7 IR-QA-MDL, Determination of Method Detection Limits

16.0 METHOD MODIFICATIONS

TABLE 4: METHOD MODIFICATIONS

Item	Method	Modification
Working Standard	*EPA 245.1 / 7470A/7471A*	*Working Standards are prepared weekly instead of daily. A stability study has been performed and demonstrated the working standards are stable for two weeks.*
Sample Weight	*EPA 7471B*	*Based on the guidance in SW 846 Draft Update method 7471B (January 1998) a single 0.5 g aliquot is used for soil rather than 3-0.2 g aliquots.*
Digestion Tube	*EPA 245.1 / 7470A/7471A*	*Plastic digestion tubes from Environmental Express can be used instead of glass tubes as Environmental Express has performed a study to show that the tubes are an acceptable alternative to glass with respect recoveries of organic mercury.*

17.0 ATTACHMENTS

17.1 **Attachment 1:** Analysis Information
17.2 **Attachment 2:** Data Review Checklist
17.3 **Attachment 3:** Metals Preparation Review Checklist
17.4 **Attachment 4:** Digestion Tube Lot Testing Form

18.0 REVISION HISTORY

18.1 Revision 3, dated 21 June 2013

- This revision supersedes IR-MET-HG, revision 2 (12/09/2011)
- Added Wipe Samples Digestion procedure
- Added traceability requirement for standards and reagents
- Change required aqua regia volume from 5ml to 4.2ml per source method.
- Revised Demonstration of Capabilities
- Corrected formulas for calculating final results
- Added volume of sample used for DI WET
- Changed Pump 1 speed to 100
- Removed Preparation Benchsheet
- Added sample RSD acceptance criteria
- Revised by DT, DD and LH.

18.2 Revision 4, dated 11 August 2014

- This revision supersedes IR-MET-HG, revision 3 (06/21/2013)
- Minor format changes and corrections
- Added foreign soil waste provisions
- Prepared by DD

Attachment 1
Analysis Information

TestAmerica Irvine

Analytical Method Information

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
Mercury - 245.1 in Water (EPA 245.1)								
Preservation: HNO3								
Container: 1 Liter Poly		**Amount Required:** 100 ml				**Hold Time:** 28 days		
Mercury	0.00010	0.00020 mg/l			70 - 130	20	85 - 115	20

TestAmerica Irvine

Analytical Method Information

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
Mercury-7470A in Water (EPA 7470A)								
Preservation: HNO3								
Container: 500 mL Poly		**Amount Required:** 100 ml				**Hold Time:** 28 days		
Mercury	0.00010	0.00020 mg/l			70 - 130	20	80 - 120	20

TestAmerica Irvine

Analytical Method Information

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
Mercury-7471 in Solid (EPA 7471A)								
Preservation: 4 C, Cool								
Container: 4 oz Jar		**Amount Required:** 100 grams				**Hold Time:** 28 days		
Mercury	0.012	0.020 mg/kg			70 - 130	20	80 - 120	20

Attachment 2
Data Review Checklist

Attachment 3
Metals Preparation Review Checklist

METALS PREPARATION REVIEW CHECKLIST
ICP, ICPMS, CVAA

Method: 200.2, 3005A, 3005A MOD, 3010A, 3050B, 3051A, 245.1, 7470A, 7471A

Preparation Date: _____ Technician Initials: _____ Prep Batch: _____

Review Date: _____ 2nd Level Reviewer: _____

Item to Review	Tech	2nd Level	Notes/Specific Criteria
Method and Matrix			
Batched with correct preparation method			
In and Out temperature entered			
Digestion temperature within range-- Non-Hg: 90-95°C for water, 90-100°C for soil on hot block, 40°C for soil in microwave **Hg** (soil and water): 95±3°C			
Sample Preparation Batch:			
Water samples have pH<2			
All prepared samples have Initial (weight or volume) and final (volume) listed.			
Batch contains no greater than 20 samples			
Method Blank and LCS digested			
MS and MSD digested. If not was LCSD digested? Reason for MS/MSD not digested			
For Hg: All calibration points (and CCV, ICV, RL check) digested and batched			
Data Documentation:			
pH recorded for each sample			
Acids / reagents / standards entered with Lot #			
Thermometer ID Number with Correction factor entered			
Digestion Tube Lot # entered			
Hood ID and Hot Block number entered			
Start Time and End Time entered for digestion step			
Paperwork includes both marked-up hand-written draft worksheet AND finalized printed worksheet			
All errors are crossed out with a single line, initialed and dated			

Comments:

G:\DATA_REV\CHCKLIST\METALS\Sample Preparation\Metals\Prep_check_r4.doc
Rev: 12/11/12

Attachment 4
Digestion Tube Lot Testing Form

FACILITY SOP ATTACHMENT

SOP NUMBER: IR-MET-ICPMS, Rev. 4 (10/07/2014)	**CHANGE FORM ID:** CF1

SOP TITLE: Metals by ICPMS – EPA Method 200.8/6020

REASON FOR ADDITION OR CHANGE (Use additional sheets if necessary):

Clarification on IDL determination.

CHANGE OR ADDITION (Use additional sheets if necessary):

Section 9.2.9 Instrument Detection Limits (IDLs)

Currently reads:

- Instrument Detection Limit studies can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of reagent blank solutions.
- IDLs should be determined at least every three months.

Revise to read:

- Instrument Detection Limits studies are performed by charting a minimum of 30 calibration blanks. The IDL will then be determined as the mean plus three times the standard deviation. The calculation can be performed using the TALS Control Chart module.
- The IDL must be compared to the current MDL and the MDL must be elevated if the IDL is higher.
- IDL studies must be performed per instrument every three months.

Prepared By: D. Dawes

APPROVED BY:

Department Manager	Date 12/1/14
Quality Assurance Manager	Date 12-2-2014
Health and Safety Coordinator	Date 12/02/2014
Laboratory Director	Date 12/2/14

Title: Metals by ICP/MS
EPA Method 200.8 / 6020

Approvals (Signature/Date):

Denny Tran Department Manager	10/7/14 Date
William Nash Health & Safety Coordinator	10/7/2014 Date
Maria Friedman Quality Assurance Manager	10-7-2014 Date
Kirk Miltimore Laboratory Director	10/07/14 Date

Facility Distribution No.: _____ **Distributed To:** _____

1.0 SCOPE AND APPLICATION

1.1 EPA Method 200.8 is used to determine trace metals in the following matrices: water, drinking water, and wastewater; EPA Method 6020 is used to determine trace metals in ground waters, surface waters, industrial wastes, soil and sludge samples.

1.2 Prior to analysis, samples must be solubilized or digested using the appropriate sample preparation method (EPA 200.2, 3005A, 3050). For dissolved metals, acid digestion is not necessary if the samples are filtered through a 0.45 µm membrane filter and acid preserved prior to analysis. For drinking water, if the measured turbidity is <1 NTU, digestion is not required but samples must be matrix matched to calibration standards. For any samples submitted under an NPDES permit, digestion is required regardless of turbidity.

1.3 If silver (Ag) analysis is requested, the sample must be digested in all cases. When silver concentrations exceed 0.1ppm the dilution must be performed by redigestion, rather than diluting the digestate at the instrument.

1.4 EPA 200.8 / 6020 may be performed in Collision Cell mode, an instrument analytical technique to remove interferences. **NOTE: Collision cell is not approved for drinking water samples**.

1.5 Drinking Water Maximum Contaminant Levels (MCL) and California Detection Limits for reporting purposes (DLR) are found below. Standard Reporting limits for all metals, attached at the end of this SOP, are either equal or less their corresponding DLRs.

Table 1: Target Analytes and Limits

Analyte	DLR (mg/L)	MCL (mg/L)	Analyte	DLR (mg/L)	MCL (mg/L)
Aluminum*	0.050	1.0/0.2	**Lead**	0.0050	0.015
Antimony	0.006	0.006	**Manganese**	0.020	0.05
Arsenic	0.002	0.050	**Nickel**	0.010	0.10
Barium	0.10	1.0	**Selenium**	0.0050	0.050
Beryllium	0.0010	0.0040	**Silver**	0.010	0.10
Cadmium	0.0010	0.0050	**Thallium**	0.0010	0.0020
Chromium (total)	0.010	0.050	**Uranium**	1 pCi/L	CA: 20 pCi/L Federal: 30 pCi/L
Copper	0.050	1.0	**Zinc**	0.050	5.0
Iron	0.1	0.3			

* Aluminum has both a primary MCL (1mg/L) and a Secondary MCL (0.2 mg/L)

1.6 See Attachment 5 for quantitation masses and associated internal standard elements.

1.7 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in “Validation of Methods” in the Quality Assurance Manual.

1.8 See Attachment 1 for MDL, reporting limit and QC information. See LIMS for current MDL and control limit values..

2.0 SUMMARY OF METHOD

2.1 For non-collision cell analysis, sample material in solution is introduced by pneumatic nebulization into radio frequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially

pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are detected by an electron multiplier detector and the ion information processed by a data handling system.

2.2 For collision cell analysis, a reaction system is used to eliminate interferences arising from plasma and sample matrix. This is an instrument mode employing Helium or Hydrogen so side reactions that would create unpredictable, new interferences are eliminated when analyzing trace metals on the ICP-MS.

3.0 DEFINITIONS

There are no specific definitions associated with this test. See the laboratory QA manual, EPA Method 200.8, and EPA Method 6020 for general definitions.

4.0 INTERFERENCES

4.1 Isobaric interferences occur when an isotope of one element is at the same nominal mass as an isotope of another element (e.g., Mo 98 and Ru 98). Most commonly used corrections are already present as default interference equations in the instrument software.

4.2 Carbon species may cause a positive interference chromium signal at mass 52 due to the formation of Ar^{40} and C^{12}. The level of interference is dependent upon the concentration of available carbon species. Digestion of the sample will remove the volatile organics through heating and remove the inorganic carbon by conversion to CO_2. Semi-volatile organics will be at least partially oxidized by the use of HNO_3 and heat.

4.3 Physical interferences are effects associated with the sample nebulization and transport process. Samples with high dissolved solids (TDS) or high acid concentrations can cause changes in viscosity and surface tension which, in turn, affects the sample nebulization and transport. Physical interference effects can be minimized through the use of a peristaltic pump and internal standard.

4.4 Molecular interferences are effects associated with the sample nebulization and transport process. Samples with high dissolved solids (TDS) or high acid concentrations can cause changes in viscosity and surface tension which, in turn, affects the sample nebulization and transport. Physical interference effects can be minimized through the use of a peristaltic pump, internal standard, and dilution.

4.5 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Optimizing the rinse time between samples and using a rinse solution with the proper acid strength can minimize memory effects. Even using these precautions, a sample may be too high to rinse completely under normal circumstances. The analyst must be aware of this situation, and samples immediately following a high sample should be re-analyzed.

4.6 For collision cell, inert gas (Helium or Hydrogen) introduced into the cell collides with the interfering ions with larger diameters, reducing their kinetic energy so they can be removed through Kinetic Energy Discrimination.

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow

appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Personal Protective Equipment Required: Safety Glasses, Labcoat, Nitrile Gloves.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

TABLE 2: PRIMARY MATERIAL HAZARDS

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 EQUIPMENT AND SUPPLIES

6.1 Instrumentation

6.1.1 Inductively coupled plasma Mass Spectroscopy (ICP-MS) - Model Elan 6100 and Agilent 7700
6.1.2 Autosampler – Cetac ASX-500 with ADX-500 or equivalent
6.1.3 Autosampler- ESI SC-4 DX Fast

6.2 Supplies

6.2.1 Sample tube racks
6.2.2 15 mL sample tubes
6.2.3 Pipettes and pipettors
6.2.4 Pipettor tips
6.2.5 Small plastic containers
6.2.6 50 mL graduated sample tubes

6.2.7 Plastic Erlenmeyer flasks
6.2.8 100 mL glass beakers
6.2.9 50 mL centrifuge tubes
6.2.10 100 mL volumetric flasks, class A.
6.2.11 500 mL volumetric flasks, class A.
6.2.12 50 mL volumetric flasks, class A

7.0 REAGENTS AND STANDARDS

All purchased and prepared reagents and standards must be made from a traceable (NIST) source material, if available, and documentation of this traceability must be maintained by the laboratory.

7.1 Reagents

7.1.1 Argon, industrial grade
7.1.2 Concentrated Nitric Acid (trace metal grade)
7.1.3 Concentrated Hydrochloric acid (trace metal grade)
7.1.4 Laboratory Reagent Grade Water (RGW)
7.1.5 Helium, industrial grade

7.2 Standards

7.2.1 SPEX Metals Stock Standards (or equivalent): 10 ppm
7.2.2 Accustandard Metals Stock Standards (or equivalent): 10 ppm
7.2.3 Single element internal standard solutions (Ge, Sc, Tb, In, Li, Y, and Bi):1000ppm
7.2.4 O2si tuning solution (or equivalent): 10 ppm
7.2.5 Agilent PA tuning 1 solution
7.2.6 Agilent PA tuning 2 solution
7.2.7 O2si Interference Check Standard A (or equivalent): 10000ppm Cl, 2000ppm C, 1000ppm Al, Fe, Mg, Ca, Na, K, P, S and 20ppm Ti, Mo.
7.2.8 O2Si CRI standard

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

TABLE 3: HOLDING TIME AND PRESERVATION

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Water	Polyethylene bottle	500 mL	Preserved with nitric acid to a pH<2	6 months	40 CFR Part 136.3
Soil	Glass Jar or Sampling Sleeve	4 oz	None	6 months	EPA SW-846

9.0 QUALITY CONTROL

Sample QC - The following quality control samples are prepared with each batch of samples. Each of these QC samples may be re-analyzed once if it doesn't pass, in order to verify the failure wasn't due to a physical or mechanical problem. Otherwise, perform corrective action and repeat the analysis.

9.1 Method Blank (MB)
Prepare and analyze a method blank (MB) for each matrix and with every batch of 20 samples, or less. Check that there are no analytes detected at ≥ RL.

If the method blank shows contamination for a requested metal, re- prepare and re-analyze the MB once unless:

- The samples are not detected (ND).
- The sample result is > 10x the blank level.

If the MB is re-analyzed, all positive samples < 10x RL must also be re-analyzed.

If the re-analyzed MB still shows contamination, re-prepare and re-digest affected samples.

9.1.1 Laboratory Control Sample (LCS).
Prepare and analyze a laboratory control sample (LCS) for every batch of 20 samples or less per matrix. The recovery must be within **85-115% for EPA 200.8** and **80-120% for EPA 6020**.

If the LCS is outside of the limit for a requested metal, re-prepare and re-analyze once:

- If the LCS is still below the acceptance limit, the effected samples must be re-digested and re-analyzed.
- If the LCS is above the acceptance limits and samples are ND, the results may be reported. The results must be flagged and a non-conformance memo (NCM) written.
- All positive samples must be re-analyzed with the LCS if the LCS is re-analyzed.

9.1.2 LCS Duplicate (LCSD)
LCS Duplicate (LCD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.
When and LCS/LCSD pair is analyzed, the RPD must also be within acceptance limits. If not, the problem must be identified and corrected before samples can be reported.

9.1.3 Samples
All samples and QC are analyzed with three replicate integrations.

- RSD must be < 5% for ICV
- RSD must be <10% for CCV
- RSD must be < 25% for sample results >2X the RL
- RSD must be < 50% for sample results ≤2X the RL

9.1.4 Matrix Spike and Matrix Spike Duplicate (MS/MSD)

- For 200.8: Analyze a Matrix Spike (MS) and a Matrix Spike Duplicate (MSD) for every batch of 10 samples or less per matrix.
- For 6020: Analyze a Matrix Spike (MS) and a Matrix Spike Duplicate (MSD) for every batch of 20 samples or less per matrix.
- A typical batch of 10 (or 20) samples will include MB, LCS, MS1, MSD1, MS2 and MSD2

- The LCS spike solution is used to spike the MS/MSD.
- The MS and MSD recoveries must be within **70-130% for EPA Method 200.8 or 75-125% for EPA Method 6020** of the actual value and the RPD must be within 20%.

9.1.5 Dilution Test

As specified in EPA 200.8, a dilution test is not required if an internal standard calibration is used. However, if required for specific client projects, the following procedures are followed:

- If the analyte concentration is sufficiently high (a factor of at least 10 times above the RL after dilution or 50 times without dilution), an analysis of a 1:5 dilution must agree within ± **10%** of the original determination.
- If the two samples differ by more than ± 10%, chemical or physical interference effect must be suspected.
- If the regular sample is reported at a dilution, then the diluted sample should be performed at 5 times that dilution (e.g., if reporting at 5X, the dilution test samples should be run at 25X)
- One dilution test must be included for each 20 samples (or less) of each batch.

9.1.6 Post Digestion Spike for 6020

If a 6020 MS and/or MSD recovery fails, a Post Digestion Spike must be performed. A spike is added to portion of a sample or its dilution and should have a recovery of within **75 to 125 %**. The spike addition should be based on the concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and re-analyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination.

9.1.7 Method of Standard Additions (MSA)

The method of standard additions is a special case of the post digestion spike and may be a special project requirement. Four aliquots of a sample are prepared. One is unspiked and three are spiked at concentrations of the target analyte that are approximately 50%, 100%, and 150% of the native sample concentration. All four aliquots are brought up to the same final volume. These four aliquots are analyzed and their known spike concentrations (including zero for the unspiked aliquot) are plotted on the x-axis against the measured concentration on the y-axis. Least-squares linear regression is then used to calculate the slope and intercept of the line. The x-intercept value (multiplied by -1) for this line is then taken as the raw concentration MSA result. Any dilution or preparation factors must be applied to yield the final concentration MSA result. The following criteria must be followed for MSA:

- The unspiked and spiked aliquots must be analyzed in the same analytical sequence
- The unspiked and spiked aliquots must all be analyzed at the same dilution
- The linear correlation coefficient (r) must be ≥0.995. If it is not, the data must be checked and/or the sample re-analyzed. If the r-value is still <0.995, the MSA result must be documented as exhibiting suspected matrix interference.
- The date analyzed, instrument ID, analysis file ID, and dilution must be documented for all 4 aliquots used in the MSA
- The name and date of the person who prepared the MSA spreadsheet must be recorded
- The MSA must have documented second-level review
- The MSA spreadsheet (see attachment) must be used for all MSA calculations

9.1.8 Method Reporting Limit (MRL) for drinking water samples

Prepare and analyze an MRL for every batch of 20 samples or less. The analyte recoveries for the MRL samples must be:

- detected for CA and Federal samples (10-200% recovery)
- ±50% of the theoretical value for Arizona samples and If the MRL is outside of the limit for a requested metal, re-prepare and re-analyze once:

If the MRL is still below the acceptance limit, the affected samples must be re-digested and re-analyzed.

- If the MRL is above the acceptance limits and samples are ND or greater than 10X the level in the MB, the results may be reported. The results must be flagged and a non-conformance memo (NCM) written.
- All positive samples must be re-analyzed with the MRL if the MRL is re-analyzed.

9.2 Instrument QC

The following instrument QC samples are run with each analytical sequence. Each of these QC samples may be re-analyzed once if it does not pass, in order to verify the failure wasn't due to a physical or mechanical problem. Re-analysis must be performed before any batch QC or client samples are analyzed.

9.2.1 Initial Calibration Verification (ICV)

Immediately after the initial calibration, analyze the secondary source. Verify that that its recovery is within **90-110%** and the RSD between replicate exposures **≤5%.**

- If the recovery for any requested analyte varies from the expected values by more than ±10% or the RSD is >10%, re-analyze the ICV using a freshly made standard.
- If the ICV is still below the acceptance limit (90%) for the requested analyte, re-calibrate and re-analyzed the ICV.
- If the ICV is above the acceptance limits (110%) and samples are ND, the results may be flagged and a non-conformance memo (NCM) written.

9.2.2 Initial Calibration Blank (ICB)

Analyze the initial calibration blank (ICB) immediately after the ICV. The ICB should be:

- <±RL for samples ≥2x RL or
- ≤ ±½ RL or MDL (whichever is greater) for samples <2x RL

If any element exceeds the limit

- Check to see if it is a requested metal; if it is not required the analysis can proceed as is.
- If the element is required, reanalyze the ICB and if it is still out of limits, re-calibrate and re-analyze ICV and ICB.
- Reanalysis is not required if the sample results are > 10x the blank result or the samples are not detected (ND).

9.2.3 Interference Check Solutions (ICSA/ICSAB) - **Required for EPA method 6020 only**
Analyze the interference check solutions (ICSA and ICSAB) immediately after the ICB to verify the inter-element corrections function properly.

TABLE 4: INTERFERENCE CHECK ACCEPTANCE CRITERIA

Target Element	ICSA Requirement (ug/L)	ICSAB Requirement (%Difference from True)
As	±2 x RL	±20
Cd	±2 x RL	±20
Cr	±2 x RL	±20
Co	±2 x RL	±20
Cu	±2 x RL	±20
Mn	±2 x RL	±20
Ni	±2 x RL	±20
Ag	±2 x RL	±20
Zn	±2 x RL	±20

If any analyte is outside a limit, then:

- Dilute the ICSA to a level that does not cause interference. If the interfering analyte (e.g. Fe) is present in a sample greater than its concentration in ICSA, dilute the sample so the interfering element concentration is below the ICSA concentration. OR
- Calculate the maximum concentration of the interfering element that can be present and not have an adverse effect on the sample results.
  [e.g. ICSA - Fe = 190mg/L, Se = 0.008mg/L; RL=0.005 (190/0.008) x 0.005= 118 mg/L Fe. If Fe exceeds this level in any sample, the sample must re-analyzed at a dilution].

Analyze the interference check solutions (ICSA and ICSAB) at the beginning of an analytical run or once every 12 hours, whichever is more frequent.

9.2.4 Internal Standard
Internal standard is added to every injection using instrument peristaltic pump. The internal standard intensities are required to meet the following criteria:

TABLE 5: INTERNAL STANDARD CRITERIA

Sample Type	EPA 200.8	EPA 6020
ICV & ICB	±20% of ICAL Standard	±20% of ICAL Standard
Batch QC	80-120%	80-120%
Client Samples	60-125%	30-120%

- If the ICV and the ICB do not meet this requirement, investigate the source of the problem before proceeding.

- If the batch QC samples do not meet these requirements, rerun once and recalibrate if necessary.

- Monitor the internal standard intensity in samples. If these criteria are not meet, dilute the sample and reanalyze. Repeat the dilution process until the IS meets the criteria.

9.2.5 Continuing Calibration Verification (CCV)

Verify the calibration curve by analyzing a CCV after the analysis of every batch of 10 samples. The recovery of the CCV must be between **90% - 110%** of the expected value and the RSD between replicate exposures **≤10%**. If the CCV is outside of acceptance limits:

- Re-prepare the CCV and re-analyze once.
- If it is acceptable, continue with the next 10 samples.
- If it is still unacceptable, re-calibrate the instrument and re-analyze the previous 10 samples.
- If a CCV fails during an overnight or unattended run, re-analyze all samples not bracketed by acceptable CCVs.
- If the CCV is out high, any ND samples may be reported.

9.2.6 Continuing Calibration Blank (CCB)

Follow every CCV with a CCB. The QC criteria for CCB are the same for ICB. Analyze a continuing calibration blank (CCB) immediately after every CCV. The CCB should be:

- <±RL for samples ≥2x RL or
- ≤ ±½ RL or MDL (whichever is greater) for samples <2x RL

If any element exceeds the limit:

- check to see if it is a requested metal; if it is not required the analysis can proceed as is.
- If CCB is still out for that element, all samples that are not detected (ND) or detected higher than 10x the contaminated CCB can be reported.

- If the element is required, reanalyze the CCB and if it is still out of limits, All positive samples bracketed by the failed CCB must be re-analyzed.

9.2.7 Calibration Acceptance Summary

Refer to the “Calibration Curves” SOP and the “Selection of Calibration Points” SOP for more information on calibrating the instrument.

Prepare and analyze a calibration curve daily for each element with 3 standards and a blank. The Correlation Coefficient must be ≥ 0.995 or the calibration must be repeated.

9.2.8 Linear Dynamic Range (LDR)

- Analyze once a year or whenever there is a change in analytical performance caused by either a change in instrument hardware or operating conditions. The upper limit of the linear calibration range should be established for each analyte by determining the

signal responses from a minimum of three different concentration standards; the highest standard is close to the upper limit of the linear range.

- For every element, calibrate the instrument as normal. Analyze standards for each element at two additional concentrations, the highest concentration being defined as the Linear Dynamic Range (LDR) of the instrument. Results of each of the standard must be within ±10% of the true value in order for the calibration range to be established.
- If ±10% cannot be achieved, a fresh standard may be prepared and reanalyzed and/or the instrument must be recalibrated and/or a lower standard may be used. The standard levels for the LDR will vary by element and must be documented after the range has been established.
- Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and analyzed.

9.2.9 Instrument Detection Limits (IDLs)

- Instrument Detection Limit studies can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of reagent blank solutions.
- IDLs should be determined at least every three months.

10.0 PROCEDURE

10.1 Reagent Preparation

10.1.1 Acidified Reagent Grade Water:

- Acidified RGW is used in the preparation of all subsequent standards.
- Acidified RGW is also used as rinse solution.
- Prepare the 1% (v/v) HNO3 and 0.5% (v/v) HCl by adding 10 mL HNO3 and 5 mL of HCL to 1L RGW in a 1L bottle.
- Prepare 3% (v/v) HNO3 and 3% (v/v) HCL by adding 20mL HNO3 and 20mL HCL to 1L bottle for analysis of Cs, Rb, Th.

10.2 Standard Preparation

All working standards are prepared daily in 100 mL/or 50mL class A volumetric flasks. Internal Standard is added at instrument by peristaltic pump.

TABLE 6: CALIBRATION CURVE*

Source	Blank	S1 0.2 ppb	S2 1 ppb	S3 10 ppb	S4 100 ppb	ICV 25 ppb	CCV 50 ppb	ICB/CCB
First Source Std	--	--	--	--	1 mL	--	2.5 mL	--
S4	--	--	--	10 mL	--	--	--	--
S3	--	2 mL	10 mL	--	--	--	--	--
Second Source Std	--	--	--	--	--	250 µL	--	--
Final Volume with Acidified Reagent Grade Water*	100 mL	100 mL	100 mL	100 mL	100 mL	100 mL	500 mL	100 mL

*Different final volumes may be used provided they are documented and the source standard volumes are scaled correspondingly.

10.2.1 Standard 1 Concentration (S1): 0.2 ppb Metals, 2 ppb Fe, 5 ppb K, Mg, Na, 10 ppb Ca.

10.2.2 Standard 2 Concentration (S2): 1 ppb Metals, 10 ppb Fe, 25 ppb K, Mg, Na, 50 ppb Ca.

10.2.3 Standard 2 Concentration (S3): 10 ppb Metals, 100 ppb Fe, 250 ppb K, Mg, Na, 500 ppb Ca.

10.2.4 Standard 3 Concentration (S4): 100 ppb Metals, 1000 ppb Fe, 2500 ppb K, Mg, Na, 5000 ppb Ca.

10.2.5 Calibration Blank, ICB, CCB: acidified Reagent Grade water

10.2.6 Second source ICV: purchased

10.2.7 Interference Check Solution A (ICSA): 1000 ppm of Cl; 200 ppm of C; 100 ppm Al, Ca, Fe, Mg, P, K, Na, S and 2ppm of Mo, Ti. Prepare the ICSA by adding 1 mL of ICSA standard to 9 mL acidified Reagent Grade water in a 15mL sample tube. Prepare daily.

10.2.8 Interference Check Solution AB (ICSAB): 1000 ppm of Cl, 200 ppm of C, 100 ppm Al,Ca, Fe, Mg, P, K, Na S, 2 ppm of Mo, Ti; It also contains 20 ppb of each of As, Cd, Cr, Co, Cu, Mn, Ni, Ag, and Zn**.** Prepare ICSAB by adding 1 mL of ICSA standard, 20 µL of 10ppm stock standard to 9 mL of acidified Reagent Grade water. Prepare daily.

10.2.9 Reporting Limit Checks

TABLE 7: REPORTING LIMIT CHECK PREPARATION

Reagent/Standard	0.2 ppb	1xRL	2xRL
100 ppb standard	20 µL		
CRI standard		0.5 mL	1 mL
Acidified Reagent Grade Water to Final Volume	50 mL	50 mL	50 mL

Note: Internal standard is added using instrument peristaltic pump.

10.2.10 Tuning check solution Agilent EPA Tune Check:
The tuning solution is prepared at 10ppb from the O2Si (or equivalent) tuning solution (10 ppm). Prepare the tuning solution with 1% (v/v) nitric acid in Reagent Grade water. Add 1mL of tuning solution (10ppm) to 1L of 1% (v/v) HNO3 solution.

10.2.11 1ppb Agilent Tuning Solution
Make a 1:10 dilution of the stock 10ppm Agilent Tune Solution to have 1ppm working standard in 1% (v/v) HNO3. Add 1mL of 1ppm standard to 1L of 1% (v/v) HNO3 solution.

10.2.12 Agilent PA Solution
Add 1mL of Agilent PA Solution 1 and 1 mL of Agilent PA Solution 2 to 100mL of 1%HNO3 and 0.5% HCl solution.

10.2.13 Internal standard solution mix:

For Agilent: The online internal standard solution mix is prepared at 1 ppm (Sc, Tb, In, Ge, Y, Bi and Li) from the 1000 ppm single element stock solutions. Add 500 ul of each of the 1000 ppm stock solutions to 500mL of acidified Reagent Grade water.

10.2.14 Linear Dynamic Range Standards

Prepare 7 standard solutions as follows: 10ppm is the stock standard

TABLE 8: LDR PREPARATION

Source	1000 ppb	1500 ppb	2000 ppb	2500 ppb	3000 ppb	3500 ppb	4000 ppb
First Source 10 mg/L std (mLs)	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Final Volume with Acidified (RGW) (mLs)	10	10	10	10	10	10	10

10.3 Sample Preparation

Batch QC samples (MB, MRL, LCS, MS/MSD) are prepared in the same manner as client samples but are spiked in accordance with the table below.

TABLE 9: SAMPLE PREPARATION

Container Matrix	QC Type	Matrix	Spike (uL)	Final Volume
Digested Water	MB	Digested RGW, prepared by Metals Prep Group		
	LCS	Digested & spiked RGW, prepared by Metals Prep Group		
	MRL			
	MS/MSD	Digested & spiked source sample, prepared by Metals Prep Group		
Digested Soil/Wipe	MB	PTFE chips or wipe digested in RGW, prepared by Metals Prep Group		
	LCS	PTFE chips or wipe spiked & digested in RGW, prepared by Metals Prep Group		
	MRL			
	MS/MSD	Source sample spiked & digested in RGW, prepared by Metals Prep Group*		
STLC	MB	0.5mL STLC Blank	N/A	10mL with acidified RGW
	LCS	0.5mL STLC Blank	80µL of 10ppm stock standard	10mL with acidified RGW
	MS/MSD	0.5mL source sample	80µL of 10ppm stock standard	10mL with acidified RGW
TCLP/SPLP	MB	Digested TCLP/SPLP Blank, prepared by Metals Prep Group		
	LCS	Digested & spiked TCLP/SPLP Blank, prepared by Metals Prep Group		
	MS/MSD	Digested TCLP/SPLP MS, prepared by Metals Prep Group		
Leachate (DI WET)	MB	DI WET Blank	N/A	10mL DI WET Blank
	LCS	DI WET Blank	80µL of 10ppm stock standard	10mL DI WET Blank
	MS/MSD	Source sample	80µL of 10ppm stock standard	10mL source sample

*MS/MSD not applicable to wipe samples.

NOTE: Internal standard is added using instrument's peristaltic pump.

10.3.1 Digested Water:

- Transfer samples into labeled corresponding centrifuge tubes.

10.3.2 Soil/Wipe

- Soil samples are diluted 20x after digestion and before analysis.
- Pipet 0.5 mL of the sample into a centrifuge tube.
- Add 9.5 mL of acidified Reagent Grade water.

10.3.3 STLC

- STLC samples (after rotation and filtration) are diluted 20x after digestion and before analysis.
- Pipet 0.5 mL of the sample into a centrifuge tube.
- Spike LCS, MS, MSD with 0.08mL calibration standard.
- Add 9.5 mL of acidified Reagent Grade water.

10.3.4 TCLP /SPLP

- TCLP / SPLP samples are diluted 10x after digestion and before analysis.
- Pipet 1.0 mL of the sample into a centrifuge tube.
- Add 9.0 mL of acidified Reagent Grade water.

10.3.5 Leachate (DI WET)

- Pour the sample into a 15mL centrifuge tube.

10.4 **Instrument Initialization:** Pre-calibration routine: instrument tuning and mass calibration. Follow instrument manual for start-up for Agilent.

- Warm-up the instrument for at least 20 minutes for Agilent.
- Analyze the tuning solution 5 times and achieve a relative standard deviation for all analytes of <5%.
- Conduct mass calibration and resolution checks using the tuning solution. Peak width should be 0.700 ± 0.010 amu at 10% peak height.
- Follow the instructions provided by the instrument manufacturer for operating conditions (see attached flow chart). For the following optimizations aspirate the tuning solution (10ppb) containing Ba, Be, Ce, Co, In, Li, Mg, Pb, Rh, Tl, U, Y.
- Run a mass tune. Measured masses should be within 0.05 atomic units of the actual masses.
- Autolens calibration is not needed for the Agilent.
- Then conduct a Daily performance check.

TABLE 10: TUNE CRITERIA

	Mass Tune Requirement (±0.1au)	Daily Performance Check
He	--	--
Mg	23.9-24.10	>2,000 cp 1/10s
Rh	102.90-103.10	>15,000 cp 1/10s
Pb	207.90-208.10	>10,000 cp 1/10s
In	114.90-115.10	>15,000 cp 1/10s
CeO/Ce	--	≤ 1%
Ba^{++}/Ba^{+}	--	≤ 3.0%
Mass 220	--	--
U	237.90-238.10	--

10.5 Calibration

Calibrate the instrument daily using a blank, S1, S2 and S3

10.6 Sample Analysis

10.6.1 Analyze the ICV, ICB at the start of the analytical run.

10.6.2 Analyze ICSA and ICSAB (only required for EPA Method 6020).

10.6.3 Analyze RL Check standards.

10.6.4 Analyze a method blank (MB) and LCS for each batch of 20 samples or less per matrix.

10.6.5 Analyze up to 8 samples after the LCS and MB.

10.6.6 For 200.8: Analyze a Matrix Spike (MS) and a Matrix Spike Duplicate (MSD) for every batch of 10 samples or less per matrix.

10.6.7 For 6020: Analyze a Matrix Spike (MS) and a Matrix Spike Duplicate (MSD) for every batch of 20 samples or less per matrix.

10.6.8 Analyze a CCV and CCB for every set of 10 client samples and at the end of the analytical run.

10.6.9 Analyze RL Checks at the end (if required by client)

10.6.10 Analyze ICA and ICSAB at the end (if required by client)

A typical daily run sequence is listed below:

TABLE 11: TYPICAL ANALYSIS SEQUENCE

Sample Name	Criteria
Blank	
S1	$r^2 \geq 0.995$
S2	
S3	
ICV	%Rec=90-110; RSD≤ 5
ICB	<±RL for samples ≥2x RL OR ≤ ±½ RL or MDL (whichever is greater) for samples <2x RL
ICSA*	±2 x RL for: As, Cd, Cr, Co, Cu, Mn, Ni, Ag, Zn
ICSAB*	±20% for: As, Cd, Cr, Co, Cu, Mn, Ni, Ag, Zn
RL Check standards	%Rec=±50
MB1	<RL
LCS1	%Rec=85-115 for 200.8 %Rec=80-120 for 6020
Source sample for MS1/MSD1	RSD≤25**
MS1	%Rec=70-130 for 200.8; RPD≤20 %Rec=75-125 for 6020; RPD≤20
MSD1	
Samples	RSD≤25 %**
CCV	%Rec=90-110; RSD≤10
CCB	<±RL for samples ≥2x RL OR ≤ ±½ RL or MDL (whichever is greater) for samples <2x RL
Source sample for MS2	RSD≤25*
MS2 (200.8 only)	%Rec=70-130; RPD≤20
MSD2 (200.8 only)	
CCV	%Rec=90-110; RSD≤10
CCB	<±RL for samples ≥2x RL OR ≤ ±½ RL or MDL (whichever is greater) for samples <2x RL
Samples	RSD≤25 %*

Sample Name	Criteria
CCV	%Rec=90-110; RSD≤10
CCB	<±RL for samples ≥2x RL OR ≤ ±½ RL or MDL (whichever is greater) for samples <2x RL
Closing ICSA (if req'd)***	±2 x RL for: As, Cd, Cr, Co, Cu, Mn, Ni, Ag, Zn
Closing ICSAB (if req'd)***	±20% for: As, Cd, Cr, Co, Cu, Mn, Ni, Ag, Zn
Closing RL check (if req'd)***	%Rec=±50

* Only required for EPA Method 6020
** For sample results >2X the RL, otherwise RSD must be ≤50%. (unless specified otherwise by client)
*** For special project

10.7 Preventative Maintenance

10.7.1 Daily

- Inspect peristaltic pump tubing and replace when needed.
- Inspect waste level and empty when necessary.
- Replace rinse solution.
- Inspect torch and injector for signs of clogging, misalignment, or deposits.
- Clean cones
- Clean or change nebulizer.

10.7.2 As Needed

- Clean or replace ion lens.
- Check gas filters for moisture and replace when necessary.
- Change rough pump oil (about monthly)

.

10.7.3 Record all performed maintenance in the instrument maintenance logbook.

10.7.4 If an instrument is unusable or has limitation to its use, it must be tagged accordingly until such a time the problem has been corrected. Record the problem, solution and verification of proper operation into the instrument maintenance logbook.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Accuracy

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\text{MS \% Recovery} = \frac{\text{(spiked sample) - (unspiked sample)}}{} \times 100$$

spiked concentration

11.2 Precision (RPD)

Matrix Duplicate (MD) = $\frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$

11.3 Calibration

$$y = mx + b \qquad C = \frac{(y - b)}{m}$$

Where y is the instrument response ratio
m is the slope
x is the concentration
b is the y-intercept
C is the raw sample concentration (instrument reading)

11.4 Concentration

$C_f = C_i \times PF \times DF$

Where C_f = Final concentration in µg/L
C_i = Concentration in µg/L from instrument
PF = Preparation (digestion) factor
DF = any additional bench Dilution Factor

11.5 Calculation / Reporting of Uranium

Uranium may be reported either as mass (ug/L) or activity (pico-Curies per liter [pCi/L]):

µg/L x conversion factor = pCi/L

conversion factor from mass to activity is 0.67

The CA DLR for uranium is 1 µg/L or 2 pCi/L.
The CA MCL for uranium is 20 pCi/L.
The Federal MCL for uranium is 30 µg/L

12.0 METHOD PERFORMANCE

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure as described in laboratory's SOP, IR-QA-MDL. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capabilities

Every analyst must perform an Initial Demonstration of Capability (IDOC) before performing analyses on any client samples. An IDOC consists of 4 consecutive LCS samples at 1 to 4 times the RL with an average recovery and RSD within laboratory acceptance limits. An on-going DOC must be performed annually. An ODOC can be 4 consecutive LCSs at mid-level or a passing PT.

12.3 Training Requirements

The analyst must have documented training, including reading of the SOP and source methods, conducted by the department manager, senior chemist, or other analyst with training documentation and a passing DOC.

13.0 POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in the "Waste Management and Pollution Prevention" section of the Corporate Environmental Health and Safety Manual (CW-E-M-001).

14.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the laboratory's Waste Disposal SOP (IR-EHS-WASTE). The following waste streams are produced when this method is carried out:

- **Metals digestates** (50 ml polytubes). Once the samples have been analyzed they are kept in the metal shelves for 30 - 60 days. After the 30 -60 days analyst transfer the digestates to a satellite 55 gallon drum in the area. When the satellite drum is full sample archive technicians will move the drum to the main waste storage area. The drum will be disposed of as the acid loosepack waste stream.
- **Acid Waste** (Hydrochloric, Nitric Acid). This waste is generated by ICP /ICP MS machines. This waste is collected behind the instruments into 4 gal Carboy satellite container. The waste is neutralized with both Sodium hydroxide and soda ash. When the waste is at a pH of 7 it is poured into a sink in the glassware wash room and drained to the sewer.
- **Unused standards.** If the standard is hazardous and can not be collected with one of the waste streams generated in the method, it must be labeled as hazardous waste with the date the material became waste. The analyst or technicians take this standard and placed it on the shelves labeled "hazardous waste" in the main waste storage area. The standard will be lab packed (example: mercury standard).
- If the standard can be collected in the satellite waste container for one of the waste streams of the method, then pour the standard in the right satellite container, rinse the original container, and collect the rinsate in the satellite container. The original container can be placed in the regular trash. (Example, buffer solutions pH 4) Sample archive technicians will bulk this waste with the nitric acid waste w/RCRA metals.

15.0 REFERENCES / CROSS-REFERENCES

15.1 EPA Method 200.8, Revision 5.4, May 1994

15.2 EPA Method 200.2, Revision 2.8, May 1994

15.3 EPA Method 6020 SW-846, Revision 0, September 1994

15.4 Manual for the Certification of Laboratories Analyzing Drinking Water, Fifth Edition, EPA, January 2005, EPA 815-R-05-004

15.5 CA-Q-S-005, Calibration Curves (General)

15.6 CA-T-P-002, Selection Of Calibration Points

15.7 Method of Standard Additions (MSA) is based on SW846 Methods 7000B (section 9.7) and 1311 (section 8.4)

16.0 METHOD MODIFICATIONS

TABLE 12: METHOD MODIFICATIONS

Item	Method Ref	Modification
1	*EPA 200.8 Sec. 10.2.1*	*For mass tuning, peak width of approximately 0.70 amu at 10% peak height is calibrated instead of 0.75 amu at 5% peak height for better performance per instrument manufacturer.*
2	*EPA 200.8 Sec. 7.4.1, 7.6.1*	*All calibration standards and calibration blank are prepared in 1% (v/v) HNO3 and 0.5% (v/v) to match with sample matrix.*
3	*EPA 200.8 Sec. 7.5*	*Germanium is used as internal standard in lieu of Yttrium and Bismuth*
4	*EPA 200.8 Sec 9.3.1*	*ICB/CCB acceptance criteria modified from 2.2 x MDL or >10% of any sample concentration, whichever is greater, to <±RL for samples ≥ 2x RL and ≤ ±½ RL (or <MDL, whichever is greater) for samples <2x RL.*
5	*EPA 200.8 6020 Sec 2.*	*The new technique, collision cell, is added to remove interferences and improve RL due to less dilution.*

17.0 ATTACHMENTS

17.1 **Attachment 1:** Analysis Information

17.2 **Attachment 2:** Agilent Data Review Checklist

17.3 **Attachment 3:** Quantitation Ions and Associated Internal Standards

18.0 REVISION HISTORY

This section has been added beginning with Revision 0. Only details of the last two revisions are incorporated into this SOP. Prior revisions are documented in the QA files.

18.1 **Revision 3, dated 30 August 2013**

This revision supersedes IR-MET-ICPMS, revision 2 (08/16/2012)

- Added digested Reporting Limit Verification (MRL) for drinking water samples that required digestion.
- Added Bismuth in the list of internal standards used in the method.
- Added standard 0.2ppb to the calibration curve

- All working standards are prepared in 100 mL class A volumetric flasks
- Added Instrument Detection Limits study
- Added Rubidium, Thorium, Tin and Strontium to the list of elements analyzed.
- Unused standards must be labeled as hazardous waste with the date the material became waste
- Added Wipe Sample Preparation
- Revised by NH, LH and DD

18.2 Revision 4, dated 07 October 2014

- This revision supersedes IR-MET-ICPMS, revision 3 (08/30/2013) and IR-MET-ICPMS_r3-CF1 (02/14/2014)
- Added revised MSA procedure
- Removed all ELAN references
- RSD requirements changed from ≤ to < for TALS compliance
- Revised analysis information in Attachment 1
- Revised ICSA & ICSAB acceptance criteria
- Revised data review checklist
- Revised by NH, DT, and DD

Attachment 1a
Analysis Information – 200.8 Water

TestAmerica Irvine

Analytical Method Information

EPA 200.8 Water - Metals by ICPMS

Analyte	CAS	MDL	RL	Units	LCS	MS/MSD
Ag	7440-22-4	0.5	1	ug/L	85-115 / 20	70-130 / 20
Al	7429-90-5	5	10	ug/L	85-115 / 20	70-130 / 20
As	7440-38-2	0.5	1	ug/L	85-115 / 20	70-130 / 20
Ba	7440-39-3	0.5	1	ug/L	85-115 / 20	70-130 / 20
Be	7440-41-7	0.25	0.5	ug/L	85-115 / 20	70-130 / 20
Cd	7440-43-9	0.25	1	ug/L	85-115 / 20	70-130 / 20
Ce	7440-45-1	0.5	1	ug/L	85-115 / 20	70-130 / 20
Co	7440-48-4	0.5	1	ug/L	85-115 / 20	70-130 / 20
Cr	7440-47-3	0.5	2	ug/L	85-115 / 20	70-130 / 20
Cs	7440-46-2	0.1	0.2	ug/L	85-115 / 20	70-130 / 20
Cu	7440-50-8	0.5	2	ug/L	85-115 / 20	70-130 / 20
Fe	7439-89-6	8	20	ug/L	85-115 / 20	70-130 / 20
Mn	7439-96-5	0.5	1	ug/L	85-115 / 20	70-130 / 20
Mo	7439-98-7	0.5	2	ug/L	85-115 / 20	70-130 / 20
Ni	7440-02-0	0.5	2	ug/L	85-115 / 20	70-130 / 20
Pb	7439-92-1	0.5	1	ug/L	85-115 / 20	70-130 / 20
Rb	7440-17-7	0.1	0.2	ug/L	85-115 / 20	70-130 / 20
Sb	7440-36-0	0.5	2	ug/L	85-115 / 20	70-130 / 20
Se	7782-49-2	0.5	2	ug/L	85-115 / 20	70-130 / 20
Sn	7440-31-5	5	10	ug/L	85-115 / 20	70-130 / 20
Sr	7440-24-6	0.25	1	ug/L	85-115 / 20	70-130 / 20
Th	7440-29-1	0.25	0.5	ug/L	85-115 / 20	70-130 / 20
Tl	7440-28-0	0.5	1	ug/L	85-115 / 20	70-130 / 20
U	7440-61-1	0.5	1	ug/L	85-115 / 20	70-130 / 20
V	7440-62-2	1	2	ug/L	85-115 / 20	70-130 / 20
Zn	7440-66-6	2.5	20	ug/L	85-115 / 20	70-130 / 20

Attachment 1b
Analysis Information – 6020 Water

TestAmerica Irvine

Analytical Method Information

SW6020 Water - Metals by ICPMS

Analyte	CAS	MDL	RL	Units	LCS	MS/MSD
Ag	7440-22-4	0.5	1	ug/L	80-120 / 20	75-125 / 20
Al	7429-90-5	5	10	ug/L	80-120 / 20	75-125 / 20
As	7440-38-2	0.5	1	ug/L	80-120 / 20	75-125 / 20
Ba	7440-39-3	0.5	1	ug/L	80-120 / 20	75-125 / 20
Be	7440-41-7	0.25	0.5	ug/L	80-120 / 20	75-125 / 20
Ca	7440-70-2	50	100	ug/L	80-120 / 20	75-125 / 20
Cd	7440-43-9	0.25	1	ug/L	80-120 / 20	75-125 / 20
Co	7440-48-4	0.5	1	ug/L	80-120 / 20	75-125 / 20
Cr	7440-47-3	0.5	2	ug/L	80-120 / 20	75-125 / 20
Cs	7440-46-2	0.1	0.2	ug/L	80-120 / 20	75-125 / 20
Cu	7440-50-8	0.5	2	ug/L	80-120 / 20	75-125 / 20
Fe	7439-89-6	8	20	ug/L	80-120 / 20	75-125 / 20
K	7440-09-7	50	100	ug/L	80-120 / 20	75-125 / 20
Mg	7439-95-4	50	100	ug/L	80-120 / 20	75-125 / 20
Mn	7439-96-5	0.5	1	ug/L	80-120 / 20	75-125 / 20
Mo	7439-98-7	0.5	2	ug/L	80-120 / 20	75-125 / 20
Na	7440-23-5	50	100	ug/L	80-120 / 20	75-125 / 20
Ni	7440-02-0	0.5	2	ug/L	80-120 / 20	75-125 / 20
Pb	7439-92-1	0.5	1	ug/L	80-120 / 20	75-125 / 20
Rb	7440-17-7	0.1	0.2	ug/L	80-120 / 20	75-125 / 20
Sb	7440-36-0	0.5	2	ug/L	80-120 / 20	75-125 / 20
Se	7782-49-2	0.5	2	ug/L	80-120 / 20	75-125 / 20
Sn	7440-31-5	5	10	ug/L	80-120 / 20	75-125 / 20
Th	7440-29-1	0.25	0.5	ug/L	80-120 / 20	75-125 / 20
Tl	7440-28-0	0.5	1	ug/L	80-120 / 20	75-125 / 20
U	7440-61-1	0.5	1	ug/L	80-120 / 20	75-125 / 20
V	7440-62-2	1	2	ug/L	80-120 / 20	75-125 / 20
Zn	7440-66-6	2.5	20	ug/L	80-120 / 20	75-125 / 20

Attachment 1c
Analysis Information – 6020 Soils

TestAmerica Irvine

Analytical Method Information

SW6020 Solid - Metals by ICPMS

Analyte	CAS	MDL	RL	Units	LCS	MS/MSD
Ag	7440-22-4	0.25	0.5	mg/Kg	80-120 / 20	80-120 / 20
Al	7429-90-5	2.5	5	mg/Kg	80-120 / 20	80-120 / 20
As	7440-38-2	0.25	0.5	mg/Kg	80-120 / 20	80-120 / 20
Ba	7440-39-3	0.25	0.5	mg/Kg	80-120 / 20	80-120 / 20
Be	7440-41-7	0.15	0.3	mg/Kg	80-120 / 20	80-120 / 20
Ca	7440-70-2	50	100	mg/Kg	80-120 / 20	80-120 / 20
Cd	7440-43-9	0.25	0.5	mg/Kg	80-120 / 20	80-120 / 20
Ce	7440-45-1	0.25	0.5	mg/Kg	80-120 / 20	80-120 / 20
Co	7440-48-4	0.25	0.5	mg/Kg	80-120 / 20	80-120 / 20
Cr	7440-47-3	0.5	1	mg/Kg	80-120 / 20	80-120 / 20
Cu	7440-50-8	0.5	1	mg/Kg	80-120 / 20	80-120 / 20
Fe	7439-89-6	5	10	mg/Kg	80-120 / 20	80-120 / 20
K	7440-09-7	50	100	mg/Kg	80-120 / 20	80-120 / 20
Mg	7439-95-4	50	100	mg/Kg	80-120 / 20	80-120 / 20
Mn	7439-96-5	0.25	0.5	mg/Kg	80-120 / 20	80-120 / 20
Mo	7439-98-7	0.5	1	mg/Kg	80-120 / 20	80-120 / 20
Na	7440-23-5	50	100	mg/Kg	80-120 / 20	80-120 / 20
Ni	7440-02-0	0.5	1	mg/Kg	80-120 / 20	80-120 / 20
Pb	7439-92-1	0.25	0.5	mg/Kg	80-120 / 20	80-120 / 20
Sb	7440-36-0	0.5	1	mg/Kg	80-120 / 20	80-120 / 20
Se	7782-49-2	0.5	1	mg/Kg	80-120 / 20	80-120 / 20
Sn	7440-31-5	2.5	5	mg/Kg	80-120 / 20	80-120 / 20
Tl	7440-28-0	0.25	0.5	mg/Kg	80-120 / 20	80-120 / 20
U	7440-61-1	0.25	0.5	mg/Kg	80-120 / 20	80-120 / 20
V	7440-62-2	0.5	1	mg/Kg	80-120 / 20	80-120 / 20
Zn	7440-66-6	5	10	mg/Kg	80-120 / 20	80-120 / 20

Attachment 1d
Analysis Information – Collision Cell

TestAmerica Irvine

Analytical Method Information

EPA 200.8 Water - Metals by ICPMS Collision Cell

Analyte	CAS	MDL	RL	Units	LCS	MS/MSD
Ag	7440-22-4	0.1	0.2	ug/L	85-115 / 20	70-130 / 20
Al	7429-90-5	5	10	ug/L	85-115 / 20	70-130 / 20
As	7440-38-2	0.1	0.2	ug/L	85-115 / 20	70-130 / 20
Ba	7440-39-3	0.1	0.2	ug/L	85-115 / 20	70-130 / 20
Be	7440-41-7	0.1	0.2	ug/L	85-115 / 20	70-130 / 20
Cd	7440-43-9	0.05	0.1	ug/L	85-115 / 20	70-130 / 20
Co	7440-48-4	0.1	0.2	ug/L	85-115 / 20	70-130 / 20
Cr	7440-47-3	0.25	0.5	ug/L	85-115 / 20	70-130 / 20
Cu	7440-50-8	0.25	0.5	ug/L	85-115 / 20	70-130 / 20
Fe	7439-89-6	5	10	ug/L	85-115 / 20	70-130 / 20
Mn	7439-96-5	0.25	0.5	ug/L	85-115 / 20	70-130 / 20
Mo	7439-98-7	0.1	0.2	ug/L	85-115 / 20	70-130 / 20
Ni	7440-02-0	0.15	0.2	ug/L	85-115 / 20	70-130 / 20
Pb	7439-92-1	0.05	0.1	ug/L	85-115 / 20	70-130 / 20
Sb	7440-36-0	0.2	0.5	ug/L	85-115 / 20	70-130 / 20
Se	7782-49-2	0.3	0.6	ug/L	85-115 / 20	70-130 / 20
Tl	7440-28-0	0.05	0.1	ug/L	85-115 / 20	70-130 / 20
U	7440-61-1	0.05	0.1	ug/L	85-115 / 20	70-130 / 20
V	7440-62-2	0.1	0.2	ug/L	85-115 / 20	70-130 / 20
Zn	7440-66-6	2	5	ug/L	85-115 / 20	70-130 / 20

TestAmerica Irvine

Analytical Method Information

SW6020 Water - Metals by ICPMS Collision Cell

Analyte	CAS	MDL	RL	Units	LCS	MS/MSD
Ag	7440-22-4	0.05	0.1	ug/L	80-120 / 20	75-125 / 20
Al	7429-90-5	5	10	ug/L	80-120 / 20	75-125 / 20
As	7440-38-2	0.05	0.1	ug/L	80-120 / 20	75-125 / 20
Ba	7440-39-3	0.1	0.2	ug/L	80-120 / 20	75-125 / 20
Be	7440-41-7	0.08	0.1	ug/L	80-120 / 20	75-125 / 20
Cd	7440-43-9	0.05	0.1	ug/L	80-120 / 20	75-125 / 20
Co	7440-48-4	0.05	0.1	ug/L	80-120 / 20	75-125 / 20
Cr	7440-47-3	0.2	0.5	ug/L	80-120 / 20	75-125 / 20
Cu	7440-50-8	0.3	0.5	ug/L	80-120 / 20	75-125 / 20
Fe	7439-89-6	7	10	ug/L	80-120 / 20	75-125 / 20
Mn	7439-96-5	0.3	0.5	ug/L	80-120 / 20	75-125 / 20
Mo	7439-98-7	0.1	0.2	ug/L	80-120 / 20	75-125 / 20
Ni	7440-02-0	0.15	0.2	ug/L	80-120 / 20	75-125 / 20
Pb	7439-92-1	0.05	0.1	ug/L	80-120 / 20	75-125 / 20
Sb	7440-36-0	0.1	0.2	ug/L	80-120 / 20	75-125 / 20
Se	7782-49-2	0.3	0.5	ug/L	80-120 / 20	75-125 / 20
Tl	7440-28-0	0.05	0.1	ug/L	80-120 / 20	75-125 / 20
U	7440-61-1	0.05	0.1	ug/L	80-120 / 20	75-125 / 20
V	7440-62-2	0.05	0.1	ug/L	80-120 / 20	75-125 / 20
Zn	7440-66-6	2	5	ug/L	80-120 / 20	75-125 / 20

Attachment 2
Agilent Data Review Checklist

DATA CHECKLIST

EPA 6020 / 200.8 – Trace Metals by ICPMS - AGILENT

Analyst: _____ 2nd Level Review: _____
Analysis Date: _____ Date: _____
ICPMS #: _____ Method used: EPA: 200.8 6020
Data Set #: _____

Analyst Rev	2nd Level Rev	
		Pre-calibration tuning and performance:
		Precision: RSD (absolute signals) < 5% from 4 to 5 runs of tuning solution
		Mass tune In: 114.90 – 115.10 Rh: 102.90 – 103.10
		Mg: 23.9 – 24.10 Pb: 207.90 – 208.10
		U: 237.90 – 238.10
		Performance In: >15,000 cp(1/10)s Oxide: ≤ 1%
		Rh: >15,000 cp(1/10)s Ba^{++}/Ba^{+}: ≤ 3%
		Mg: >2,000 cp(1/10)s mz/ RSD: < 10%
		Pb: >10,000 cp(1/10)s
		Daily calibration: 3-point, 3-replicate run, linear and forced through zero. r≥ 0.995
		2nd source ICV (25ppb) / **1st source CCV** (50ppb):
		• ICV immediately after calibration. CCV every 10 samples and at the end of analysis
		• %REC = 90 – 110
		• %RSD ≤ 5 for ICV
		• %RSD ≤ 10 for CCV
		Reporting Limit (RL) Check: 50-150%
		ICS: for 6020, run before sample analysis **ICSA** **ICSAB**
		• As,Cd,Cr, Co,Cu,Mn,Ni,Ag,Zn: ±2 x RL ±20%
		• Analyze ISCA/ICSAB once every 12 hours
		ICB/CCB/MB:
		• Run after ICV/CCV
		• ICB/CCB : <±RL for samples ≥2x RL or ≤ ±½ RL or MDL (whichever is greater) for samples <2x RL
		• MB: <RL
		LCS/LFB: every batch of 20 samples or less
		• EPA 6020: %REC = 80 – 120 (or in-house)
		• EPA 200.8: %REC = 85 – 115
		MS/MSD: EPA 6020: every 20 samples or less
		EPA 200.8: every 10 samples or less
		• EPA 6020: %REC = 75 - 125 (or in-house) and %RPD (MS/MSD) ≤ 20
		• EPA 200.8: %REC = 70 – 130 and %RPD (MS/MSD) ≤ 20
		Post-Digestion Spike (EPA 6020 only): Analyze if MS or MSD fail. % REC = 75 - 125
		Dilution Test: (for special project)
		Internal Standard:
		• EPA 200.8: 60 – 125% (80-120% in ICB/ICV)
		• EPA 6020B: 30 – 120% (80-120% in ICB/ICV)
		All samples checked for replicates (3), precision (RSD if applicable), accuracy, dilution, linear range (<=90% of LDR), correct bracket (<=10 samples) between compliant CCV/CCB and transcription errors

Comments: _____

ICPMS_AGILENT_CHK_r2
Rev. 10/03/2014

Attachment 3
Quantitation Ions and Associated Internal Standards

Element Name	Quant Ion Mass	Internal Standard
Beryllium (Be)	9	Germanium (Ge) and/or Scandium(Sc)
Aluminum (Al)	27	Germanium(Ge) and/or Scandium(Sc)
Vanadium (V)	51	Germanium(Ge) and/or Scandium(Sc)
Chromium (Cr)	52	Germanium(Ge) and/or Scandium(Sc)
Manganese (Mn)	55	Germanium(Ge) and/or Scandium(Sc)
Cobalt (Co)	59	Germanium(Ge) and/or Scandium(Sc)
Nickel (Ni)	60	Germanium(Ge) and/or Scandium(Sc)
Copper (Cu)	63	Germanium(Ge) and/or Scandium(Sc)
Copper (Cu)	65	Germanium(Ge) and/or Scandium(Sc)
Zinc (Zn)	66	Germanium (Ge)
Arsenic (As)	75	Germanium (Ge)
Selenium (Se)	82	Germanium (Ge)
Krypton (Kr)	84	No IS. Monitoring purposes only*
Molybdenum (Mo)	98	Germanium (Ge) and/or Indium(In)
Silver (Ag)	107	Germanium (Ge) and/or Indium(In)
Cadmium (Cd)	114	Germanium (Ge) and/or Indium(In)
Antimony (Sb)	121	Germanium (Ge) and/or Indium(In)
Barium (Ba)	135	Germanium (Ge) and/or Indium(In)
Thallium (Tl)	205	Terbium (Tb) and/or Bismuth (Bi)
Lead (Pb)	208	Terbium (Tb) and/or Bismuth (Bi)
Uranium (U)	238	Terbium (Tb)
Sodium (Na)	23	Scandium (Sc)
Magnesium (Mg)	24	Scandium (Sc)
Potassium (K)	39	Scandium (Sc)
Calcium (Ca)	44	Scandium (Sc)
Iron (Fe)	54	Scandium (Sc)
Rubidium	85	Indium (In)
Thorium	232	Terbium (Tb)
Tin	118	Indium (In)
Strontium	88	Indium (In)
Cesium (Ce)	140	Indium (In)

*Krypton should read > 5000 – 10000 counts as daily monitoring response

Title: ALKALINITY
SM 2320B

Approvals (Signature/Date):

Tung Nguyen Department Manager 10/2/14 Date	William Nash Environmental Health & Safety Coordinator 10/02/2014 Date
Maria Friedman Quality Assurance Manager 10-3-2014 Date	Kirk Miltimore Laboratory Director 10/02/2014 Date

Facility Distribution No. _____ **Distributed To:** _____

1.0 SCOPE AND APPLICATION

1.1 SM2320B is applicable the analysis of alkalinity in drinking water, surface water, saline water, domestic waste, and industrial waste.

1.2 This method has been modified to report alkalinity for solids.

1.3 See Attachment 1 for reporting limit and QC information. See LIMS for current RL and control limit values.

1.4 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in "Validation of Methods" in the Quality Assurance Manual.

2.0 SUMMARY OF METHOD

2.1 An unaltered sample is titrated with standardized hydrochloric acid to potentiometrically determined endpoints of pH 8.3 and/or 4.5.

2.2 For solids, a specific weight of solid is mixed with reagent water and the aqueous portion is titrated.

3.0 DEFINITIONS

3.1 Alkalinity of water is its acid-neutralizing capacity. It is the sum of all the titratable bases.

3.2 Alkalinity results can be expressed as total alkalinity as calcium carbonate and as the component bases, bicarbonate as calcium carbonate, carbonate as calcium carbonate, and hydroxide as calcium carbonate.

3.3 There are no additional specific definitions associated with this test. See the laboratory QA manual and Standard Methods 2320B for general definitions.

4.0 INTERFERENCES

4.1 Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause sluggish response. Allow additional time between titrant additions or clean the electrode occasionally.

4.2 Temperature has an effect on the pH readings. Be sure the samples are allowed to come up to room temperature prior to analysis.

4.3 **Do not filter** (except for dissolved Alkalinity)**, dilute, concentrate or alter sample**.

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Personal Protective Equipment Required: Safety Glasses, Labcoat, Nitrile Gloves

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

TABLE 1: PRIMARY MATERIAL HAZARDS

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 EQUIPMENT AND SUPPLIES

6.1 Instrumentation

6.1.1 pH meter
6.1.2 ManTech auto-titrator

6.2 Supplies

6.2.1 Magnetic stirrer with Teflon stir bars
6.2.2 10 mL and 25 mL Pyrex microburets, Class A
6.2.3 5 mL graduated pipette
6.2.4 50 mL and 100 mL Beakers
6.2.5 25 mL and 50 mL graduated cylinders, class A
6.2.6 Ultra-Pure PTFE boiling stones

7.0 REAGENTS AND STANDARDS

7.1 Reagents

All purchased and prepared reagents must be made from a traceable (NIST) source material, if available, and documentation of this traceability must be maintained by the laboratory

7.1.1 0.02 N HCl, Fisher Scientific or equivalent
7.1.2 0.1 N HCl, Fisher Scientific or equivalent
7.1.3 1.0 N HCl, Fisher Scientific or equivalent
7.1.4 Reagent Grade Water (RGW) (Ultrapure water)

7.1.5 1:10 dilution of household bleach

7.2 Standards

All purchased standards must be accompanied by a Certificate of Analysis (C of A) which is kept available at the laboratory in order to demonstrate traceability of the standard to certified (NIST-traceable, if available) source material. All prepared standards must be made from a traceable (NIST) source material, if available, and documentation of this traceability must be maintained by the laboratory.

7.2.1 Alkalinity Reference Standard (used as LCS), Ultra Scientific or equivalent. Alternatively, prepare from solid sodium carbonate, ACS grade or equivalent. For a 100 mg/L Total Alkalinity as $CaCO_3$, dissolve 0.530 g of Na_2CO_3 (dried for 4 hours at 250°C) in 1L of laboratory reagent water. Store at room temperature with a shelf life of 2 months. Standardize before use.

7.2.2 Buffer solutions, pH 4, pH 7, pH 10 (primary source)

7.2.3 Buffer solution, pH 7 (secondary source)

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

TABLE 2: HOLDING TIME AND PRESERVATION

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	Glass or plastic container	250 mL	Cool >0 to 6°C	14 Days	40 CFR Part 136.3
Solids	Brass sleeve or jars	10g	Cool >0 to 6°C	14 Days	N/A

9.0 QUALITY CONTROL

9.1 Sample QC

The following quality control samples are prepared with each batch of samples. Each of these QC samples may be re-analyzed once if it doesn't pass, prior to sample analysis, in order to verify the failure wasn't due to a physical or mechanical problem. Otherwise, perform corrective action and repeat the analysis

9.1.1 Method Blank (MB)

Analyze a method blank (MB) for each matrix and with every batch of 20 samples, or less to ensure that water is not contributing to the alkalinity result. If the method blank shows contamination (>RL), re-prepare all samples in the batch unless:

- The samples are ND (flag the result accordingly and write an NCM).
- The sample result is > 10x the blank level (flag the result accordingly and write an NCM).

9.1.2 Laboratory Control Sample (LCS).

Analyze the laboratory control sample (LCS) for every batch of 20 samples or less. Because this is a reference standard and is available only in an aqueous matrix, it is reported in mg/L regardless of the associated sample matrices. If the LCS is outside of vendor-specified limits, re-prepare the entire batch and/or re-calibrate the system unless:

- The LCS recovery is above the upper limit and samples are ND. Flag sample results accordingly and initiate an NCM.

9.1.3 Sample Duplicate

Analyze a sample duplicate with every batch of 20 or fewer samples. The sample duplicate is randomly selected, unless specifically requested by a client. The RPD must be ≤ 20% or the analysis must be repeated one more time. If it still is > 20% flag the source sample and initiate an NCM.

9.2 Instrument QC

The following instrument QC samples are run with each analytical sequence. Each of these QC samples may be re-analyzed once if it does not pass, in order to verify the failure wasn't due to a physical or mechanical problem. Re-analysis must be performed before the analysis of any associated batch QC or client samples.

9.2.1 Initial Calibration

For both the manual and automated titration procedure, the pH meter is calibrated with three pH buffers.

- The calibration slope, if available, must meet manufacturer's specifications.
- Intercept and linearity coefficient meet manufacturer's specifications (if applicable).
- If the calibration does not meet acceptance criteria, use fresh buffer aliquots to recalibrate. If criteria are still not met, instrument maintenance must be performed.
-

TABLE 3: CALIBRATION ACCEPTANCE CRITERA

Procedure	ICAL Buffers	Slope	Intercept	Linearity Coeff.
Manual	pH 4, pH 7, pH 10	90 to 105%	N/A	N/A
ManTech		-63 to -53 mV	±100 mV	r≥0.995

9.2.2 Initial Calibration Verification (ICV)

Verify the Calibration daily with the pH 7 buffer solution, which is from a secondary source. The pH must agree within ± 0.05 pH units or the calibration must be repeated. If the result of the buffer is outside of 0.05 pH units, the calibration curve must be re-analyzed before the sample can be analyzed.

9.2.3 Continuing Calibration Verification (CCV)

Analyze a pH 7.0 buffer after every 10 readings. The buffer must read within ± 0.1 pH units or the instrument must be recalibrated and any affected samples reanalyzed.

10.0 PROCEDURE

10.1 Alkalinity reference Standardization

- If a laboratory-prepared reference standard is used, it must be titrated prior to use.
- Using a graduated cylinder, measure 25 mL of the sample into a graduated cylinder.

- Add the 0.02 N HCl standard acid, dropwise. Stir thoroughly but gently to allow the probe/meter to equilibrate.
- Titrate to pH 4.5 endpoint. Record the volume of the titrant used in LIMS or logbook
- Repeat this titration with a second 25 mL volume of standard.
- Replicate titration volumes must agree to within ±0.1 mL.
- Calculate the standard concentration using the Total Alkalinity equation listed below under "Calculations/Data Reduction." Use the average of the two titration volumes in the calculation. Document this final concentration as the assigned standard concentration in LIMS or logbook.

10.2 Sample Preparation

Samples must not be diluted (waters or solids). If a sample indicates high alkalinity (>2000 mg/L waters or 50,000 mg/Kg), use the appropriate normality titrant.

10.2.1 Water Alkalinity

- Mix the sample well. Using a graduated cylinder, measure 25 mL of the sample into a graduated cylinder.
- For manual titration, transfer into a beaker and add a stir bar.
- For automated titration, transfer into an autosampler tube.

10.2.2 Dissolved Alkalinity

Filter sample with 0.45µm filter before analysis.

10.2.3 Solid Alkalinity

- Weigh 1 g sample to the nearest 0.01 g into a beaker and record the exact weight.
- Add 25 mL of laboratory reagent water and a stir bar.
- NOTE 1: Solid samples CANNOT be analyzed on the ManTech auto-titrator
- NOTE 2: All waste generated during the weighing process must be disposed of in a separate container from other soil sample waste. (This includes, spatulas, Kimwipes, gloves, etc). When finished weighing samples, wipe balance and surrounding area with a paper towel, and dispose of the paper towel in the foreign soil waste container. Wipe surrounding area with a 10% household bleach solution to disinfect the surrounding areas and dispose of wipes in the foreign soil waste container. When the container is full, notify sample archive technicians.

10.3 Batch QC Preparation

10.3.1 Method Blank

- Water Alkalinity: consists of 25 mL of laboratory reagent water
- Dissolved Alkalinity: consists of 25 mL of laboratory reagent water filtered in the same manner as samples.
- Solid Alkalinity: consists of 1 g of PTFE boiling stones in 25 mL of laboratory reagent water.

10.3.2 LCS

Water Alkalinity: consists of 25 mL of alkalinity reference standard.
Dissolved Alkalinity: consists of 25 mL of alkalinity reference standard filtered in the same manner as samples.
Solid Alkalinity: consists of 1 g of PTFE boiling stones in 25 mL of alkalinity reference standard.

10.3.3 Sample Duplicate

All matrices: consists of a second aliquot of one sample in the batch prepared in the same manner as the original aliquot.

10.4 Manual Sample Analysis

10.4.1 Total Alkalinity

- Turn on stir plate.
- Measure and record the initial pH of the sample in the logbook or TALS batch notes.

  NOTE: if the initial pH is 4.50 or less, the alkalinity result will be reported as ND.
- Add the 0.02 N HCl standard acid, dropwise. Stir thoroughly but gently to allow the probe/meter to equilibrate.
- Due to buffering nature of most soil/solid samples, equilibration takes considerably longer than for waters.
- Titrate to pH 4.5 endpoint. Record the volume of the titrant used in LIMS or logbook.
- Calculate the total alkalinity.
- If the total alkalinity is less than 20 mg/L or 500 mg/Kg (i.e. titrated with < 0.5mL HCl), then the sample must be re-analyzed with the "low alkalinity" procedure described below.
- If the total alkalinity greater than 2000 mg/L or 50,000 mg/Kg (i.e. titrated with >50mL HCl), then the sample must be re-analyzed with the "high alkalinity" procedure described below.

10.4.2 High Alkalinity (≥ 2000 mg/L)

- If the alkalinity of the sample is greater than 2000 mg/l (50, 000 mg/Kg), the sample must be re-analyzed using either 0.1N or 1.0 N HCl solution as the titrant.

10.4.3 Low Alkalinity (< 20 mg/L)

- If the alkalinity of the sample is less than 20 mg/L (500 mg/Kg), then use a larger sample volume, 100 mL to 200 mL (2 g for solids). Titrate the sample using a 10 mL microburet and 0.02 N acid solution. Stop titration at pH in range of 4.3 to 4.7 and record the titrant volume and, if other than 4.5, the exact pH. Record the pH, in parentheses, next to the volume.
- Carefully titrate to lower the pH by exactly 0.3 pH units. Record the titrant volume and, if other than 4.2, the exact pH. Record the pH, in parentheses, next to the volume.

10.4.4 Component Base Alkalinity

- For determination of Alkalinity relationships [Carbonate (CO3), Bicarbonate (HCO3), Hydroxide (OH)]
- Follow the procedure outlined above except titrate to an 8.3 endpoint (P alkalinity) as well as the 4.5 endpoint (T alkalinity) Record the volumes at each endpoint.

10.5 Automated Sample Analysis (Mantech)

- Load QC and the samples on the auto-sampler tray in the following order:

TABLE 4: TYPICAL ANALYSIS SEQUENCE

#	Sample Description
1	ICV (pH7 check, second source)
2	LCS
3	MB
4	Sample
5	Sample Duplicate
6	8 samples
7	CCV (pH7 check)
8	10 samples
9	CCV (pH7 check)

- Start the analysis. Titrate the samples with 0.02N titrant.
- For all details on the Mantech operation, refer to PC Titration Plus System Operator's Manual.

10.6 Instrument Initialization

10.6.1 Fill the buret with titrant.
10.6.2 Calibrate the pH meter.

10.7 Calibration

10.7.1 Manual Titration Procedure: Using the calibration mode, calibrate the pH meter with pH 4, and pH 10 buffer solutions. Document these readings in the pH Calibration Logbook.

10.7.2 ManTech Titration System: Calibrate the pH meter for the instrument using pH 4, pH 7 and pH10.

10.7.3 Manual and ManTech Procedures: Verify the calibration with pH7 buffer from a second source. The buffer solution must read within ± 0.05 pH unit of the actual value. For the manual titration procedure, record the pH in the pH Calibration Logbook.

10.8 Preventative Maintenance

10.8.1 Record all performed maintenance in the instrument maintenance logbook.
10.8.2 If an instrument is unusable or has limitation to its use, it must be tagged accordingly until such a time the problem has been corrected. Record the problem, solution and verification of proper operation into the instrument maintenance logbook.
10.8.3 Mantech Titration System Maintenance.

TABLE 5: MANTECH MAINTENANCE SCHEDULE

Frequency	Tasks
Daily	Check electrode filling solution Check hardware (all components turned on; buret tip placed correctly) Check chemicals (reagent and waste container levels)
Weekly	Check electrode (drain and refill)

Frequency	Tasks
	Check hardware
Monthly	Clean the buret valve Clean the stirrer Clean the dosing pump Check the pump flow rates
Annually	Change seals and washers Replace tubing and fittings on the pumps Replace tubing and fittings on the burets
As Needed	Replace electrodes Replace the stirrer

For all details on Mantech Titration System Maintenance, refer to the maintenance manual.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Accuracy

$$\text{LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

11.2 Precision (RPD)

$$\text{Duplicate (MD)} = \frac{|\text{orig. sample value} - \text{dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

11.3 Concentration

The potentiometric titration to pH 4.5 results in the total alkalinity as follows:

Total Alkalinity (Water):

$$\text{mg/L } CaCO_3 = \frac{V \times N \times 50{,}000}{\text{sample volume (mL)}}$$

where: V = Volume of titrant in milliliters
N = Normality of titrant (0.02N or 0.1N)

Total Alkalinity (Solid):

$$\text{mg/Kg } CaCO_3 = \frac{V \times N \times 50{,}000}{\text{leachate vol titrated (mL)}} \div \frac{\text{sample Wt (g)}}{\text{leachate vol (mL)}}$$

where: V = Volume of titrant in milliliters
N = Normality of titrant (0.02N or 0.1N)

Low Alkalinity (Water):

$$mg/L\ CaCO_3 = \frac{(2V_I - V_F) \times N \times 50{,}000}{\text{sample volume (mL)}}$$

where: V_I = Volume of titrant to Initial pH 4.5 in milliliters
V_F = Volume of titrant to Final pH 4.2 in milliliters
N = Normality of titrant (0.02N)

Low Alkalinity (Solid):

$$mg/L\ CaCO_3 = \frac{(2V_I - V_F) \times N \times 50{,}000}{\text{leachate vol titrated (mL)}} \div \frac{\text{sample Wt (g)}}{\text{leachate vol (mL)}}$$

where: V_I = Volume of titrant to Initial pH 4.5 in milliliters
V_F = Volume of titrant to Final pH 4.2 in milliliters
N = Normality of titrant (0.02N)

Alkalinity Relationships

Calculate P alkalinity using the Total alkalinity equation above except the Volume is the volume of titrant used to the 8.3 pH endpoint. Compare the P alkalinity result with the T alkalinity result. Use the following table to calculate the alkalinity relationships:

TABLE 6: ALKALINITY RELATIONSHIP CALCULATIONS

Result of the Titration	Bicarbonate Alkalinity Concentration as $CaCO_3$	Carbonate Alkalinity Concentration as $CaCO_3$	Hydroxide Alkalinity Concentration as $CaCO_3$
P = 0	T	0	0
P < 1/2 T	T - 2P	2P	0
P = 1/2 T	0	2P	0
P > 1/2 T	0	2(T-P)	2P - T
P = T	0	0	T

Reporting Components as Specific Ions (e.g. Carbonate as Carbonate)

Standard Methods 2320B is written to report Total Alkalinity and three principal forms of alkalinity (carbonate, bicarbonate, and hydroxide) as calcium carbonate. In order to report the component as the specific anion (e.g. “carbonate as carbonate”) it is necessary to convert the various calcium carbonate results. This is done by multiplying the required calcium carbonate component result by the ratio of the equivalent weight of the component to be reported to the equivalent weight of calcium carbonate:

TABLE 7: ALKALINITY COMPONENT EQUIVALENT WEIGHTS

Component to be Reported	Component Equivalent Weight	Calcium Carbonate Equivalent weight	Equivalent Weight Ratio
Carbonate as Carbonate (CO_3)	30	50	0.6
Bicarbonate as Bicarbonate	61	50	1.22

Component to be Reported	Component Equivalent Weight	Calcium Carbonate Equivalent weight	Equivalent Weight Ratio
(HCO_3)			
Hydroxide as Hydroxide (OH)	17	50	0.34

12.0 METHOD PERFORMANCE

12.1 Method Detection Limit Study (MDL)

For this titrimetric method, an MDL is not applicable as the lowest discernable unit of measure that can be observed (0.1 mL in a 25 ml sample) is defined as the reporting limit (RL) or 4 mg/L.

12.2 Demonstration of Capabilities

Every analyst must perform an Initial Demonstration of Capability (IDOC) before performing analyses on any client samples. An IDOC consists of 4 consecutive LCS samples with an average recovery and RSD within laboratory acceptance limits. An on-going DOC (ODOC) must be performed annually. An ODOC can be 4 consecutive LCSs or a passing PT.

12.3 Training Requirements

The analyst must have documented training, including reading of the SOP and source methods, conducted by the department manager, senior chemist, or other analyst with training documentation and a passing DOC.

13.0 POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in the "Waste Management and Pollution Prevention" section of the Corporate Environmental Health and Safety Manual (CW-E-M-001).

14.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the laboratory's Waste Disposal SOP (IR-EHS-WASTE). The following waste streams are produced when this method is carried out:

Non-Hazardous Waste

Non-Hazardous waste is disposed of by pouring the samples water that have been extracted into the sink, measuring the pH and neutralizing the water using soda ash, and then draining the neutralized contents into the sewer system. Wetchem analysts/technicians are responsible for neutralizing this waste in the glassware washing room.

Solid waste

Solid waste is generated by analyst/technicians after samples have been prepared and analyzed in the WetChem area. This waste is stored in 55-gallon closed head metal drum in the WetChem area. Sample archive technicians label the drum with a preprinted label of Non-RCRA Hazardous waste solid. The drum is removed from the WetChem area to the main waste storage area by sample archive technicians. Analyst/technicians let the sample archive technicians know when

they need to removed this drum. All foreign soil waste must be collected separately from soil waste.

Unused standards or reagents. If the standard or reagent is hazardous and can not be collected with one of the waste streams generated in the method, then the analysts and technicians will take this standard or reagent and place it on the shelves labeled "hazardous waste" in the main waste storage area. The waste material must be labeled with the words "Hazardous Waste", contents and the date taken to the waste storage area. The waste material will be lab packed (example: mercury standard).

If the waste material can be collected in the satellite waste container for one of the waste streams of the method, then pour the standard in the right satellite container, rinse the original container, and collect the rinsate in the satellite container. The original container can be placed in the regular trash. (Example, buffer solutions pH 4).

15.0 REFERENCES / CROSS-REFERENCES

15.1 Standard Methods for the Analysis of Water and Wastewater, SM2320B (1997).

15.2 TestAmerica Irvine high concentration alkalinity study, 11/19/2013.

16.0 METHOD MODIFICATIONS

TABLE 8: METHOD MODIFICATIONS

Item	Reference	Modification
1	*2320A sec 1*	*This method has been modified to include the analysis of solids.*
2	*2310 sec 1e*	*The threshold for changing from 0.02N to 0.1N titrant has been increased from 1000mg/L to 2000mg/L. The laboratory has data on file for both manual titration and the ManTech that demonstrates accurate results up to this increased level.*
3	*2310 sec 1e*	*For extremely high alkalinity samples, the use of 1.0N titrant has been added to the method. This serves to reduce the possibility of large titrant volumes that might cause difficulty measuring the endpoint.*

17.0 ATTACHMENTS

17.1 **Attachment 1:** Analysis Information

17.2 **Attachment 2:** Alkalinity Benchsheet

17.3 **Attachment 3:** pH Calibration Log

17.4 **Attachment 4:** Data Review Checklist

18.0 REVISION HISTORY

This section has been added beginning with Revision 0. Only details of the last two revisions are incorporated into this SOP. Prior revisions are documented in the QA files.

18.1 Revision 5, dated 19 September 2013

- This revision supersedes IR-WET-ALK, revision 4 (07/02/2013)
- Added the ManTech Titration System: Calibration, Analysis and Maintenance
- Added slope criteria

- Revised Demonstration of Capabilities section
- Added and updated pH calibration logbook page
- Manual titration now requires a 3 buffer pH calibration
- Added requirement of a LCS and MB prepared for solids using PTFE chips
- If a sample indicates high alkalinity, use 0.1N HCl or 0.1N H_2SO_4 as the titrant, do not add water.
- Revised by YZ, XL, LH and DD

18.2 Revision 6, dated 03 October 2014

- This revision supersedes IR-WET-ALK, revision 5 (09/19/2013) and IR-WET-ALK_r5-CF1 (10/14/2013)
- Removed MDL requirement
- Increased 0.02N titrant limit from 1000mg/L to 2000mg/L
- Changed soil preparation procedure from 2 grams to 1 gram of sample
- Added allowance for use of 1.0N titrant on high concentration samples
- Added foreign soil procedures
- Revised by DD and YZ

Attachment 1
Analysis Information

TestAmerica Irvine

Analytical Method Information

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
Alkalinity-All forms (as CaCO3) in Water (SM2320B)								
Preservation: 4 C, Cool								
Container: 1 Liter Poly		**Amount Required:** 100 ml				**Hold Time:** 14 days		
Alkalinity as CaCO3	N/A	4.0 mg/l		20				
Bicarbonate Alkalinity as CaCO3	N/A	4.0 mg/l		20				
Carbonate Alkalinity as CaCO3	N/A	4.0 mg/l		20				
Hydroxide Alkalinity as CaCO3	N/A	4.0 mg/l		20				
Alkalinity-All forms (as CaCO3) in Soil (SM2320B Mod.)								
Preservation: 4 C, Cool								
Container: 4 oz Jar/BrassSleeve		**Amount Required:** 10 g				**Hold Time:** 14 days		
Alkalinity as CaCO3	N/A	500 mg/kg		20				
Bicarbonate Alkalinity as CaCO3	N/A	500 mg/kg		20				
Carbonate Alkalinity as CaCO3	N/A	500 mg/kg		20				
Hydroxide Alkalinity as CaCO3	N/A	500 mg/kg		20				

TestAmerica Irvine

Analytical Method Information

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
Alkalinity-All forms in Water (SM2320B)								
Preservation: 4 C, Cool								
Container: 1 Liter Poly		**Amount Required:** 100 ml				**Hold Time:** 14 days		
Alkalinity as CaCO3	N/A	4.0 mg/l		20				
Bicarbonate as HCO3	N/A	4.8 mg/l		20				
Carbonate as CO3	N/A	2.4 mg/l		20				
Hydroxide as OH	N/A	1.4 mg/l		20				

Attachment 2
Benchsheet

RL: 4.0 mg/L as CaCO3 (water)
100 mg/Kg as CaCO3 (soil)

Method SM 2320B

Analysis Date: _____
Analyst's Initials: _____
Batch #: _____
Balance ID: _____

^If the preliminary alkalinity result is greater than 20 mg/L but less than 1000 mg/L, then report this result.
^If the preliminary alkalinity result is greater than or equal to 1000 mg/L, then re-analyze with 0.1N HCl.
^If the preliminary alkalinity result is less than 20 mg/L, re-analyze by Low Alkalinity procedure

Sample Number	Sample Size ml or g	Matrix S or W	Initial pH	Preliminary		High Level		Low Level	
				0.02 N HCl Vol* to pH 8.3(P)	0.02 N HCl Vol* to pH 4.5 (T)	0.1 N HCl Vol* to pH 8.3(P)	0.1 N HCl Vol* to pH 4.5 (T)	0.02N HCl Vol* / pH pH (4.3 to 4.7)	0.02N HCl Vol* / pH pH (0.3 lower)
LCS									
BLK									
pH 7 Check									
pH 7 Check									

2320B (Rev. 9)

*All volumes in mL

1

Attachment 3
pH Calibration Logbook

pH METER CALIBRATION LOGBOOK

Instr. ID: _____

Slope criteria: _____

ICV Criteria: _____

ICAL-pH 4 TALS ID/Exp date: _____

ICAL-pH 7 TALS ID/Exp date: _____

ICAL-pH 10 TALS ID/Exp date: _____

ICV-pH 7 TALS ID/Exp date: _____

Date	ICAL pH 4	ICAL pH 7	ICAL pH 10	ICV pH 7	Slope	PASS/FAIL Comments	Initials

pH_meter_cal.xls_r2
Rev. 09/17/13

1 of 100

Attachment 4
Data Review Checklist

ALKALINITY DATA REVIEW CHECKLIST
SM 2320B

Batch ID: _____ Analysis Date: _____ 2nd Level Reviewer: _____

Analyst Initials: _____ Review Date: _____

Item to Review	Analyst	2nd Level	Notes/Specific Criteria
Calibration			
pH meter calibrated with 3 buffer solutions: pH 4, pH 7, and pH 10			
Verify the calibration with a second source pH 7 buffer solution. pH must be within ± 0.05 pH units			
Analyze a pH 7.0 buffer after every 10 readings. pH must be within ± 0.1 pH units			
Sample Preparation Batch:			
Water samples are un-preserved			
All samples prepared and analyzed within holding time of 14 days			
Batch contains no greater than 20 samples			
Method Blank reads < RL			
Solid matrix MB and LCS prepared in the same manner as solid samples			
LCS recovery within vendor-specified limits			
Sample Dup RPD ≤20%			
If the alkalinity of the sample is greater than 2000 mg/l (50,000 mg/Kg), the sample must be re-analyzed using 0.1N HCl or 0.1N H_2SO_4 as the titrant.			
If the alkalinity of the sample is less than 20 mg/L (500 mg/Kg), then use a larger sample volume, 100 mL to 200 mL (2 g for solids) and follow Low Alkalinity procedure			
Data Documentation:			
All standards used are uniquely identified and are not expired			
All errors are crossed out with a single line, initialed and dated			
The analyst's signature/initials are on the logsheet page			
All flags correctly applied and NCM written, as required			
Analysis time accurately entered into LIMS			

Alkalinity_2320B_Check_r4
03/2014

Title: HARDNESS BY TITRATION
SM 2340C

Approvals (Signature/Date):

Tung Nguyen 4/1/15
Department Manager — Date

William Nash 04/01/2015
Environmental Health & Safety Coordinator — Date

Marie Friedman 4-1-2015
Quality Assurance Manager — Date

Ben Beachaine 4/1/2015
Interim Laboratory Director — Date

Facility Distribution No. _____ **Distributed To: _____**

1.0 SCOPE AND APPLICATION

Method SM 2340C is used to determine hardness by EDTA titration in drinking, surface and saline water, domestic and industrial wastes. On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in "Validation of Methods" in the Quality Assurance Manual.

1.1 Analytes, Matrix(s), and Reporting Limits

These methods can be used to determine hardness in drinking, surface and saline water, domestic and industrial wastes. Hardness in solids can be determined following a deionized water leaching procedure. See Attachment 1 for reporting limits.

2.0 SUMMARY OF METHOD

Calcium and magnesium ions in the sample are sequestered upon the addition of Ethylene-diamine-tetraacetic acid (EDTA) by forming a chelated soluble complex. The end point of the reaction is detected by means of Erichrome Black T indicator, which has a red color in the presence of calcium and magnesium at a pH of 10.0 ±0.01 and a blue color when the cations are sequestered.

3.0 DEFINITIONS

3.1 Total hardness is defined as the sum of calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrams per liter.

3.2 There are no additional specific definitions associated with this test. See the QAPM and SM2340C for general definitions.

4.0 INTERFERENCES

Some metal ions interfere by causing indistinct endpoints. MgEDTA reduces this interference.

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Personal Protective Equipment Required: Safety Glasses, Labcoat, Nitrile Gloves

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Ammonium Hydroxide	Corrosive Poison	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Ammonium chloride	Irritant	None listed	Causes irritation to the respiratory tract, skin and eyes. Symptoms may include coughing, shortness of breath. Symptoms include redness, itching, and pain.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 EQUIPMENT AND SUPPLIES

6.1 Supplies

6.1.1 10 mL buret, class A
6.1.2 100 mL glass beakers
6.1.3 50 mL graduated cylinders
6.1.4 Stirbars
6.1.5 Magnetic stirrer
6.1.6 pH strips
6.1.7 5mL pipets

7.0 REAGENTS AND STANDARDS

7.1 Standard

All purchased standards must be accompanied by a Certificate of Analysis (C of A) which is kept available at the laboratory in order to demonstrate traceability of the standard to certified (NIST-traceable, if available) source material.

7.1.1 Hardness WasteWatR standard from ERA (or equivalent), used to prepare LCS

7.2 Reagents

All purchased and prepared reagents must be made from a traceable (NIST) source material, if available, and documentation of this traceabililty must be maintained by the laboratory

7.2.1 Reagent grade water
7.2.2 Buffer solution with MgEDTA, purchased, certified APHA Standard.
7.2.3 Eriochrome Black T
7.2.4 EDTA Titrant 0.01M, purchased, certified traceable to NIST SRM 915
7.2.5 NaCl, reagent grade
7.2.6 Ammonium hydroxide
7.2.7 Ammonium chloride
7.2.8 1:10 dilution of household bleach

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding time and the reference that includes preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	Polyethylene bottle	100 ml	HNO_3, pH < 2;	Six months	40CFR 136
Solids	Glass jar	50 g	0-6°C	Six months	N/A

Notify the Project Manager if the hold time has been exceeded.

9.0 QUALITY CONTROL

9.1 Sample QC

The following quality control samples are prepared with each batch of samples. Each of these QC samples may be re-analyzed once if it doesn't pass, prior to sample analysis, in order to verify the failure wasn't due to a physical or mechanical problem.

9.1.1 Method Blank (MB)

Prepare and analyze a method blank (MB) for each matrix and with every batch of 20 samples, or less. Check that there are no analytes detected at or above the reporting limit. If the method blank shows contamination, re-prepare all samples in the batch unless:

- The samples are ND (flag the result accordingly).
- The sample result is > 10x the blank level (flag the result accordingly).

9.1.2 Laboratory Control Sample (LCS).

Prepare and analyze a primary source laboratory control sample (LCS) for every batch of 20 samples or less. The LCS recovery must be within the vendor's specified limits (or ±10% of vendor's certified value if limits are not provided). If the LCS is outside of these limits, re-prepare the whole batch unless:

- The LCS recovery is above the upper limit and samples are ND. Flag sample results accordingly and write an NCM.

9.1.3 Sample Duplicate

- Analyze a sample duplicate with every batch of twenty samples or less. The RPD between the sample and the duplicate must be within ±20 %.
- For drinking water, analyze a sample duplicate with every batch of ten samples or less.

9.1.4 Batch QC for Solid Samples

Prepare a solid matrix MB and LCS in the same manner as solid samples but using Teflon chips or glass beads.

10.0 PROCEDURE

10.1 Reagent and Standard Preparation

10.1.1 Eriochrome Black T Indicator

Weight 0.5g Eriochrome Black T and 100g NaCl. Mix well in a beaker. Store in a tightly stopper plastic bottle.

10.1.2 Buffer Solution (if not purchased)

Dissolve 16.9g NH_4Cl in 143 mL concentrated NH_4OH in a 250mL volumetric flask. Add 1.25g of MgEDTA and bring up to volume with Reagent grade water. Store in a tightly stopper plastic bottle. Shelf life is one month. Discard when 1 or 2 mL added to sample fails to produce a pH of 10.0± 0.1 at end point of titration.

10.1.3 Laboratory Control Sample-LCS

Prepare the LCS by adding to 25 mL Hardness WasteWatR standard from ERA (or equivalent) QC Standard to 25 mL Reagent grade water.

10.2 Preparation of Water Samples

- The sample must be preserved with HNO_3 to a pH<2
- The sample must be at room temperature before analysis. Mix the sample well.
- Measure 25mL of sample with a graduated cylinder. Transfer to a glass beaker. Add 25mL Reagent grade water to the beaker.

10.3 Preparation of Solid Samples

- Weigh 4 ± 0.1 grams of the well mixed sample into a disposable 50 mL centrifuge tube.
- Add 40mL Laboratory Reagent Grade water using a Class A graduated cylinder. All initial and final amounts must be documented.
- Shake samples by hand to ensure water and soil are mixed and then place on an orbital shaker for minimum of 10 minutes. If necessary, centrifuge for 3 – 5 min or until separation of the phases occurs.
- Filter the resultant supernatant water through a 0.2um filter.
- NOTE: For foreign soil, all waste generated during the weighing process must be disposed of in a separate container from other soil sample waste. (This includes, spatulas, Kimwipes, gloves, etc). When finished weighing samples, wipe balance and surrounding area with a paper towel, and dispose of the paper towel in the foreign soil waste container. Wipe surrounding area with a 10% household bleach solution to disinfect the surrounding areas and dispose of wipes in the foreign soil waste container.

10.4 Sample Analysis

- Add a stir bar. Turn on the stir plate and mix well.
- Add 1-2mL buffer solution. Measure pH to ensure it is at 10.0 ±0.1
- Add 1 small scoop of indicator
- Titrate sample slowly with standard EDTA titrant with continuous stirring. At the endpoint the solution is blue.

- NOTE: The titration must be completed within 5 min of buffer addition.
- Record the volume of EDTA titrant used in the logbook.
- If the EDTA used for titration is more than 10mL, use a smaller aliquot of sample and re-analyze the sample. Record the volume of EDTA titrant used in the logbook.
- For waters of low hardness (less than 5 mg/L), take a larger aliquot of sample (50-100 mL), add proportionally larger amount of buffer, inhibitor and indicator and re-analyze the sample. Record the volume of EDTA titrant used in the logbook.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Accuracy

$$\text{LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

11.2 Precision (RPD)

$$\text{Sample Duplicate RPD} = \frac{|\text{orig. sample value} - \text{dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

11.3 Concentration

$$\text{Hardness (EDTA) as mg } CaCO_3/L = \frac{A \times N \times 50000}{\text{mL sample}}$$

where A= mL of EDTA titrant
N= Normality of EDTA titrant

Hardness result may be calculated using the Excel spreadsheet and attach the sheet to the logbook.

11.4 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure as described in laboratory's SOP, IR-QA-MDL. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. For this titrimetric method, an MDL is not applicable as the lowest discernable unit of measure that can be observed (0.1 mL in a 25 ml sample) is defined as the reporting limit (RL) or 4 mg/L.

11.5 Demonstration of Capabilities

Every analyst must perform an Initial Demonstration of Capability (IDOC) before performing analyses on any client samples. An IDOC consists of 4 consecutive LCS samples with an average recovery and RSD within laboratory acceptance limits. An on-going Demonstration of

Capability must be documented annually and consists of 4 consecutive passing LCS samples or a passing PT.

11.6 Training Requirements

The analyst must have documented training, including reading of the SOP and source methods, conducted by the department manager, senior chemist, or other analyst with training documentation and a passing DOC.

12.0 POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in the "Waste Management and Pollution Prevention" section of the Environmental Health and Safety Manual (CW-E-M-001).

13.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the laboratory's Waste Disposal SOP (IR-EHS-WASTE). The following waste streams are produced when this method is carried out:

Titrated sample waste. This is generated during the analysis of the sample. The waste is collected in a 5 gallon satellite container. The waste is bulked as base waste.

Sample waste. Non-Hazardous waste is disposed of by pouring the samples water that have been titrated into the sink, measuring the pH and neutralizing the water using soda ash, and then draining the neutralized contents into the sewer system. The soil generated in these tests is collected in the 55-gallon closed head metal drum in the wetchem area. Sample archive technicians label the drum with a preprinted label of Non-RCRA Hazardous waste solid. All foreign soil waste must be collected separately from soil waste.

Unused standards or reagents. If the standard or reagent is hazardous and can not be collected with one of the waste streams generated in the method, then the analysts and technicians will take this standard or reagent and place it on the shelves labeled "hazardous waste" in the main waste storage area. The waste material must be labeled with the words "Hazardous Waste", contents and the date taken to the waste storage area. The waste material will be lab packed (example: mercury standard).

If the waste material can be collected in the satellite waste container for one of the waste streams of the method, then pour the standard in the right satellite container, rinse the original container, and collect the rinsate in the satellite container. The original container can be placed in the regular trash. (Example, buffer solutions pH 4).

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14.0 REFERENCES / CROSS-REFERENCES

14.1 SM2340C (1997), "Hardness: EDTA Titration Method", Standard Methods for the Analysis

of Water and Wastewater.

15.0 METHOD MODIFICATIONS

Item	Method 2340C	Modification
1.	*2340C – Sec 2.a.2*	*The Laboratory uses purchased Certified APHA Buffer solution with specified Expiration Date. Solution will be discarded when 1 or 2 mL added to sample fails to produce a pH of 10.0± 0.1 at end point of titration.*
2.	*2340C – Sec 2.d*	*The Laboratory uses purchased Certified traceable to NIST EDTA Titrant solution with specified Expiration Date.*

16.0 ATTACHMENTS

16.1 **Attachment 1:** Analysis Information
16.2 **Attachment 2:** Logbook
16.3 **Attachment 3:** Data Review Checklist

17.0 REVISION HISTORY

This section has been added beginning with Revision 0. Only details of the last two revisions are incorporated into this SOP. Prior revisions are documented in the QA files.

17.1 Revision 5, dated 07 March 2014

- This revision supersedes IR-WET-HARD, revision 4 (02/28/2013)
- Clarified that there is no MDL for this method
- Removed logbook; data entered directly into LIMS
- Revised data review checklist
- Revised by DD

17.2 Revision 6, dated 01 April 2015

- This revision supersedes IR-WET-HARD, revision 5 (03/07/2014)
- Corrected acid reference in data review checklist
- Added details on solid prep and foreign soil
- Revised method reference
- Revised by DD

Attachment 1
Analysis Information

TestAmerica Irvine

Analytical Method Information

Analyte	Reporting Limit	Duplicate RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
Hardness in Water by Titration (SM2340C)				
Preservation: HNO3				
Container: 500 mL Poly	**Amount Required:** 100 ml		**Hold Time:** 180 days	
Hardness (as CaCO3)	4.0 mg/l	20	90 - 110	

TestAmerica Irvine

Analytical Method Information

Analyte	Reporting Limit	Duplicate RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
Hardness in Solid by Titration (SM2340C)				
Preservation: None				
Container: 4 oz jar	**Amount Required:** 10 grams		**Hold Time:** 180 days	
Hardness (as CaCO3)	40.0 mg/l	20	90 - 110	

Attachment 2
Data Review Checklist

Title: Electrometric pH
EPA Method 150.1 /9040B /9040C /9041A /9045C /SM4500-H+B

Approvals (Signature/Date):

Priyuni Patel 11/17/14
Priyuni Patel Date
Department Manager

William Nash 11/17/2014
William Nash Date
Environmental Health & Safety Coordinator

Maria Friedman 11-21-2014
Maria Friedman Date
Quality Assurance Manager

Kirk Miltimore 11/18/14
Kirk Miltimore Date
Laboratory Director

Facility Distribution No. _____ **Distributed To: _____**

1.0 SCOPE AND APPLICATION

1.1 EPA Methods 150.1 and Standard Method 4500-H+B are used to determine the pH of drinking water, surface water, saline water, domestic and industrial waste.

1.2 NOTE: Although, effective 04/11/07, the EPA Method Update Rule (MUR) deleted 150.1 from the Federal Register, as of September 2010, State of California still certifies Method 150.1 under the SDWA.

1.3 EPA Method 9040B / 9040C is used to measure the pH of aqueous wastes and those multiphase wastes where the aqueous phase constitutes at least 20% of the total volume of the waste.

1.4 EPA Method 9041A may be used to measure pH as an alternative to Method 9040 or in cases where pH measurements by Method 9040 are not possible. Method 9041 is not applicable to wastes that contain components that may mask or alter the pH paper color change. It also cannot be used to define a waste as corrosive or non-corrosive because pH paper is not considered to be as accurate a form of pH measurement as a pH meter.

1.5 EPA 9045C is used to measure the pH of soils and waste samples. Wastes may be solids, sludges or non-aqueous liquids. If water is present, it must constitute less than 20% of the total volume of the sample.

1.6 For samples with pH values less than 1 or greater than 13, bracketing standards at the extremes are not feasible.

1.7 pH is generally reported to the nearest 0.1 unit but can be reported to two decimal places per client request.

2.0 SUMMARY OF METHOD

2.1 The pH of a water or aqueous sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. The measurement device is calibrated using a series of standard solutions of known pH.

2.2 The soil or waste sample is mixed with reagent water and the resulting aqueous solution is measured.

2.3 For Method 9041A, the pH determination is made using “narrow-range” pH paper.

3.0 DEFINITIONS

There are no additional specific definitions associated with this test. See the laboratory QA manual and EPA methods 150.1, 9040B, 9045C and Standard Methods 4500-H+B for general definitions.

4.0 INTERFERENCES

4.1 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by rinsing with distilled water. An additional treatment with 10% HCl may be necessary to remove any remaining film. See electrode manufacturer information for more detail.

4.2 The electrode output can be influenced by varying temperatures. Be sure the calibration solutions and samples are allowed to warm to room temperature prior to analysis.

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Personal Protective Equipment Required: Safety Glasses, Lab Coat and Nitrile Gloves

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Low pH buffers (pH<4)	Corrosive Irritant	5 ppm-Ceiling	May be hazardous in case of skin contact (irritant). Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.
High pH buffers (pH>10)	Corrosive Irritant	Not established	May be hazardous in case of skin contact (irritant). Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes
Hydrochloric Acid	Corrosive Poison	5 ppm Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions. 2 - Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 EQUIPMENT AND SUPPLIES

6.1 Instrumentation

6.1.1 pH meter with Automatic temperature compensation feature – Mettler Toledo or equivalent

6.1.2 pH combination electrode

6.1.3 Magnetic stirrer

6.1.4 Analytical balance

6.2 Supplies

6.2.1 Teflon coated stirring bars

6.2.2 Plastic beakers

6.2.3 Wooden spatula

6.2.4 pH indicator strips – 1 to 14

7.0 REAGENTS AND STANDARDS

All purchased and prepared reagents and standards must be made from a traceable (NIST) source material, if available, and documentation of this traceability must be maintained by the laboratory

7.1 Reagents

7.1.1 Electrode filling solution (see specific manufacturer's recommendation)

7.1.2 Electrode storage solution (see specific manufacturer's recommendation)

7.1.3 Laboratory Reagent Grade Water (purified laboratory deionized water)

7.1.4 Methanol

7.1.5 Hydrochloric acid

7.1.6 Household bleach 1/10 dilution

7.2 Standards

7.2.1 Primary source buffer solutions at the following pH levels:

- 1.00
- 2.00
- 4.00
- 7.00
- 10.00
- 12.00
- 12.45
- 13.00

7.2.2 Secondary source buffer solutions as needed for each calibration range used.

7.2.3 NOTE: Because buffers are uniquely prepared and identified by vendor lot number, the typical distinction between primary and secondary sources is not relevant. All standards (buffers) are independent sources.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Before analysis, check the label on the sample bottle to make sure that the sample is unpreserved. If preserved with acid, contact the project manager for further instructions.

8.2 Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	Plastic or glass	100 ml	Cool >0 to 6°C	As soon as possible after receipt*	40 CFR Part 136.3
Soils	Glass or boring	50 g	Cool >0 to 6°C	7 Days	EPA 9045C

*pH of water samples is considered a field test with a listed holding time of 15 minutes. Although this is a field test and must be flagged as such, the laboratory must analyze within 48 hours of receipt.

9.0 QUALITY CONTROL

9.1 Sample QC

The following quality control sample is prepared with each batch of samples. This QC sample may be re-analyzed once if it doesn't pass, in order to verify the failure wasn't due to a physical or mechanical problem.

9.1.1 Sample Duplicate.

A sample duplicate must be analyzed with every 10 or fewer samples. The duplicate reading must be within ± 0.1 pH units or a third analysis must be performed. If the third analysis still does not fall within 0.1 pH units, report the results with an NCM.

9.2 Instrument QC

The following instrument QC is required for each analytical sequence. Each of these QC samples may be re-analyzed once if it does not pass, in order to verify the failure wasn't due to a physical or mechanical problem. Re-analysis must be performed before the analysis of any associated batch QC or client samples.

9.2.1 Calibration

- The instrument is calibrated with two buffers
- The high and low buffers must bracket the pH values of any samples reported. The following calibration points are recommended*:

Calibration Buffers	ICV/CCV Buffer
1 and 4	2
2 and 7	4
4 and 10	7
7 and 12	10
10 and 13	12 or 12.45

*The ManTech auto-titrator is calibrated using 4, 7, and 10 buffers, and the calibration is good for 24 hours. It is possible to adjust calibration parameters for high or low ranges.

- The follow calibration criteria must be met:

Procedure	Slope	Intercept	Linearity Coeff.
Manual	Per manuf.	N/A	N/A

ManTech auto-titrator	-63 to -53 mV	±100 mV	r≥0.995

- Initial Calibration Verification (ICV)

  Verify the Calibration daily with the middle buffer solution from a secondary source. The pH must agree within ± 0.1 pH units or the calibration must be repeated. If the result of the buffer is outside of 0.05 pH units, the calibration curve must be re-analyzed before the sample can be analyzed.

- Continuing Calibration Verification (CCV)

  Analyze the middle buffer (primary or secondary) after every 10 readings. The buffer must read within ± 0.1 pH units or the instrument must be recalibrated and any affected samples reanalyzed.

10.0 PROCEDURE

10.1 Manual Electrode Method

10.1.1 Instrument Preparation

Soak the electrode in storage solution for at least two hours before performing the analysis of any sample.

10.1.2 Calibration

Using the calibration mode (refer to manufacturer instructions), calibrate the pH meter at room temperature with the appropriate buffers (typically 4, 7, and 10). Record the pH and the temperature of the buffer solutions. Verify the calibration with the appropriate second-source buffer near the middle of the calibration range. Verify that all calibration criteria are met before proceeding.

10.1.3 Water Sample Analysis

- Allow samples to equilibrate at room temperature. Sample temperature must not differ by more than 2°C from the buffer solutions.

  NOTE: For samples with pH>12, the measurement must be taken at a temperature of 25±1°C.

  Pour a water sample directly into a plastic beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar. Allow the sample to warm to room temperature. Stir the sample while taking the pH. Record the pH and temperature once the reading stabilizes. Be sure to rinse and gently wipe the electrodes between measurements.

- Repeat measurements on sample until values differ by no more than ±0.1 pH units.

10.1.4 Soil Sample Analysis

- Prepare a soil sample by weighing 20 ± 0.2 g of the soil into a 50 mL centrifuge tube. Add 20 mL of Reagent Grade Water to the centrifuge tube using a Class A graduated cylinder. All initial and final amounts must be documented. Shake the sample on an orbital shaker

for approximately 15 minutes or until the sample is well-mixed. Let the sample suspension stand for up to 1 hour until most of the solid has settled, or centrifuge for approximately15 minutes then decant the aqueous phase for the pH measurement.

- Immerse the pH electrode just deep enough into the clear supernatant solution to completely submerge the sensing element without allowing it to contact the settled solid material.
- Record the pH and the temperature once the reading stabilizes. Be sure to rinse and gently wipe the electrodes between measurements.
- Repeat measurements on sample until values differ by no more than ±0.1 pH units.
- For foreign soil, all waste generated during the weighing process must be disposed of in a separate container from other soil sample waste. (This includes, spatulas, Kimwipes, gloves, etc). When finished weighing samples, wipe balance and surrounding area with a paper towel, and dispose of the paper towel in the foreign soil waste container. Wipe surrounding area with a 10% household bleach solution to disinfect the surrounding areas and dispose of wipes in the foreign soil waste container. When the container is full, notify sample archive technicians.

10.1.5 Non-Aqueous Waste / Oil Samples

- Prepare a non-aqueous waste/oil sample by weighing 20 ± 0.2 g of the soil into a 50 mL centrifuge tube. Add 20 mL of Reagent Grade Water to the centrifuge tube using a Class A graduated cylinder. All initial and final amounts must be documented. Shake the sample on an orbital shaker for approximately 15 minutes or until the sample is well-mixed. Transfer the sample to a separatory funnel. Let the waste suspension stand for approximately 15 minutes to allow most of the suspended waste to settle out and/or the oil to collect at the top. Drain the portion of the sample below the oil into a 50 mL centrifuge tube. If necessary, centrifuge for approximately 15 minutes then decant the aqueous phase for the pH measurement.
- If the waste absorbs all the reagent water, begin the procedure again using 20 g of waste and 40 mL of water.
- Immerse the pH electrode just deep enough into the clear supernatant solution to completely submerge the sensing element without allowing it to contact the settled solid material.
- Record the pH and the temperature once the reading stabilizes. Be sure to rinse and gently wipe the electrodes between measurements.
- Repeat measurements on sample until values differ by no more than ±0.1 pH units.

10.1.6 Lime Grit Samples

Lime grit is composed primarily of Calcium Hydroxide. Calcium Hydroxide has a standardized pH of 12.44. Regulations require material with pH higher than 12.5 to be declared as hazardous. Since pH is temperature dependent, a set of preparation instructions is necessary to eliminate errors and variables that occur in the measurement of high range pH. Lime Grit samples are required to run for pH above 25℃. The laboratory needs to be informed of the nature of the sample (or that it is required to run at 25℃) via notes entered into LIMS.

SET UP

- Set up water bath with temperature control to maintain temperature between 25-27℃. Use a water thermometer that is directly dipped into the water of the water bath.
- Pour out a buffer series into flat bottom tubes (digestion tube or VOA vial).
    - High range calibration buffers 10 and 13
    - ICV/CCV buffer 12.45
- pH probe storage solution is poured into a flat bottom tube (digestion or VOA vial). The pH probe is placed into the storage solution in the flat bottom tube.
- Buffers and storage solution with probe are placed in a rack. The rack is transferred to the water bath.
- RGW rinse bottle is placed in the water bath.
- Wait 15 to 30 minutes for the buffers, solution, and RGW to equilibrate with water bath temperature.

SAMPLE PREPARATION

- Sample(s) are prepared according to the Soil Sample Analysis section of this SOP.
- Sample(s) are decanted into flat bottom tube (digestion tube).
- Pour RGW to the same level as the buffers in the flat bottom tube. Place the thermometer in this RGW tube. This will measure the actual temperature of the solution in the flat bottom tube.
- Before calibrating or taking readings, verify that both thermometers - one that is placed directly in the water bath, and the other in the flat bottom tube containing RGW - show the water bath temperature is 25-27℃. Do not take any readings below 25℃.
- All calibration and analysis is done directly in the water bath. Do not remove any sample(s) or buffers when calibrating or taking readings.
- Calibrate the pH meter using pH buffer 10 and 13. Run ICV using pH buffer 12.45.
- Take pH of the sample and duplicate, following the procedures in the Soil Analysis section of this SOP.

10.2 pH Paper Method

10.2.1 Aqueous wastes do not require leaching for 9041A.

10.2.2 Prepare the sample in the same manner as specified for electrometric pH determination.

10.2.3 Dip the pH paper into the sample aliquot and then determine the pH by matching the color to the index supplied with the paper.

10.2.4 Perform the pH paper check in duplicate for each sample.

10.3 Auto-Titrator Method (ManTech)

10.3.1 Load QC and the samples on the auto-sampler tray in the following order:

1	ICV (pH7 check, second source)
4	Sample
5	Sample Duplicate
6	8 samples
7	CCV (pH7 check)
8	10 samples
9	CCV (pH7 check)

10.3.2 Start the analysis.

10.3.3 For all details on the ManTech operation, refer to PC Titration Plus System Operator's Manual.

10.4 Data Entry and Review

10.4.1 Sample Results in LIMS

- Enter the replicate pH readings and temperatures into LIMS.
- If a sample pH is less than 4 or greater than 10, verify it has not been taken from a preserved container.
- In the LIMS worksheet, enter the final sample volume (nominally 50 mL for waters, 20 mL for DI leach of solids).
- Under Batch Information, enter the start and end date/time, analyst name, instrument ID, Calibration Date, Slope, and any batch comments if applicable

10.4.2 Sample Results in Logbook

Data entry in a logbook is available if workload requirements prevent an analyst from having real-time access to LIMS.

- Enter analyte name, date/time, pH buffer IDs, pH buffer readings and temperatures, and slope (if applicable) in the logbook page header.
- Record the sample ID, matrix, and replicate pH and temperature readings for each sample.
- All sample data must be transcribed into LIMS and a copy of the logbook page scanned and placed and an attached document in LIMS.

10.4.3 Flags and NCMs

- All water samples are automatically flagged "HF" to indicate this is a field test.
- For solids and wastes, if any sample is analyzed past the method-specified holding time, it will be flagged "H" and an NCM must be written. The NCM type may be " Holding Time - Analysis", "Holding Time - Receipt", Holding Time - Requested Late", or "Holding Time - Received >50%" depending on circumstances.
- NOTE 1: for EDF (LaMP) flagging suite, blank detects are flagged MB or CQ and holding time exceedances are flagged BU, BV. NCM types remain the same.
- NOTE 2: For Arizona flagging suite blank detects are flagged B1 or B7 and holding time exceedances are flagged H1 or H3. NCM types remain the same.

10.4.4 Reagents
In the LIMS Reagents tab, enter the LIMS IDs and amounts for all buffers used.

10.4.5 Sample Status
If all results are entered correctly and deemed reportable, update the status to "primary" in LIMS.

10.4.6 Second-Level Review
Perform second-level review using the Data Review Checklist (attachment 3)

10.5 Preventative Maintenance

10.5.1 Manual Electrode

- Inspect the electrode for scratches, cracks, salt crystal build-up, or junction/membrane deposits.
- Rinse off any salt build-up with distilled water.
- For storage between pH measurements, and for short-term storage (up to one week), store the electrode in pH electrode storage solution. If pH electrode storage solution is not available, store the electrode in pH 7 buffer. Add 1 gram of KCL to 200 mL of the pH 7 buffer to use in place of the electrode storage solution
- For long term storage (longer than one week), fill the electrode with filling solution and cover the filling hole. Put a few drops of storage solution into the protective cap and cover the electrode tip.
- For grease and oil deposits, rinse the electrode with methanol
- If the electrode does not meet calibration criteria or appears to have a slow or unstable response, additional cleaning may be necessary. Consult the manufacturer's manual for specific electrode cleaning procedures.
- After any cleaning procedure, soak the electrode in storage solution for at least two hours before performing the analysis of any sample.

10.5.2 Auto-Titrator (ManTech)

Frequency	Tasks
Daily	Check electrode filling solution Check hardware (all components turned on; buret tip placed correctly) Check waste container level
Weekly	Check electrode (drain and refill) Check hardware
Monthly	Clean the stirrer
Annually	Change seals and washers
As Needed	Replace electrodes Replace the stirrer

For all details on ManTech Titration System Maintenance, refer to the maintenance manual.

10.5.3 If the pH meter or electrode is unusable or has limitation to its use, it must be tagged accordingly until such a time the problem has been corrected. Record the problem, solution, and verification of proper operation into the equipment maintenance logbook.

10.5.4 Record all performed maintenance in the instrument maintenance logbook.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Results are reported as read off the instrument along with the temperature at which the reading was taken.

11.2 Final reported results are normally reported to 0.1 pH units but may be reported to 0.01 pH units if requested.

12.0 METHOD PERFORMANCE

12.1 Demonstration of Capabilities

Every analyst must perform an Initial Demonstration of Capability (IDOC) before performing analyses on any client samples. An IDOC consists of 4 consecutive pH 7 readings within ±0.1 pH units of the assigned value.

12.2 Training Requirements

The analyst must have documented training, including reading of the SOP and source methods, conducted by the department manager, senior chemist, or other analyst with training documentation and a passing DOC.

13.0 POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in the "Waste Management and Pollution Prevention" section of the Corporate Environmental Health and Safety Manual (CW-E-M-001).

14.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the laboratory's Waste Disposal SOP. The following waste streams are produced when this method is carried out:

- **Water waste:** This waste is disposed of by pouring the water waste that have been analyzed into the sink, measuring the pH and neutralizing the water using soda ash or acid, and then draining the neutralized contents into the sewer system. Extraction analysts/technicians are responsible for neutralizing this waste in the glassware washing room.

- **Soil waste:** Generated by analyst/technicians after samples have been prepared and analyzed. This waste is stored in 55-gallon closed head metal drum in the wetchem

area. Sample archive technicians label the drum with a preprinted label of Non-RCRA Hazardous waste solid. The drum is removed from the wetchem area to the main waste storage area by sample archive technicians. Analyst/technicians let the sample archive technicians know when they need to removed this drum. All foreign soil waste must be collected separately from soil waste. The foreign soil waste is collected in a red step-on container located in the balance room. This waste is bulked as foreign soil for incineration.

- **Unused standards or reagents:**
  - If the standard or reagent is hazardous and can not be collected with one of the waste streams generated in the method, then the analysts and technicians will take this standard or reagent and place it on the shelves labeled "hazardous waste" in the main waste storage area. The waste material must be labeled with the words "Hazardous Waste", contents and the date taken to the waste storage area. The waste material will be lab packed (example: mercury standard).
  - If the waste material can be collected in the satellite waste container for one of the waste streams of the method, then pour the standard in the right satellite container, rinse the original container, and collect the rinsate in the satellite container. The original container can be placed in the regular trash. (Example, buffer solutions pH 4)

15.0 REFERENCES / CROSS-REFERENCES

15.1 EPA Method 9040B, EPA SW-846, Revision 2, January 1995

15.2 EPA Method 9040C, EPA SW-846, Revision 3, August 2002

15.3 EPA Method 9041A, EPA SW-846, Revision 1, July 1992

15.4 EPA Method 9045C, EPA SW-846, Revision 3, January 1995

15.5 EPA 150.1, EPA Methods for Chemical Analysis of Water and Wastes, Revision 1982.

15.6 SM4500 H^+B (2000), "Electrometric Method", Standard Methods for the Examination of Water and Wastewater

16.0 METHOD MODIFICATIONS

Item	Method Ref	Modification
1	*EPA 150.1 Sec 8.4 EPA 9040B Sec 7.4*	*Each sample is measured two times and each reading is recorded instead of repeating the measurement on successive aliquot of the sample. However, the two readings must not be differed more than ± 0.1 pH units.*
2	*EPA 9045C Sec. 7.2.1*	*Soil samples are stirred from one to five minutes depending upon the sample. Each sample is stirred until it is well mixed.*
3	*EPA 150.1 EPA 9040B EPA 9045C*	*Addition of buffer solutions pH 1 and pH 13 to verify pH for samples with pH <2 and pH >12*

17.0 ATTACHMENTS

17.1 Attachment 1: Analysis Information
17.2 Attachment 2: Logbook Page
17.3 Attachment 3: Data Review Checklist

18.0 REVISION HISTORY

This section has been added beginning with Revision 0. Only details of the last two revisions are incorporated into this SOP. Prior revisions are documented in the QA files.

18.1 Revision 5, dated 02 December 2013

- This revision supersedes IR-WET-PH, revision 4 (11/16/2012)
- Added requirement that ICV be from a second source
- Added procedure for use of ManTech to measure pH
- Added procedure for Lime Grit samples
- Added Data Entry and Review section
- Updated logbook page and data review checklist

18.2 Revision 6, dated 21 November 2014

- This revision supersedes IR-WET-PH, revision 5 (12/02/2014)
- Added requirement for water sample analysis within 48 hours of receipt
- Added foreign soil procedures
- Updated Standard Methods reference
- Revised by DD

Attachment 1
Analysis Information

TestAmerica Irvine

Analytical Method Information

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
pH - in Water (SM4500-H,B, EPA 150.1, EPA 9040B, EPA 9040C)								
Preservation: 4 C, Cool								
Container: 1 Liter Poly			**Amount Required:** 100 ml				**Hold Time:** 15 minutes	
pH	N/A	0.100 pH Units		5				

TestAmerica Irvine

Analytical Method Information

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
pH in Soil (EPA 9045C)								
Preservation: 4 C, Cool								
Container: 4 oz Jar			**Amount Required:** 100 grams				**Hold Time:** 7 days	
pH	N/A	0.100 pH Units		5				

Attachment 2
Logbook Page

pH

EPA Method 150.1/9040B/9040C/SM4500-H,B (water)
EPA Method 9045C (soil)

Analyst Initials: _____

Date/Time: _____

Instr. ID: _____

Batch Number: _____

Calibration Point	pH Value	Standard ID	Temperature	pH Reading
Cal 1	_____	_____	_____	_____
Cal 2	_____	_____	_____	_____
ICV	_____	_____	_____	_____

Slope: _____ Slope acceptance: _____

#	Sample Number	Matrix	Temperature #1 (°C)	pH #1	Temperature #2 (°C)	pH #2	Comments
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							

pH.xls Rev2_nov2013

Attachment 3
Data Review Checklist

pH DATA REVIEW CHECKLIST
EPA 150.1 & 9040B & 9040C & 9041A & 9045C & SM 4500-H B

Method: _____ Analysis Date: _____ 2nd Level Reviewer: _____

Batch: _____ Analyst Initials: _____ Review Date: _____

Item to Review	Analyst	2nd Level	Notes/Specific Criteria
Calibration			
2-point calibration performed			
Initial verification (ICV) reads within limits of ± 0.10			
ICV is from a second source			
CCVs every 10 readings (including Duplicates) and at end of run			
CCVs read within limits of ± 0. 1			
Slope is within manufacturer's specified limits (if applicable)			
Sample Preparation Batch:			
All water samples prepared and analyzed as soon as possible after receipt			
All soil samples prepared and analyzed within 7 days			
Batch contains no greater than 20 samples			
Sample result and duplicate result are within ± 0. 1 units			
All sample readings are within the calibration range used			
All sample temperatures are ±2°C of buffer temperatures			
Data Documentation:			
The analyst's name is on the batch editor page			
Analysis and prep times accurately entered into LIMS			
All standards used are uniquely identified and are not expired			
All flags correctly applied and NCMs written, as required			
All unused fields in the logbook (if used) are z-ed out			

G:\DATA_REV\CHCKLIST\WETCHEM\pH_check_r4.doc
Rev 11/25/2013

Title: Total Dissolved Solids; Filterable Residue
Method SM2540C

Approvals (Signature/Date):

for Tung Nguyen — Date
Department Manager

William Nash — Date
Environmental Health & Safety Coordinator

Maria Friedman — Date
Quality Assurance Manager

Kirk Miltimore — Date
Laboratory Director

Facility Distribution No. _____ **Distributed To: _____**

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the filterable residue (total dissolved solids) in drinking water, surface water, saline water, domestic waste and industrial waste.

1.2 This method has been modified for the analysis of soils in one of two ways:

- Based on soil ("soluble" TDS), by preparing a 10-fold leachate prior to filtration. Results are reported as mg/kg.
- Based on a leachate, by preparing a leachate using a 1:1 preparation factor prior to filtration. Results are reported as mg/L.

1.3 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in "Validation of Methods" in the Quality Assurance Manual

1.4 The reporting limit is for waters and leachates is 10 mg/L when using 100 mL sample aliquot. The reporting limit for soils is 100 mg/kg. Note: Although lower reporting limits may be achieved using larger sample aliquots, the logistics of handling significantly large volumes may make the analysis impractical.

2.0 SUMMARY OF METHOD

A measured aliquot of aqueous sample is filtered through a glass fiber filter into a tared glass beaker. The filtrate is evaporated to near dryness in an oven below 100°C. It is then dried to constant weight at 180℃. The weight of residue di vided by the sample aliquot volume yields Total Dissolved Solids in the sample.

3.0 DEFINITIONS

3.1 Filterable residue is defined as those solids capable of passing through a glass fiber filter and dried to constant weight at 180°C.

There are no additional specific definitions associated with this test. See the laboratory QA manual Standard Methods 2540C for general definitions.

4.0 INTERFERENCE

4.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.

4.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.

4.3 Wear gloves to pick up a weighing dish since oil from your skin can slightly increase the weight of the dish.

4.4 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue allowable residue is limited to 200 mg.

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all

samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Personal Protective Equipment Required: Safety Glasses, Labcoat, Nitrile gloves

5.1.2 When working with the drying oven use temperature resistant gloves to handle hot material

5.2 Primary Materials Used

There are no materials used in this method that have a significant or serious hazard rating.

6.0 EQUIPMENT AND SUPPLIES

6.1 Equipment

6.1.1 Glass fiber filter disc, Whatman 934AH, Gelman A/E, Millipore AP40, Environmental Express ProWeigh, or equivalent

6.1.2 Filter holder, membrane filter funnel

6.1.3 500 mL suction flask

6.1.4 Drying oven, 180± 2°C

6.1.5 Desiccator

6.1.6 Analytical balance

6.2 Supplies

6.2.1 Graduated cylinders, class A

6.2.2 150 mL glass beakers

7.0 REAGENTS AND STANDARDS

7.1 Standards

7.1.1 Sodium chloride, 1000 mg/L

7.1.2 1:10 dilution of household bleach

All purchased standards must be accompanied by a Certificate of Analysis (C of A) which is kept available at the laboratory in order to demonstrate traceability of the standard to certified (NIST-traceable) source material, if available.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

TABLE 1: HOLDING TIME AND PRESERVATION

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	1L Poly	150 mL	Cool >0 to 6°C	7 Days	40 CFR Part 136.3
Soils	4 oz. Jar	100 g	Cool >0 to 6°C	28 Days	N/A

9.0 QUALITY CONTROL

9.1 **Sample QC** - The following quality control samples are prepared with each batch of samples.

9.1.1 Method Blank (MB)

Prepare and analyze a method blank (MB) for each matrix and with every batch of 20 samples, or less. Check that there are no analytes detected at or above the reporting limit. If the method blank shows contamination, re-prepare all samples in the batch unless:

- The samples are ND (qualify the result accordingly).
- The sample result is > 10x the blank level (qualify the result accordingly).

9.1.2 Laboratory Control Sample (LCS)

Prepare and analyze a primary source laboratory control sample (LCS) for every batch of 20 samples or less. The LCS recovery must be within laboratory acceptance limits of (see attachment 1). If the LCS is outside of these limits, re-prepare the entire batch unless:

- The LCS recovery is above the upper limit and samples are ND. Qualify sample results accordingly.

9.1.3 Sample Duplicate

Prepare and analyze a sample duplicate for each matrix and with 10 samples, or less. The relative percent difference (%RPD) must be ≤ 5% of the average result of the pair if the sample residue is ≥ than 10 mg or a third analysis must be performed. If the third analysis still does not ≤ 5% of the average, report the results with an NCM.

If the residue is < 10 mg then the RPD must be ≤ 20%.

10.0 PROCEDURE

10.1 Standard Preparation

Prepare the 1000 mg/L laboratory control sample solution by dissolving 1.000 g of NaCl in 1000 mL of Laboratory Reagent Grade. Store the standard at 4±2℃ with a shelf life of six months.

10.2 Sample Analysis

10.2.1 Heat the evaporating glass beakers 180± 2°C for 1 hour.

10.2.2 Cool the evaporating glass beakers in a desiccator and store until needed. Weigh and record the weight of each weighing dish immediately before use. .

10.2.3 Assemble the filtering apparatus with a glass fiber filter. Prepare the glass fiber filter disc by placing the disc on the filter apparatus and wetting it to help it adhere. Rinse the disc with three successive 20 mL aliquots of Laboratory Reagent Grade water while applying a vacuum after the water has passed through the filter. Discard the resulting rinse water.

10.2.4 For all samples, Method Blank and LCS, the analysis volume must be measured in a graduated cylinder and recorded prior to filtration. In addition, after filtration of the initial aliquot, the graduated cylinder must be rinsed with three successive 10 mL aliquots of

Laboratory Reagent Grade water. Each 10 mL aliquot is to be poured through filtration apparatus, allowing complete drainage between rinses. After the final rinse, suction must be maintained for approximately 1 minute.

10.2.5 Measure 100 mL of Laboratory Reagent Grade water in a clean graduated cylinder. Filter and rinse. This will be used as the method blank.

10.2.6 Measure 50 mL of the LCS solution into graduated cylinder. Filter and rinse

10.2.7 Check and record the pH and conductivity of all samples.

- If sample pH is <2 or >9, verify correct (unpreserved) container is being used. Notify the project manager and write an NCM indicating that the sample may be improperly preserved.
- Use sample conductivity to determine the volume to filter.

10.2.8 Water Samples: Shake the sample vigorously and then transfer 100 mL (or less) of sample into a graduated cylinder or use a pipette for smaller volume (20 mL or less). Record the volume. Transfer this volume to the filtration apparatus. Vacuum filter the sample directly into a 150 mL glass beaker. Rinse the graduated cylinder with three successive 10 mL aliquots of water. If the total filterable residue is expected to be high, based on conductivity results (>2000 umhos/cm), use smaller volume as follows:

TABLE 2: CONDUCTIVITY SCREENING LEVELS

Sample conductivity (uS)	Sample volume to use (mL)
<2,000	100
2,000 to 4,000	50
4,000 to 5,000	20
5,000 to 20,000	10
20,000 to 50,000	5
>50,000	1

10.2.9 Solid Samples

- For soluble TDS in soil, a 10X RGW leachate of the soil is analyzed at an appropriate volume in the same manner as water samples. Report in mg/Kg.
- For leachable TDS in soil, a 1:1 RGW leachate of the soil is analyzed an appropriate volume in the same manner as water sample. Report in mg/L.
- Weigh an appropriate amount of the well mixed sample into a clean containter.
- Add Laboratory Reagent Grade water using a Class A graduated cylinder. (10x the solid aliquot weight for soluble TDS and 1x the solid aliquot weight for leachable TDS.)
- All initial and final amounts must be documented.
- Shake samples by hand to ensure water and soil are mixed and then place on an orbital shaker for minimum of 30 minutes.
- Remove sample from the shaker and allow settling to occur.
- A measured volume of the supernatant can now be analyzed in the same manner as regular water samples.

NOTE 1: All batch QC samples must be processed in the same manner, using baked sand in lieu of solid sample for the MB and LCS.

Note 2: For foreign soils, all waste generated during the weighing process must be disposed of in a separate container from other soil sample waste. (This includes, spatulas, Kimwipes, gloves, etc). When finished weighing samples, wipe balance and surrounding area with a paper towel, and dispose of the paper towel in the foreign soil waste container. Wipe surrounding area with a 10% household bleach solution to disinfect the surrounding areas and dispose of wipes in the foreign soil waste container. When the container is full, notify sample archive technicians.

10.2.10 Evaporate the filtrate to near dryness in an oven below 100°C to prevent splattering. After the filtrate has been evaporated to near dryness, dry the filtrate for 2 hours at **180 ± 2°C** to obtain a constant weight.

10.2.11 Cool the sample in a desiccator. Weigh the sample after it is cool. Repeat the drying cycle until a constant weight is obtained or until the weight loss is less than 0.5 mg. Use the lowest of the final two constant weights weighing in the calculation.

10.2.12 The final residue weight must be no greater than 200mg. If it the residue exceeds this level, there is a potential for high bias in the result. Samples must be either re-analyzed or qualified as estimates.

10.3 Preventative Maintenance

If any equipment is unusable or has limitation to its use, it must be tagged "out of service" until such a time the problem has been corrected. Record the problem, solution and verification of proper operation into the instrument maintenance logbook.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Accuracy

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

11.2 Concentration

$$\text{TDS (mg/L)} = \frac{(A - B) \times 1{,}000{,}000}{C} \qquad \text{TDS (mg/Kg)} = \frac{(A - B) \times 1{,}000{,}000}{D}$$

Where:
A = weight of dried residue + dish (g)
B = weight of dish (g)
C = volume of sample or leachate (mL)
D = weight of sample in leachate volume filtered (g)

12.0 METHOD PERFORMANCE

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure as described in laboratory's SOP, IR-QA-MDL.

12.2 Demonstration of Capabilities

Every analyst must perform an Initial Demonstration of Capability (IDOC) before performing analyses on any client samples. An IDOC consists of 4 consecutive LCS samples at 1 to 4 times the RL with an average recovery and RSD within laboratory acceptance limits. An on-going DOC must be performed annually. An ODOC can be 4 consecutive LCSs at mid-level or a passing PT.

12.3 Training Requirements

The analyst must have documented training, including reading of the SOP and source methods, conducted by the department manager, senior chemist, or other analyst with training documentation and a passing DOC.

13.0 POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in the "Waste Management and Pollution Prevention" section of the Corporate Environmental Health and Safety Manual (CW-E-M-001).

14.0 WASTE MANAGEMENT

- **Non-Hazardous Waste**

Non-Hazardous waste is disposed of by pouring the samples water that have been extracted into the sink, measuring the pH and neutralizing the water using Soda ash, and then draining the neutralized contents into the sewer system. The soil generated in these tests is collected in the 55-gallon closed head metal drum in the wetchem area. Sample archive technicians label the drum with a preprinted label of Non-RCRA Hazardous waste solid. Foreign soil waste must be kept separate from domestic soil waste. See the note above for the solid sample procedures.

Wetchem analysts/technicians are responsible for neutralizing this waste in the glassware washing room.

15.0 REFERENCES / CROSS-REFERENCES

15.1 Standard Methods for the Examination of Water and Wastewater, 2540C (1997).

16.0 METHOD MODIFICATIONS

TABLE 4: METHOD MODIFICATIONS

Item	Method	Modification
1	*SM 2540C*	*The method has been modified to report TDS in solid samples based on the weight of sample in the leachate volume filtered.*
2	*SM2540C 3.d*	*Sample/Sample Duplicate RPD for samples with residues less than 10 mg is allowed to be up to 20%.*

17.0 ATTACHMENTS

17.1 **Attachment 1**: Analysis information
17.2 **Attachment 2:** Data Review Checklist
17.3 **Attachment 3:** Datatypes

18.0 REVISION HISTORY

This section has been added beginning with Revision 0. Only details of the last two revisions are incorporated into this SOP. Prior revisions are documented in the QA files.

18.1 Revision 5, dated 30 September 2013

- This revision supersedes IR-WET-TDS, revision 4 (09/28/2012)
- Updated signatories to the SOP
- Added reference to EPA 160.1
- Changed SA/DU requirement from every 20 to every 10 samples
- Revised by DD

18.2 Revision 6, dated 06 October 2014

- This revision supersedes IR-WET-TDS, revision 5 (09/30/2013)
- Removed references to EPA 160.1
- Revised Standard Methods reference
- Revised soil preparation section
- Added foreign soil procedures
- Updated section 14 to include handling of foreign soil waste
- Revised by DD

Attachment 1
Analysis Information

TestAmerica Irvine

Analytical Method Information

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
TDS - in Water (SM2540C)								
Preservation: 4 C, Cool								
Container: 1 Liter Poly			**Amount Required:** 100 ml			**Hold Time:** 7 days		
Total Dissolved Solids	5	10 mg/l		5			90 - 110	10
TDS – in Solid (SM2540C Mod.)								
Preservation: 4 C, Cool								
Container: 4 oz Jar			**Amount Required:** 100 g			**Hold Time:** 28 days		
Total Dissolved Solids	50	100 mg/kg		5			90 - 110	10

Attachment 2
Data Review Checklist

DAILY DATA CHECKLIST
Total Dissolved Solids –SM2540C & EPA 160.1

Analyst: _____ 2nd Level Review: _____
Analysis Date: _____ Date: _____
Batch ID: _____

Analyst Rev	2nd Level Rev	
		Calibration
_____	_____	Daily balance calibration verification is recorded
_____	_____	Beginning and ending oven temperatures are recorded in LIMS
_____	_____	Time IN and time OUT are recorded in LIMS
_____	_____	Temperatures within the required temperature range of the method
		Sample Preparation Batch
_____	_____	Batch contains no greater than 20 samples
_____	_____	Batch contains a passing Method Blank (< 10 mg/L)
_____	_____	Batch contains a passing LCS (%R= 85-115)
_____	_____	Batch contains a Duplicate (SA/DU RPD<5)
_____	_____	Duplicate pair (SA/DU) analyzed every 10 samples
		Analysis
_____	_____	Constant weight is achieved for all samples and QC (diff <0.5mg or 5%)
_____	_____	Final residue no greater than 200 mg

Comments: _____

_____

_____

TDS_check_r3.DOC
8/30/2012

Attachment 3
Datatypes

Method Code	Level	Datatype Description	Value to Enter	Units
2540C_Calcd	BATCH	Nominal Amount Used	[100]	mL
2540C_Calcd	BATCH	Oven ID	[Specify]	None
2540C_Calcd	BATCH	Date samples were placed in the oven	Date/time	None
2540C_Calcd	BATCH	Oven Temperature Verification	N/A	Celsius
2540C_Calcd	BATCH	Oven Temp when samples are put in	[Specify]	Celsius
2540C_Calcd	BATCH	Uncorrected In Temperature	N/A	Celsius
2540C_Calcd	BATCH	Date samples were removed from oven	Date/time	None
2540C_Calcd	BATCH	Oven Temp when samples removed from oven	[Specify]	Celsius
2540C_Calcd	BATCH	Uncorrected Out Temperature	N/A	Celsius
2540C_Calcd	BATCH	Balance ID	[Specify]	None
2540C_Calcd	BATCH	Pipette ID	[Specify]	None
2540C_Calcd	BATCH	ID number of the thermometer	[Specify ID and CF]	None
2540C_Calcd	BATCH	Filter Paper Lot Number	[Specify]	None
2540C_Calcd	BATCH	Constant Weight (WT2) Date/Time in	Date/time	None
2540C_Calcd	BATCH	Constant Weight (WT2) Temp In	[Specify]	Celsius
2540C_Calcd	BATCH	Constant Weight (WT2) Date/Time Out	Date/time	None
2540C_Calcd	BATCH	Constant Weight (WT2) Temp Out	[Specify]	Celsius
2540C_Calcd	BATCH	Constant Weight (WT3) Date/time In	Date/time	None
2540C_Calcd	BATCH	Constant Weight (WT3) Temp In	[Specify]	Celsius
2540C_Calcd	BATCH	Constant Weight (WT3) Date/Time Out	Date/time	None
2540C_Calcd	BATCH	Constant Weight (WT3) Temp Out	[Specify]	Celsius
2540C_Calcd	BATCH	Batch Comment	Enter as needed	None

FACILITY SOP ATTACHMENT

SOP NUMBER: IR-WET-TSS, Rev 5 (9/12/2014)	**CHANGE FORM ID:** CF1

SOP TITLE: SM 2540D/ASTM D 3977 TOTAL SUSPENDED SOLIDS (NON-FILTERABLE RESIDUE) AND SEDIMENT CONCENTRATION

REASON FOR ADDITION OR CHANGE (Use additional sheets if necessary):

1) Clarify that filter drying time is a minimum of 2 hours, remove mention of "overnight"
2) Update Attachment 2 (Datatypes)

CHANGE OR ADDITION (Use additional sheets if necessary):

Update Section 10.3.10 as follows:

10.3.10 Dry the filter for a minimum of 2 hours~~, or overnight~~ at 103°C to 105°C. Record the time in, time out, and the temperature of the oven into the TALS Batch Notes when the sample is in the oven.

Replace Attachment 2 with the Attachment from Page 2 of this Change Form.

Prepared By: Maria Friedman

APPROVED BY:

Department Manager	Date 5/7/15
Quality Assurance Manager	Date 5-7-2015
Environmental Health and Safety Coordinator	Date 5/7/2015
Laboratory Director	Date 5-7-2015

Control Copy Number _____

Attachment 2
Datatypes

Method Code	Datatype Description	Value to Enter	Units
2540D	Perform Calculation (0=No, 1=Yes)	Enter [1]	NONE
2540D	Nominal Amount Used	Enter volume	mL
2540D	Pipette ID	[Specify]	NONE
2540D	Balance ID	[Specify]	NONE
2540D	Filter Paper Lot Number	[Specify]	NONE
2540D	Oven ID	[Specify]	NONE
2540D	ID number of the thermometer	Enter ID# and Correction factor	NONE
2540D	Date/Time Samples placed in Oven	Enter date & time IN	NONE
2540D	Corrected Temperature in Oven	Enter corrected temp	Celsius
2540D	Uncorrected In Temperature	N/A	Celsius
2540D	Date samples removed from oven	Enter date & time OUT	NONE
2540D	Corrected Temperature out of Oven	Enter corrected temp	Celsius
2540D	Uncorrected Out Temperature	N/A	Celsius
2540D	Constant Weight (WT2) Date/Time In Oven	Enter date & time	NONE
2540D	Constant Weight (WT2) Temp In	Enter temperature	Celsius
2540D	Uncorrected CW (WT2) Temp In	NA	Celsius
2540D	Constant Weight (WT2) Date/Time Out	Enter date & time	NONE
2540D	Constant Weight (WT2) Temp Out	Enter temperature	Celsius
2540D	Uncorrected CW (WT2) Temp Out	N/A	Celsius
2540D	Constant Weight (WT3) Date/time In	Enter date & time	NONE
2540D	Constant Weight (WT3) Date/Time Out	Enter date & time	NONE
2540D	Constant Weight (WT3) Temp In	Enter temperature	Celsius
2540D	Uncorrected CW (WT3) Temp In	NA	Celsius
2540D	Constant Weight (WT3) Temp Out	Enter temperature	Celsius
2540D	Uncorrected CW (WT3) Temp Out	NA	Celsius

Title: Total Suspended Solids (Non-filterable residue) and Sediment Concentration
SM2540D

Approvals (Signature/Date):

Tung Nguyen Department Manager	Date 9/3/14	William Nash Environmental Health & Safety Coordinator	Date 09/05/2014
Maria Friedman Quality Assurance Manager	Date 9-12-2014	Kirk Miltimore Laboratory Director	Date 09/03/14

Facility Distribution No. _____ **Distributed To: _____**

1.0 SCOPE AND APPLICATION

1.1 This procedure is used to determine the non-filterable residue (Total Suspended Solids) in drinking water, surface water, saline water, domestic waste and industrial waste.

1.2 The standard reporting limit for water is 10 mg/L. Lower reporting limits can be achieved using a larger sample volume. Note that RLs are subject to change based on annual method detection limit (MDL) studies.

1.3 On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in "Validation of Methods" in the Quality Assurance Manual.

2.0 SUMMARY OF METHOD

2.1 For TSS, a well-mixed sample is filtered through a glass fiber filter and the residue retained on the filter is dried to constant weight at 103°C to 105°C.

2.2 For sediment concentration, a thoroughly mixed aliquot of sample is either weighed or measured volumetrically and then filtered through a tared glass-fiber filter. Dry the filter and filtrate to constant weight at 105°C.

3.0 DEFINITIONS

3.1 Total Suspended Solids is also referred to as non-filterable residue. It is those solids that are retained by a glass fiber filter and dried to a constant weight at 103°C to 105°C.

3.2 Sediment concentration is defined as either the ratio of the mass of dry sediment in a water-sediment mixture to the mass of the mixture or, as the ratio of the mass of the dry sediment to the volume of the mixture. At concentrations below 8000 mg/L these two definitions are the same.

4.0 INTERFERENCES

4.1 Filtration apparatus, filter material, pre-washing, post-washing and drying temperature are specified because these variables have been shown to affect the results.

4.2 Sample high in Filterable Residue (dissolved solids), such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids in the filter minimizes this potential interference.

4.3 Large floating particles or agglomerates of non-homogeneous material can lead to erratic TSS results. These types of artifacts must be evaluated and removed if deemed not representative of the sample as a whole.

4.4

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples

and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

Personal Protective Equipment Required: Safety Glasses/Face Shield, Lab coat, Nitrile/Cut-resistant Gloves

5.2 Primary Materials Used

There are no materials with a health rating of 3 or 4 used in this method. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material	Hazards	Exposure Limit (1)	Signs and symptoms of exposure
Sigmacell Cellulose	Irritant	15 mg/m3 TWA	May be harmful if inhaled. May cause respiratory tract irritation. May be harmful if absorbed through skin. May cause skin irritation. May cause eye irritation. May be harmful if swallowed.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 EQUIPMENT AND SUPPLIES

6.1 Instrumentation

6.1.1 Filtering apparatus: filter holder, membrane filter funnel

6.1.2 Suction Flask

6.1.3 Drying oven

6.1.4 Desiccator

6.1.5 Analytical balance, capable of weighing to 0.1mg

6.2 Supplies

6.2.1 Glass fiber filter disc, Environmental Express PreWeigh F93447MM pre-weighed 47mm, pore size: 1.5µm, or equivalent

6.2.2 Graduated cylinder

6.2.3 50mL aluminum weighing dishes

6.2.4 Tongs and gloves

7.0 REAGENTS AND STANDARDS

7.1.1 Laboratory reagent water

7.1.2 SigmaCell® Cellulose, 20µm

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Waters	Poly	1L	Cool >0 to 6°C	7 Days	40 CFR Part 136.3
Soils	4 oz. Jar	100 g	Cool >0 to 6°C	7 Days	N/A

9.0 QUALITY CONTROL

9.1 Sample QC - The following quality control samples are prepared with each batch of samples.

9.1.1 Method Blank (MB)

Prepare and analyze a method blank (MB) for each matrix and with every batch of 20 samples, or less. Check that there are no analytes detected at or above the reporting limit. If the method blank shows contamination, re-prepare all samples in the batch unless:

- The sample is ND (flag and write an NCM).
- The sample result is > 10x the blank level (flag and write an NCM).

9.1.2 Laboratory Control Sample (LCS).

Prepare and analyze a primary source laboratory control sample (LCS) for every batch of 20 samples or less. The LCS recovery must be within laboratory acceptance limits (see attachment 1). If the LCS is outside of these limits, re-prepare the whole batch and/or re-calibrate the system unless:

- The LCS recovery is above the upper limit and samples are ND. Flag and write an NCM.

9.1.3 Sample Duplicate.

Prepare and analyze a sample duplicate for every 10 samples or less. The RPD between the sample and duplicate readings should be 10% if the sample residue is ≥ 10 mg or a third analysis must be performed.

- If the third analysis still does not fall within10%, report the result with an NCM.

If the residue is < 10 mg, flag the data to indicate “due to the low levels of analyte in the sample, the duplicate RPD calculation does not provide useful information”.

For result with a final residue of more than 10 mg, duplicate analysis results must agree within 5% of the average result of the pair. This is equivalent to an RPD of 10%.

9.1.4 Reporting Limit Check Standard (MRL Check)
Prepare and analyzed an MRL check with each batch of 20 samples or less only if required by a specific program or client project. MRL check recovery must be within the specified program or client recovery limits.

9.1.5 Minimum Residue Requirement

A full 1L* of sample must be filtered if the final residue is less than 2.5 mg. If the final residue is less than 2.5 mg AND less than 1 L of sample is filtered, an NCM must be written to state why this method requirement was not followed. The 2.5 mg requirement must be met REGARDLESS of the reporting limit requested for the sample.
(*at a minimum, 950 mL. Final result rounding to the required significant figures will yield a result indistinguishable from that determined using a full liter.)

9.2 Instrument QC

9.2.1 Balance Calibration Verification Tolerance Levels

The tolerance levels for the balance are indicated in the following table.

Tolerance Levels		
	Top Loaders (Balances with 2 and 3 decimal places)	Analytical balances
0.5g	0.49 g – 0.51 g	0.4999 g – 0.5001 g
1 g	0.99 g – 1.01 g	0.9999 g – 1.0001 g
50 g	49.95 g – 50.05 g	49.9995 g – 50.0005 g
100 g	99.90 g – 100.10 g	99.9990 g – 100.0010 g

10.0 PROCEDURE

10.1 Standard Preparation

10.1.1 LCS Stock Standard

Prepare a 1000 mg/L LCS standard by adding 1.00 g of cellulose to 1 L of DI Water. Shake thoroughly before use. Discard after one month. Store the solution in the refrigerator at >0 to 6℃.

10.1.2 Method Blank-MB

A method blank is processed by filtering 1000 mL of Reagent Grade water through a filter in the same manner as the samples. 1000 mL is always filtered for the method blank regardless of the program or client-specified RL.

10.1.3 Laboratory Control Sample-LCS

An LCS is processed by filtering 100 mL of TSS LCS solution through a filter in the same manner as the samples.

10.1.4 Reporting Limit Standard (MRL Check)

MRL check levels are prepared, if required, at the program or client-specified RL. Prepare an X mg/L MRL Check Standard (where X= the reporting limit required) by pipetting X mL of 1000 mg/L LCS Stock Standard into a 1 L volumetric flask and bringing to volume with laboratory reagent grade water. Store at >0 to 6℃ for up to one month.

10.2 Instrument Initialization and Calibration

Verify the analytical balance has been leveled and its calibration checked prior to use.

10.3 Sample Preparation and Analysis

10.3.1 Purchase pre-rinsed and pre-weighed filters from the supplier. Each filter comes in its own aluminum weighing dish.

10.3.2 Wear gloves when handling a weighing dish since oils from your skin can slightly increase the weight of the dish.

10.3.3 Label each dish with the sample number prior to filtering the sample.

10.3.4 Rinse the filtering apparatus prior to use. Apply a vacuum while rinsing the disc with a minimum of 60 mL of laboratory reagent water applied using the directed spray from a wash bottle. Remove all traces of water by continuing to apply vacuum after the water has passed through the filtration device. Discard the resulting rinse water.

10.3.5 Assemble the filtering apparatus by placing the pre-rinsed and pre-weighed glass fiber filter disc on the membrane filter apparatus.

10.3.6 Observe the sample with respect to both the amount of suspended solid present and whether or not the sample contains non-representative artifacts such as floating materials or submerged agglomerates. Non-representative artifacts must be physically removed and the removal documented with an NCM. An artifact is considered non-representative if it would not always be included in multiple aliquots of the same volume to be used for filtration

10.3.7 Shake the sample vigorously and transfer an appropriate volume of sample to the filter using a graduated cylinder.

- Final residues must be at least 2.5 mg (up to a filtered volume of 1L) but no more than 200 mg
- Rely on analyst judgment and experience to adjust the filtered volume in order to meet these residue criteria.
- If the final residue exceeds 200mg, re-analyze the sample with a smaller aliquot. To estimate the re-analysis volume, divide 200 by the actual residue; multiply this by the volume originally used and round down to an easily measured multiple of 10.

$$new\_vol = \frac{200}{residue} \times original\_vol$$

- If the final residue is less than 2.5mg, re-analyze the sample with a larger aliquot (not to exceed 1L). To estimate the re-analysis volume, divide 2.5 by the actual residue; multiply this by the volume originally used and round UP to an easily measured multiple of 10. If the re-analysis volume is greater than 1L, use 1L for re-analysis.

$$new\_vol = \frac{2.5}{residue} \times original\_vol$$

10.3.8 Filter the sample through a glass fiber filter. Rinse the graduated cylinder, the filter, the non-filterable residue and the funnel walls with a minimum of 60 mL of laboratory reagent water applied using the directed spray from a wash bottle while applying a vacuum. Continue to apply a vacuum until the filtration is complete to remove as much water as possible. Allow time for complete drainage between each rinsing.

10.3.9 Remove the filter from the filter support and transfer it to its aluminum weighing dish using tongs only.

10.3.10 Dry the filter for a minimum of 2 hours, or overnight at 103°C to 105°C. Record the time in, time out, and the temperature of the oven into the TALS Batch Notes when the sample is in the oven.

10.3.11 Cool the sample in a desiccator for about 30 minutes. Weigh the sample after it is cool.

10.3.12 Repeat the drying cycle until constant weight is obtained (weight loss is less than 0.5 mg). Record all the weights directly into TALS worksheet. Use the lowest dried residue weight in the final calculation.

10.3.13 Procedure for soil samples

Weigh 5 ± 0.05 grams of the well mixed sample into a disposable 50 mL centrifuge tube. Add 40mL Laboratory Reagent Grade water using a Class A graduated cylinder. All initial and final amounts must be documented. Shake samples by hand to ensure water and soil are mixed and then place on an orbital shaker for minimum of 10 minutes. If necessary, centrifuge for 3 – 5 min or until separation of the phases occurs. Filter the resultant supernatant water through a 0.2um filter. This filtrate can now be analyzed in the same manner as regular water samples.

10.4 Preventative Maintenance

10.4.1 Clean the balance after every use. This is a courtesy as well as a safety matter. This also adds to the operational life of the balance.

10.4.2 If the balance is unusable or has limitation to its use, it must be tagged immediately and reported to QA staff.

11.0 CALCULATIONS / DATA REDUCTION

11.1 Accuracy

$$\text{LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

11.2 Precision (RPD)

$$\text{Sample Duplicate} = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

11.3 TSS Concentration

$$\text{TSS (mg/L)} = \frac{(A - B) \times 1{,}000{,}000}{C}$$

Where:
A = weight of filter + residue in grams (the lowest of the replicate weightings)
B = weight of filter (gram)
C = volume of sample filtered (ml)

11.4 Reporting limit Calculation

$$\text{Final RL} = RL_{base} \times \frac{V_{no\,min\,al}}{V_{sample}}$$

Where RL_{base} = the requested RL (mg/L)

$V_{nominal}$ = the nominal or "final" volume in the TALS batch (mL)
V_{sample} = the volume of sample filtered (mL)

12.0 METHOD PERFORMANCE

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure as described in laboratory's SOP, IR-QA-MDL.

12.2 Demonstration of Capabilities

Every analyst must perform an Initial Demonstration of Capability (IDOC) before performing analyses on any client samples. An IDOC consists of 4 consecutive LCS samples at 1-4 times the RL with an average recovery and RSD within the in-house statistical limits. An ODOC can be 4 consecutive LCSs or a passing PT.

12.3 Training Requirements

The analyst must have documented training, including reading of the SOP and source methods, conducted by the department manager, senior chemist, or other analyst with training documentation and a passing DOC.

13.0 POLLUTION CONTROL

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in the "Waste Management and Pollution Prevention" section of the Corporate Environmental Health and Safety Manual (CW-E-M-001).

14.0 WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to the laboratory's Waste Disposal SOP (IR-EHS-WASTE). The following waste streams are produced when this method is carried out:

Non-Hazardous Waste: Total Suspend Solids.
Non-Hazardous waste is disposed of by pouring the samples water that have been extracted into the sink, measuring the pH and neutralizing the water using soda ash, and then draining the neutralized contents into the sewer system. The soil generated in these tests is collected in the 55-gallon closed head metal drum in the wetchem area. Sample archive technicians label the drum with a preprinted label of Non-RCRA Hazardous waste solid.

Wetchem analysts/technicians are responsible for neutralizing this waste in the glassware washing room.

Unused standards All these departments generate unused and expired standards. If the standard is hazardous and can not be collected with one of the waste streams generated in the method, it must be labeled as hazardous waste with a date that the material became waste. The analyst or technicians take this standard and placed it on the shelves labeled “hazardous waste” in the main waste storage area. The standard will be lab packed (example: mercury standard). If the standard can be collected in the satellite waste container for one of the waste streams of the method, then pour the standard in the right satellite container, rinse the original container, and collect the rinsate in the satellite container. The original container can be placed in the regular trash. (Example, buffer solutions pH 4)

15.0 REFERENCES / CROSS-REFERENCES

15.1 Method 2540D, Standard Methods for the Examination of Water and Wastewater, 20th Edition 1998.

16.0 METHOD MODIFICATIONS

None

17.0 ATTACHMENTS

17.1 **Attachment 1:** Analysis Information

17.2 **Attachment 2:** Datatypes

17.3 **Attachment 3:** Data Review Checklist

18.0 REVISION HISTORY

This section has been added beginning with Revision 0. Only details of the last two revisions are incorporated into this SOP. Prior revisions are documented in the QA files.

18.1 Revision 4, dated 28 August 2013

- This revision supersedes IR-WET-TSS, revision 3 (08/01/2012) and IR-WET-TSS_r3-CF1 (07/02/2013)
- Specify that a minimum residue of 2.5mg is required and to increase filtered volume up to 1000mL to meet this minimum.
- Removed requirement that MDL is based on lowest discernable unit of measure on the balance.
- Removed the nominal sample volume used
- Removed ASTM D 3977-97
- RLs are subject to change based on annual method detection limit (MDL) studies.
- Revised by DK, LH and DD.

18.2 Revision 5, dated 12 September 2014

- This revision supersedes IR-WET-TSS, revision 4 (08/28/2013) and IR-WET-TSS_r3 change forms CF1 (10/25/2013), CF2 (12/06/2013), and CF3 (02/14/2014)
- Changed requirement of duplicate to one per 10 instead of 1 per 20
- Added MRL check standard
- Added minimum residue requirement
- Added RL calculation formula
- Revised by DD

Attachment 1
Analysis Information

TestAmerica Irvine

Analytical Method Information

Analyte	MDL	Reporting Limit	Surrogate %R	Duplicate RPD	Matrix Spike %R	Matrix Spike RPD	Blank Spike / LCS %R	Blank Spike / LCS RPD
TSS - in Water (SM 2540D)								
Preservation: 4 C, Cool								
Container: 1 Liter Poly			**Amount Required:** 100 ml			**Hold Time:** 7 days		
Total Suspended Solids	5	10 mg/l		10			85 - 115	

Attachment 2
Datatypes

Method Code	Datatype Description	Value to Enter	Units
2540D	Perform Calculation (0=No, 1=Yes)	Enter [1]	NONE
2540D	Nominal Amount Used	Enter volume	mL
2540D	Oven ID	[Specify]	NONE
2540D	ID number of the thermometer	Enter ID# and Correction factor	NONE
2540D	Date samples were placed in the oven	Enter date & time IN	NONE
2540D	Uncorrected In Temperature	N/A	Celsius
2540D	Oven Temp when samples are put in oven	Enter corrected temp	Celsius
2540D	Date samples were removed from oven	Enter date & time OUT	NONE
2540D	Uncorrected Out Temperature	N/A	Celsius
2540D	Oven Temp when samples removed from oven	Enter corrected temp	Celsius
2540D	Filter Paper Lot Number	[Specify]	NONE
2540D	Constant Weight (WT2) Temp In	Enter temperature	Celsius
2540D	Uncorrected CW (Wt2) Temp In	NA	Celsius
2540D	Constant Weight (WT2) Temp Out	Enter temperature	Celsius
2540D	Uncorrected CW (Wt2) Temp Out	N/A	Celsius
2540D	Constant Weight (WT3) Date/time In	Enter date & time	NONE
2540D	Constant Weight (WT3) Date/Time Out	Enter date & time	NONE
2540D	Constant Weight (WT3) Temp In	Enter temperature	Celsius
2540D	Uncorrected CW (Wt3) Temp In	NA	Celsius
2540D	Constant Weight (WT3) Temp Out	Enter temperature	Celsius

Attachment 3
Data Review Checklist

DAILY DATA CHECKLIST
Total Suspended Solids –SM2540D

Analyst: _____ 2nd Level Review: _____
Analysis Date: _____ Date: _____
Batch ID: _____

Analyst Rev	2nd Level Rev	
		Calibration
_____	_____	Daily balance calibration verification has been performed
_____	_____	Beginning and ending oven temperatures are recorded
_____	_____	Date/Time IN and time OUT are recorded
_____	_____	Temperatures within the required temperature range of the method
		Sample Preparation Batch
_____	_____	Batch contains no greater than 20 samples
_____	_____	Batch contains a passing Method Blank (< 10 mg/L)
_____	_____	Batch contains a passing LCS (%R= 85-115)
_____	_____	Batch contains a Duplicate (SA/DU RPD<5)
		Analysis
_____	_____	Constant weight is achieved for all samples and QC (diff <0.5mg)
_____	_____	Total mg residue for each sample does not exceed 200
_____	_____	Final residues less than 2.5mg must be based on 1000 mL of filtered sample
		Documentation
_____	_____	All required TALS datatypes are entered
_____	_____	All standards used are uniquely identified and are not expired
		All data flags correctly applied and NCMs written, as required

Comments: _____

TSS_check_r2.DOC
Rev 08/07/13

APPENDIX D
TESTAMERICA, DENVER, CO, SOPs

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

TestAmerica Denver

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Title: Acid Digestion of Aqueous Samples for Metals Analysis by ICP

Approvals (Signature/Date):

Doug Gomer 6/26/15 Doug Gomer Date Technical Specialist	Adam W Alban 26 June 15 Adam Alban Date Health & Safety Manager / Coordinator
Margaret S. Sleevi 6/29/15 Margaret S. Sleevi Date Quality Assurance Manager	L&L 6/26/15 William S. Cicero Date Laboratory Director

Facility Distribution No. _____ **Distributed To: _____**

1.0 Scope and Application

1.1 This standard operating procedure (SOP) describes the acid digestion of aqueous samples by EPA Method 200.7, SW-846 Method 3005A or SW-846 Method 3010A prior to the determination of the concentration of individual metallic elements by inductively coupled plasma atomic emission spectroscopy (ICP). These methods include digestions for total, total recoverable, dissolved, and potentially dissolved analytes (see definitions in Section 3).

1.2 This SOP is applicable to ground water, surface water, domestic and industrial wastewater, TCLP leachates, and other aqueous media. This SOP is not applicable to oils or other liquids that are not miscible with water.

NOTE: Samples that are found to be immiscible with water, e.g., contain oil or other immiscible organic solvents, are subcontracted to other labs that are capable of handling such samples. If during the preparation process it is discovered that the sample is immiscible with water or is biphasic, the analyst notifies the Technical Specialist and Project Manager, who can subcontract the samples to a laboratory with the capability to handle the sample.

1.3 The following table summarizes the applicability of the various digestion methods referenced in this SOP. All sample digestates are analyzed by ICP in accordance with SOPs DV-MT-0012, DV-MT-0019 and DV-MT-0021.

Method	Title	Summary	SOP Section
3005A/200.7_Prep	Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by ICP	Preparation of surface and ground water samples for total recoverable or dissolved metals for analysis by ICP.	10.5
3010A	Acid Digestion of Aqueous Samples and Extracts for Total Metals Analysis by ICP	Preparation of aqueous samples, EP and mobility procedure extracts, and wastes that contain suspended solids for total metals analysis by ICP.	10.7

1.4 Sample digestion requirements are established by the laboratory Project Manager before samples are received. TestAmerica LIMS (TALS) method codes are applied to samples at Login to indicate which digestion is to be used for each sample.

1.5 This procedure can be used for all of the elements listed in Table 1. Additional elements may be analyzed using the digestion methods in this SOP provided the method performance criteria specified in Section 12 and the Quality Control (QC) acceptance criteria specified in Section 9 of this SOP and the ICP determinative SOPs DV-MT-0012, DV-MT-0019 and DV-MT-0021 are met.

1.6 All samples require digestion prior to analysis, with the possible exception of "direct analysis" of dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators do require digestion of dissolved samples. This must be determined by the laboratory Project Manager before projects start, and is communicated to the analysts through Method Comments in TALS.

2.0 Summary of Method

2.1 Method 3005A/200.7_Prep, Total Recoverable, Dissolved Metals or Potentially Dissolved Metals

A representative portion of sample is heated with diluted nitric and hydrochloric acids until substantially reduced in volume. The digestate is filtered (if necessary) and diluted to volume.

2.2 Method 3010A Total Metals

A representative portion of sample is refluxed with nitric acid. This step is repeated until the digestate is light in color or until its color has stabilized. After the digestate has been reduced to a low volume, it is refluxed with hydrochloric acid, filtered (if necessary), and brought up to volume.

3.0 Definitions

3.1 Dissolved Analyte: The concentration of analyte in an aqueous sample that will pass through a 0.45-µm membrane filter prior to acidification (sample is acidified after filtration).

3.2 Potentially Dissolved Metals: The concentration of elements in solution after acidifying the sample with nitric acid to pH < 2, holding at room temperature for 8 to 96 hours, and then filtering through a 0.45-µm membrane filter. This definition is based on the Colorado surface water regulations.

3.3 Total Recoverable Analyte: The concentration of analyte determined by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s).

3.4 Total Metals: The concentration of elements in an unfiltered sample subject to a more rigorous nitric acid / hydrochloric acid digestion than is used for total recoverable metals.

3.5 General Analytical Terms: Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and policy DV-QA-003P, “Quality Assurance Program,” for definitions of general analytical and QA/QC terms.

4.0 Interferences

4.1 Potential sources of trace metals contamination include metallic or metal-containing labware (e.g., talc powdered gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work

areas, and atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2 Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents, and other matrices may not be digested using these methods if they are not miscible with acids. If physical interferences are present, they should be documented in the final report case narrative.

4.3 Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented in the final report case narrative.

4.4 Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs, the sample must be re-prepared. Antimony is easily lost by volatilization from hydrochloric acid media.

4.5 Precipitation of silver chloride (AgCl) may occur when chloride ions and high concentrations of silver (i.e., greater than 1 mg/L) are present in the sample. Method 3005 or 3010 samples containing more than 1 mg/L silver are redigested at a reduced sample volume and reanalyzed to produce more accurate results. Method 200.7 requires samples to be redigested if the silver is greater than 0.1 mg/L.

4.6 Specific analytical interferences are discussed in the ICP determinative methods. See SOPs DV-MT-0012, DV-MT-0019, and DV-MT-0021.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.3.2 Samples that contain high concentrations of carbonates or organic material, or samples that are at elevated pH can react violently when acids are added.

5.3.3 Care must be taken when handling the digestion tubes. The tubes may become very hot during the digestion procedure. Allow the tubes to cool before attempting to touch the digested samples.

5.4 Primary Materials Used

5.4.1 The following is a list of the materials used in this method which have a serious or significant hazard rating.

5.4.2 A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time.

Material (1)	Hazards	Exposure Limit(2)	Signs and Symptoms of Exposure
Stock Standard Solutions	Oxidizer Corrosive Poison	5 mg/m^3 as HNO_3	Toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Nitric Acid (HNO_3)	Corrosive Oxidizer Poison	2 ppm (TWA) 4 ppm (STEL)	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid (HCl)	Corrosive Poison	5 ppm (Ceiling)	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
(1) Always add acid to water to prevent violent reactions. (2) Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 EQUIPMENT AND SUPPLIES

6.1 Instrumentation

6.1.1 Digestion blocks, with adjustable heating, capable of maintaining a sample temperature of 90 - 95 °C.

6.1.2 Thermometer that covers a temperature range of at least 80 - 110 °C, in increments of 1 °C.

6.1.3 Liquid-filled thermometers must have a tag indicating that the accuracy was checked by the QA group within the last 12 months.

6.1.4 Digital thermometers must have a tag showing that they were checked within the last three months.

6.1.5 See SOP DV-QA-0001 for details of the thermometer calibration procedure.

6.1.6 Centrifuge (when the desired method of removing particulates is centrifugation).

6.1.7 Calibrated mechanical pipettes with disposable pipette tips. Pipette calibration is checked in accordance with SOP DV-QA-0008.

6.2 Supplies

6.2.1 Disposable digestion tubes, with volume accuracy verified to ± 3% gravimetrically prior to use. See SOP DV-QA-0008.

6.2.2 Watch glasses, ribbed or equivalent, or disposable digestion tube covers.

6.2.3 Whatman GD/XP - PVDF membrane, 0.45-micron syringe filters (No. 6973-2504), for trace metal analysis, or equivalent. When used to filter any sample in a preparation batch or analytical batch, filters of the same type are also used to filter the method blank and the LCS in the batch. Acceptable results for the QC samples demonstrate that the filters neither add nor subtract analytes.

6.2.4 Syringes or equivalent filtration apparatus.

6.2.5 Re-pipettors or suitable reagent dispensers.

6.2.6 Class A volumetric graduated cylinders.

6.2.7 pH indicator strips.

6.2.8 Plastic digestate storage bottles.

7.0 Standards and Reagents

7.1 Standards must be NIST traceable, where available. Multi-element standards are verified against a second-source standard before they are put into use (the only exception is standards purchased directly from NIST), which is described in SOP DV-QA-0015.

7.2 Stock standards are purchased as custom multi-element mixes or as single-element solutions. Standards are logged into the TALS Reagent Module and are assigned unique identification numbers that can be used to access traceability information.

7.3 All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles.

7.4 Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.5 Standards containing silver must be protected from light using either a cardboard box or amber containers.

7.6 Shelf-Life

7.6.1 Stock standards, standards as received from the vendor, expire on the date assigned by the vendor. If no date is assigned by the vendor, then a one-year expiration will be assigned by the laboratory.

7.6.2 Intermediate concentration standards or working standards may be used for up to six months. The expiration date cannot be later than the date assigned to the stock standard.

7.6.3 Any suspect standards are re-verified, and replaced if re-verification fails.

7.7 Laboratory Control Sample (LCS) Spike Stock Standards

The LCS spike stock standards are custom-made standards purchased from Inorganic Ventures. The standards are designated ICP-SPK-3A (ICP-1) and ICP-SPK-2B (ICP-2) and contain the following elements at ready-to-use concentrations:

LCS Spike Stock Standards

Elements in LCS Spike	Concentration in ppm (µg/mL)
Ca, K, Mg, Na	5,000
P, Si	1,000
Al, Ba, Bi, Se, Tl, U, Sn, S	200
Fe, Sr, Li, B, Mo, Ti, As, Th	100
Co, Mn, Ni, Pb, V, Zn, Sb, Zr	50
Cu	25

Elements in LCS Spike	Concentration in ppm (µg/mL)
Cr	20
Cd	10
Ag, Be	5

7.8 TCLP Spike Stock Standard (TCLP Spike)

The TCLP spike stock standard is purchased from commercial sources. The stock is a custom-made standard purchased at ready-to-use concentrations and designated as TCLP Spike, as follows:

TCLP Spike Stock Standard

Elements in TCLP Spike	Concentration in ppm (µg/mL)
Ba	1,000
Cr, Pb	500
As	300
Cu, Zn	200
Ag, Cd, Se	100

7.9 TCLP Mercury Spike Solution

TCLP leachate matrix spike samples are spiked for both ICP elements and mercury at the time of sample preparation but before preservation. The mercury spike standard is prepared by the mercury analyst as the mercury daily spike solution (Hg Daily Spk) at a concentration of 100 µg/L (SOP DV-MT-0015).

7.10 Reagent Water

Reagent water must be produced by a Millipore de-ionized system or equivalent and must achieve the performance specifications for ASTM Type II water, i.e., conductivity < 1.0 µmhos/cm; resistivity > 1.0 megohms-cm; silica < 3.0 µg/L. In addition, the reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs DV-MT-0012, DV-MT-0019, and DV-MT-0021.

7.11 Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.12 Hydrochloric acid (HCl), concentrated, trace metal grade or better.

8.0 Sample Collection, Preservation, Shipment and Storage

Preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Water	HDPE	500 mL	HNO_3, pH < 2	180 Days	40 CFR Part 136.3

[1] Inclusive of digestion and analysis.

9.0 Quality Control

9.1 The minimum required QC, acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the TALS Method Comments to determine which specific QC requirements apply to each job.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Control Program.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, QA/QC Requirements for Federal Programs.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in TALS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Initial Performance Studies

Before analyzing samples, the laboratory must establish a method detection limit (MDL). In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument he/she will be using. Ongoing proficiency must be demonstrated by each analyst on an annual basis. See Section 12 for more details on initial demonstrations of capability, analyst training and qualification.

9.3 Preparation Batch

A preparation batch is a group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, an LCS, a matrix spike (MS), and a matrix spike duplicate (MSD). In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify samples for the MS/MSD pair, then the batch may contain multiple MS/MSD pairs to accommodate client requests. Clients may also request a duplicate LCS (LCSD). In cases where the client has not provided sufficient sample to prepare an MS and MSD, an LCS and LCSD will be prepared instead.

9.4 Sample Count

Laboratory-generated QC samples (method blanks, LCSs) are not included in the sample count for determining the size of a preparation batch. The MS and MSD are not included in the sample count unless specifically requested by the client. The prep batch consist of the laboratory generated QC and no more than twenty field samples.

9.5 Method Blank (MB)

9.5.1 The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. When samples are filtered in the laboratory for determination of dissolved metals, then the blank is filtered using a filter of the same type that was used for the samples.

9.5.2 TCLP method blanks are prepared by taking 50 mL of TCLP leachate fluid (see SOP DV-IP-0012) through the appropriate procedure as described in Section 10. TCLP method blanks are referred to as LB (extraction fluid 1) and LB2 (extraction fluid 2) in TALS and on the final reports.

9.5.3 One method blank must be processed with each preparation batch. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false-positive data. Method blank results are evaluated by the ICP analysts as described in SOPs DV-MT-0012, DV-MT-0019 and DV-MT-0021.

9.5.4 Acceptance Criteria

The method blank should not contain any analyte of interest at or above ½ the reporting limit (RL) or at or above 10% of the measured concentration of that analyte in associated samples, whichever is higher. In other words, the sample result must be a minimum of 10 times higher than the blank contamination level. Method blank results that are greater than ½ the RL may also be reported if the associated sample results fall below the RL and the client accepts the data.

9.5.5 Corrective Action

If the method blank does not meet the acceptance criteria, the blank and all associated samples in the batch must be re-digested and reanalyzed.

9.6 Laboratory Control Sample (LCS)

9.6.1 One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. When samples are filtered in the laboratory for determination of dissolved metals, then the LCS is filtered using a filter of the same type that was used for the samples.

9.6.2 An LCS for a batch of aqueous samples is prepared by adding 0.5 mL of each of the LCS spike stock standards, ICP-1 and ICP-2 (Section 7.7), to 50 mL of reagent water. This produces the final concentrations shown in Table 1.

9.6.3 An LCS for a TCLP batch is prepared by adding 0.5 mL of each of the LCS spike stock standards, ICP-1 and ICP-2 (Section 7.7), plus 0.5 mL of the TCLP Spike stock standard (Section 7.8) to 50 mL of the TCLP leachate solution (see SOP DV-IP-0012). This produces the final concentrations shown in Table 2.

9.6.4 The LCS is used to monitor the accuracy of the analytical process. LCS results are evaluated by the ICP analyst as described in SOP DV-MT-0012. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

9.6.5 Acceptance Criteria

LCS recovery control limits are set at ± 3 standard deviations about the historical mean. These limits must not be wider than 85 - 115 % recovery for Method 200.7 or 80 - 120 % for Method 6010. The control limits are maintained in the LIMS system.

9.6.6 Corrective Action

If the LCS percent recovery falls outside of the control limits for any analyte, that analyte is judged to be out of control. All associated samples must be reprocessed for analysis. One possible exception is a recovery for a given element above the upper control limit with no

detection for the same element in the samples. This latter case must be documented in an NCM and explained in the case narrative.

9.7 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.7.1 A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Normally, one MS/MSD pair is digested with each preparation batch. Samples identified as field blanks, equipment blanks, or rinse blanks are not appropriate for use as the batch MS/MSD.

9.7.2 Some programs (e.g., South Carolina and North Carolina) require that MS/MSD pairs are run at a 10% frequency. Also, some clients may require unspiked duplicate samples in place of or in addition to an MS/MSD pair. Check special project instructions attached as Method Comments in TALS and any project QASs before starting the batch.

NOTE: This method does not require a sample duplicate. Precision is measured using the MS/MSD. Use of the MS/MSD precision is preferred as not all samples will contain measurable concentrations of target analytes. Samples that have target analytes at low concentrations or non-detectable levels do not provide useful precision data. When an MS/MSD is not available, the LCS and LCSD are used to measure precision.

9.7.3 If insufficient sample is available to process an MS/MSD pair, then a duplicate LCS must be processed and an NCM generated. The LCS pair is then evaluated according to the MS/MSD criteria.

9.7.4 The purpose of analyzing matrix spike samples is to assess the effect of the sample matrix on the accuracy and precision of the analysis. MS/MSD results are evaluated by the ICP analysts as described in SOPs DV-MT-0012, DV-MT-0019 and DV-MT-0021. If the MS/MSD results fail to meet control limits while the LCS results are in control, then something about the sample matrix is interfering with the analysis.

9.7.5 Matrix spikes for aqueous sample batches are prepared by adding 0.5 mL of each of the LCS spike stock standards, ICP-1 and ICP-2 (Section 7.7), to a digestion tube containing 50 mL of the selected sample. The final spike concentrations are shown in Table 1.

9.7.6 Matrix spikes for TCLP batches are prepared by adding 0.5 mL of the TCLP Spike stock standard (Section 7.8) plus 0.5 mL of each of the LCS spike stock standards, ICP-1 and ICP-2 (Section 7.7), to 50 mL of the parent TCLP aliquot. A second aliquot is spiked for mercury analysis at by adding 1.5 mL of the 100 mg/L Hg standard (Hg Daily Spk) to 30ml of parent sample. The matrix spike samples are then preserved with HNO_3 to pH < 2. The final spike concentrations are shown in Table 2.

NOTE: The MS and MSD must be spiked prior to preservation of the leachate.

9.7.7 Acceptance Criteria

The recovery for each analyte must fall within established limits. The relative percent difference (RPD) between the MS and MSD must be less than or equal to the established RPD limit. If any analyte recovery or relative percent difference (RPD) between the MS and MSD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS.

9.7.8 Corrective Action

If MS/MSD results fail to meet control limits, but the LCS results are within limits, then samples do not require re-preparation and reanalysis unless the results indicate that a spiking error may have occurred. If the recovery of the LCS also failed acceptance criteria, then corrective action must be taken. Corrective action will include re-preparation and reanalysis of the batch. One possible exception is an LCS recovery for a given element above the upper control limit with no detection for the same element in the samples. This latter case must be documented in an NCM and explained in the case narrative.

9.8 Continuing Calibration Verification Standard (CCV)

Continuing calibration verification standards (CCVs) are not digested but are instead created and evaluated by the ICP analysts as described in SOPs DV-MT-0012, DV-MT-0019 and DV-MT-0021.

9.9 Second-Source Initial Calibration Verification (ICV) Standard

Initial calibration verification standards (ICVs) are not digested but are instead created and evaluated by the ICP analysts as described in SOPs DV-MT-0012, DV-MT-0019 and DV-MT-0021.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 All data shall be recorded directly on the described forms, logbooks, electronic forms, or directly in TALS at the time of data generation. It is not acceptable to record data on loose papers, scraps of paper, gloves, sample vials, or "Post-It" notes. Data may be recorded on paper bench sheets if the sheets are subsequently scanned and saved in a designated folder on the company server.

10.4 Sample Preparation

10.4.1 Samples are typically logged in as either water or solid. Waste such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating sample preparation, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous, but it appears to be a waste (biphasic, oil, sludge-like, organic liquid, lots of sediment, etc.), contact the project manager and the laboratory Technical Specialist for further instructions. It may be necessary to subcontract these samples to a laboratory with the capability to digest organic matrices.

NOTE: TestAmerica Denver has not implemented digestion methods for water-immiscible organic matrices, e.g., oils. Samples that are known to be incompatible with TestAmerica Denver digestion techniques are typically subcontracted to other laboratories.

10.4.2 All samples are to be electronically checked out of sample control using the TALS Internal Chain of Custody (ICOC) module.

10.4.3 Proper sample identification is extremely important in any preparation procedure. Labeling of beakers, digestion tubes, and bottles must be done in a manner to ensure connection with the proper sample.

10.4.4 If possible, prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab, data review and reporting.

10.4.5 Guidelines are provided in Appendix 1 on procedures to minimize contamination of samples and standards.

10.5 Aqueous Sample Preparation Setup

The following setup procedure must be followed for all aqueous samples prior to performing the specific digestion procedure. The sample preparation procedures for Methods 3005A and 3010A detailed in the following sections are also summarized in work instruction WI-DV-016.

10.5.1 Verify sample pH

10.5.1.1 Measure the sample pH with pH paper using a separate aliquot of sample. This can be done using disposable plastic droppers or pouring the sample on to the pH paper. Do not put the pH paper directly into the bottle. Record the pH on a

copy of the internal chain of custody (ICOC). When all of the samples have been tested, initial and date the copy of the ICOC, scan it, and save it to the Metals folder on the G: drive.

10.5.1.2 All water sample pH's must be verified and documented before digestion.

10.5.1.3 If the pH>2 for a sample requiring acidic preservation, record the job in the Sample Filtration and Preservation Logbook.

10.5.1.4 If laboratory preservation is required, add 1-2 mL of conc. HNO_3 to the sample. Replace the lid and mix the sample. If the pH is still >2 add another addition of HNO_3. Do not add more than 5 mL. If the pH is still >2 create an NCM saying the sample will not preserve.

10.5.1.5 Allow the sample to sit for 8-16 hours following acidification.

10.5.1.6 Recheck the pH of the sample. If the pH>2, repeat Section 10.5.1.4 until the pH holds at <2 or 5 mL of HNO_3 has been added. If the pH is still >2 after the addition of 5 mL of HNO_3 create an NCM saying the sample will not preserve.

10.5.1.7 Samples cannot be digested for 24 hours after preservation. Note the date/time of this pH recheck in the Metals Prep Log in the LIMS.

10.5.1.8 Leachates or portions of leachates for metallic analyte deteminations must be acidified with nitric acid to a pH <2 unless precipitation occurs. Test a small portion of sample to see if precipitation occurs. If a precipitate forms do not acidify the leachate and analyze as soon a possible. Leachates may be digested as soon as they are acidified.

10.5.2 Select the unfiltered fraction for a total or total recoverable analysis or the filtered fraction for a dissolved analysis. If requested by the client, select the filtered fraction for a total dissolved analysis. For TCLP and SPLP, select the proper sample leachates.

NOTE: Samples requiring dissolved metals determination are either filtered and preserved in the field or are filtered and preserved by the laboratory as soon as possible after receiving the samples. When filtered in the laboratory, the filtration and preservation are recorded in the Laboratory Sample Filtration and Preservation Logbook, including the preservative type and lot number. Filter acceptability is demonstrated by using filters of the same type to filter samples and batch QC samples when preparation batches include samples that were filtered in the laboratory. The results of the analysis of the batch QC samples are used to demonstrate that the filtration process neither adds nor subtracts target analytes from samples. The performance of

the filtration process is recorded in TALS.

10.5.3 Mix the sample by shaking the container.

10.5.4 Measure and transfer 50 mL of the sample into a digestion tube (record the lot number of the digestion tubes used in the LIMS). When using calibrated digestion tubes, pour the sample into the tube to the 50 mL mark. For TCLP sample batches pour 10 mL of samples and bring to 50 mL with reagent water. Unless specifically required for a project, all samples are measured by volume and not by weight. Record the volume and units on the preparation bench sheet in TALS. If the digestion cup is filled beyond the required mark, the excess sample must not be poured back into the original container, but must be disposed of as waste.

10.5.5 Mix the sample by shaking the container and then measure two extra aliquots of the sample that is selected for the MS/MSD analysis. Spike each aliquot as described in Section 9.7. Refer to Section 9.7.6 for specific instructions for spiking the selected TCLP sample. Record the standards and pipette identifications in TALS.

10.5.6 Measure and transfer 50 mL of reagent water into a digestion tube for the method blank. If a determination of dissolved metals is requested (LIMS 3005A), use filtered reagent water for the method blank. For TCLP sample batches, measure 10 mL of the TCLP leachate solution and bring to 50 mL with reagent water for the blank. See Section 9.5 for a detailed description of the method blank.

10.5.7 Measure and transfer 50 mL of reagent water into a digestion tube for the LCS and add the spiking solutions as described in Section 9.6.2. For TCLP sample batches, use 10 mL of TCLP leachate fluid and bring to a final volume of 50ml with reagent water for preparing the LCS (Section 9.6.3). Record the standards and pipette identifications in TALS. If determination of dissolved metals is requested and one or more samples were filtered in the laboratory, then filter the LCS using a filter of the same type that was used to filter the sample(s).

10.5.8 If the analysis is for total recoverable, dissolved metals, or potentially dissolved metals, continue on with Section 10.5. If the analysis is for total metals, skip Section 10.6 and go to Section 10.7.

10.6 Total Recoverable, Dissolved, or Potentially Dissolved Digestion for Waters by 3005A and 200.7_Prep.

10.6.1 Add 1 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl to the sample in the digestion tube.

10.6.2 Heat at 90-95 °C until the volume is reduced to between 15 and 20 mL. Record the start and stop times, digestion block temperature (observed and corrected) and the thermometer ID in TALS.

CAUTION: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be re-prepared.

10.6.3 Allow the digestion tube to cool in a fume hood.

10.6.4 Wash down the digestion tube walls with reagent water.

10.6.5 Add 1.5 mL of concentrated HNO_3 to the digestate.

10.6.6 Revolume to 50 mL with reagent water. Cap and shake to mix.

10.6.7 If insoluble materials are present, the sample will be filtered at the instrument by the analyst.

NOTES: If any samples in a preparation batch are filtered, the method blank and LCS associated with that batch must also be filtered.

Instead of filtering, the samples may be diluted and mixed and then centrifuged or allowed to settle overnight to remove insoluble material from the supernatant solution.

10.6.8 The sample is now ready for analysis.

10.7 Total Metals Digestion for Waters or TCLP Leachates by 3010A

10.7.1 Add 1.5 mL of concentrated HNO_3 to the sample in the digestion tube.

10.7.2 Heat at 90-95 °C until volume is reduced to 10 ± 5 mL. Record the start and stop times, digestion block temperature (observed and corrected) and the thermometer ID in TALS.

CAUTION: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be re-prepared.

10.7.3 Allow the digestion tube to cool in a fume hood.

10.7.4 Add another 1.5 mL portion of concentrated HNO_3 and cover the sample with a watchglass.

10.7.5 Continue refluxing until the digestion is complete.

NOTE: Digestion is complete when the digestate is light in color or does not change in appearance. For most samples the addition of two nitric acid aliquots is sufficient. Additional aliquots of nitric acid may be added if necessary.

10.7.6 Evaporate to a low volume of 5 to 10 mL. If the sample does go to dryness, the digestion must be started over using a fresh portion of sample.

10.7.7 Allow the digestion tube to cool in a fume hood.

10.7.8 Add 2.5 mL of concentrated HCl.

10.7.9 Cover and reflux for an additional 15 minutes to dissolve any precipitate or residue.

10.7.10 Wash down the digestion tube walls and watch glass (or digestion tube cover) with reagent water.

10.7.11 Adjust to 50 mL final volume with reagent water. This must be done volumetrically, and not using a balance.

10.7.12 If insoluble materials are present, the sample will be filtered at the instrument by the analyst.

NOTES: If any samples in a preparation batch are filtered, the method blank and LCS associated with that batch must also be filtered.

Instead of filtering, the samples may be diluted and mixed and then centrifuged or allowed to settle overnight to remove insoluble material from the supernatant solution.

10.7.13 The sample is now ready for analysis.

10.8 Calibration

10.8.1 The digestion block temperature must be maintained between 90 and 95 °C. The temperature must be monitored continuously while in use and must be recorded in TALS. The temperature must be monitored by measuring the temperature of reagent water contained in a capped digestion tube that is placed in each digestion block. The thermometer used and the start and end times for all temperature cycles are recorded in TALS.

10.8.2 The thermometer is calibrated in accordance with SOP DV-QA-0001, Thermometer Calibration Procedures.

11.0 Calculations / Data Reduction

11.1 This SOP does not produce any analytical data. See the determinative method SOPs DV-MT-0012, DV-MT-0019 or DV-MT-0021 for data analysis and applicable calculations.

11.2 Documentation

11.2.1 All of the preparation information is recorded and stored in TALS.

11.2.2 The preparation information includes:

11.2.2.1 Batch number, job and sample numbers, preparation date, and analyst name;

11.2.2.2 Matrix and prep type;

11.2.2.3 Initial sample pH, Initial sample volume and final volume;

11.2.2.4 Reagent manufacturer and lot number for each reagent used;

11.2.2.5 Digestion tube lot information;

11.2.2.6 Standard identification number for each standard used;

11.2.2.7 Start and stop times for digestions;

11.2.2.8 Observed and corrected temperature readings during digestion;

11.2.2.9 Identification numbers of calibrated measuring equipment used (thermometers, balances, pipettes, etc.).

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

12.1.1 An initial method detection limit study is performed for each analyte and each sample matrix type in accordance with Policy DV-QA-005P. An MDL verification is performed once a year to satisfy NELAC 2003/2009 requirements. For DoD, AFCEE and Texas TRRP projects, an MDL verification is performed quarterly. MDLs are stored in TALS.

12.1.2 The current MDL value is maintained in TALS.

12.2 Demonstration of Capabilities

An initial demonstration of capability for each method must be performed prior to analyzing samples.

12.2.1 For the standard analyte list, the initial demonstration consists of the preparation and analysis of a QC check sample containing all of the standard analytes for the method, as well as a method detection limit (MDL) study.

12.2.2 Four aliquots of the QC check sample are analyzed with the same procedures used to analyze samples, including sample preparation.

12.2.3 The mean recovery and standard deviation are calculated for each analyte of interest. These results are compared with the established or project-specific acceptance criteria. All four results must meet acceptance criteria before the method can be used to analyze samples.

12.2.4 For non-standard analytes, an MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event, the minimum initial demonstration required is successful analysis of an extracted standard at the reporting limit and a single point calibration.

12.3 Training Requirements

12.3.1 The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

12.3.2 Each analyst performing the method must complete a demonstration of capability (DOC) by successfully preparing and/or analyzing four consecutive LCSs, or a blind performance evaluation (PE) sample, or other acceptable QC samples. The results of the DOC study are summarized in the NELAC format, as described in SOP DV-QA-0024. DOCs are approved by the Quality Assurance Manager and the Technical Director. DOC records are maintained by the QA staff in the central training files. Analysts who continue to perform the method must successfully complete a demonstration of capability annually.

13.0 Pollution Control

13.1 This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

13.2 Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in Section 13, *Waste Management and Pollution Prevention*, of the Environmental Health and Safety Manual, and DV-HS-001P, *Waste Management Plan*.

14.2 The following waste streams are produced when this method is carried out:

14.2.1 Expired Chemicals/Reagents/Standards: Contact Waste Coordinator

14.2.2 Acidic waste from sample digests: Waste Stream J.

NOTE: Radioactive, mixed waste and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure

15.0 References / Cross-References

15.1 SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

15.1.1 Method 3005A, Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy, Revision 1, July 1992.

15.1.2 Method 3010A, Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy, Revision 1, July 1992.

15.2 Method 200.7, Determination of Metals And Trace Elements In Water And Wastes By Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, 1994.

16.0 Method Modifications

16.1 Modifications Specific to MCAWW Methods (200.7_Prep)

It was determined by technical review that several of the MCAWW methods were equivalent to the SW-846 methods and therefore were combined under the scope of this SOP as described in Section 10.0. The nature of the differences were deemed insignificant in regards to the amount of acid added and the evaporative volume based on the flexibility allowed by the methods (i.e., add additional acid as required) and the subjective wording of the methods (i.e., evaporate to near dryness versus an exact volume).

16.2 Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above ½ the reporting limit. Common laboratory contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

16.3 The referenced methods use 100 mL of sample for digestion. This SOP uses a 50 mL aliquot, with a proportional reduction in digestion reagents. This change is made to allow better control of temperature and potential sample contamination with the use of the digestion block. It is also considered one of the laboratory's hazardous waste reduction initiatives.

16.4 The use of reduced sample volumes are supported in EPA's document "Response to Public Comments Background Document, Promulgation of the Second Update to SW-846, Third Edition" dated November 3, 1994. This document states "flexibility to alter digestion volumes is addressed and 'allowed' by the table (3-1)

and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples..." EMSL-Ci has also taken the stance that "reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology."

17.0 Attachments

Table 1. Matrix Spike and Aqueous Laboratory Control Sample Levels

Table 2. TCLP Reporting Limits, Regulatory Limits, and Matrix Spike Levels

Appendix 1. Contamination Control Guidelines

18.0 Revision History

- Revision 8 dated 30 June 2015
  - Updated Section 10.5.1.1 to include statement about not putting the pH paper into the bottle
  - Added language to Section 4.5 for clarification
  - Added new Section 10.3 reminding analysts to enter data directly at time of acquisition

- Revision 7 dated 31 October 2014
  - Annual technical review
  - Removed reference to SOP DV-IP-0017 for oils in section 1.2
  - Added maximum silver concentration to section 4.5 for method 200.7
  - Updated standard ID's for sections 7.7 and 7.8 and added Sulfur to the spike list
  - Corrected intermediate standard expirations from three months to six months
  - Removed duplicate analyte spike levels in ICP spike standards
  - Changed references from LIMS to TALS
  - Corrected concentration of Hg Daily spike standard
  - Removed Figures 1 and 2
  - Corrected various grammar and language errors
  - Corrected analyte spike levels in Table 1

- Revision 6 dated 08 October 2013
  - Updated sections 10.4.1.3, 10.4.1.4 and 10.4.1.6 about preservation procedure and removed the comment about recording the amount of acid added in the preservation logbook

- Revision 5, dated 15 July 2013
  - Annual review
  - Changed section 10.5.5, 7.3, 9.4, 9.5.2, 9.5.4, 10.3.1, 10.3.2, 10.4, 10.4.4, 10.5.2, 10.6.2, 11.2.2, 12.1.1 and 12.3 to reflect current practices
  - Corrected formatting and grammatical errors
  - Clarified sample matrices for this method in section 1.2
  - Corrected references in table associated with section 1.3
  - Added ICP determinative SOPs to sections 1.5, 4.6, 7.10, 9.5.3, 9.7.4
  - Added 200.7_Prep whenever 3005A was referenced
  - Edited section 3.5 to reflect current reference
  - Removed note associated with section 5.4.1
  - Added SOP reference to section 6.2.1
  - Removed references to Denver Standards Log and replaces those references with TALS reagent module

- Correct standard names in section 7.7
- Removed references to Supplemental Metals Prep Sheet
- Updated sections 10.4.4, 10.4.6 and 10.4.7 for 10 mL TCLP sample aliquot
- Added reference to 200.7 in Section 15

- Revision 4.7, dated 18 July 2012
  - Annual review
  - Updated Section 9.1, 10.1 and 10.2 to reflect current practice
  - Updated Section 9.7.6 on spiking TCLP aliquots
  - Added section 10.4.1.9 for TCLP preservation
  - Removed Appendix 2. Added reference to work instruction in Section 10.4
  - Updated Figures 1 and 2 to reflect current practice.
  - Formatting and editorial changes throughout

- Revision 4.6, dated 24 August 2011
  - Added recommendation to use disposable bulbs for pH checking in section 10.8.1.
  - Added requirement to store samples with a Rush form after preserving in section 10.8.1.2.

- Revision 4.5, dated 31 January 2011
  - Change note in section 10.8.1.8 to be 24 hours before preparation.

Earlier revision histories have been archived and are available upon request.

Table 1.

Matrix Spike and Aqueous Laboratory Control Sample Levels

Element	LCS Concentration (ug/L)	Matrix Spike Concentration (ug/L)
Aluminum	2,000	2,000
Antimony	500	500
Arsenic	1,000	1,000
Barium	2,000	2,000
Beryllium	50	50
Bismuth	2,000	2,000
Boron	1,000	1,000
Cadmium	100	100
Calcium	50,000	50,000
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1,000	1,000
Lead	500	500
Lithium	1,000	1,000
Magnesium	50,000	50,000
Manganese	500	500
Molybdenum	1,000	1,000
Nickel	500	500
Phosphorous	10,000	10,000
Potassium	50,000	50,000
Selenium	2,000	2,000
Silicon	10,000	10,000
Si (as SiO2)	21,400	21,400
Silver	50	50
Sodium	50,000	50,000
Strontium	1,000	1,000
Thallium	2,000	2,000
Tin	2,000	2,000
Titanium	1,000	1,000
Uranium	2,000	2,000
Vanadium	500	500
Zinc	500	500
Zirconium	500	500

Table 2.

TCLP Reporting Limits, Regulatory Limits, and Matrix Spike Levels

Element	RL (mg/L)	Regulatory Limit (mg/L)	Spike Level (mg/L)
Arsenic	0.1	5,000	5.0
Barium	1.0	100,000	12.0
Cadmium	0.05	1,000	1.05
Chromium	1.0	5,000	5.2
Lead	0.03	5,000	5.5
Selenium	0.05	1,000	3.0
Silver	0.1	5,000	1.05

Appendix 1.

Contamination Control Guidelines

The following procedures are strongly recommended to prevent contamination:

- All work areas used to prepare standards and spikes should be cleaned before and after each use.
- All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.
- Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.
- Powdered or latex gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.
- Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.
- Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

- Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.
- Improper cleaning of glassware can cause contamination.
- Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

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Title: Determination of Solids in Waters and Wastes [SM 2540B, SM 2540C, SM 2540D, and EPA 160.4]

Approvals (Signature/Date):

Andrew Allen — Date 6/17/15
Technical Specialist

Adam Alban — Date 22 June 15
Health & Safety Manager / Coordinator

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Quality Assurance Manager

William S. Cicero — Date 6/23/15
Laboratory Director

Facility Distribution No. _____ **Distributed To:** _____

1.0 Scope and Application

1.1 This SOP is applicable to the determination of total solids, total suspended solids, total dissolved solids, volatile solids, and volatile suspended solids using gravimetric techniques. This SOP is applicable to drinking, surface, and saline waters and domestic and industrial wastes.

1.2 The methods cover a practical range of 10 mg/L to 20,000 mg/L (TSS: 4 mg/L - 20,000 mg/L). As a practical matter, the final residue weight should be limited to about 200 mg.

1.3 Reporting limits for each method are:

Reported Analyte	RL (mg/L)
Total Solids	10
Total Dissolved Solids	10
Total Suspended Solids	4
Total Volatile Solids	10
Volatile Suspended Solids	10

1.4 The procedure for settleable solids is found in SOP DV-WC-0032.

1.5 The procedure for percent moisture in solid samples is found in SOP DV-WC-0023.

1.6 The method is extended to solid matrices for Total Solids and Total Volatile Solids. For these applications the result is reported as a percentage.

2.0 Summary of Method

2.1 **Total Solids (TS):** A well-mixed aliquot of the sample is quantitatively transferred to a preweighed evaporating dish and evaporated to dryness at 103-105 °C. The increase in weight over that of the empty dish represents the total solids.

2.2 **Total Dissolved Solids (TDS):** A well-mixed sample is filtered through a glass fiber filter. The filtrate is quantitatively transferred into a preweighed evaporating dish and is evaporated to dryness and then dried to constant weight at 180 °C. The increase in weight over that of the empty dish represents the total dissolved solids. The filter from this procedure may also be used for TSS/VSS determination.

2.3 **Total Suspended Solids (TSS):** A well-mixed sample is filtered through a pre-weighed glass fiber filter. The residue on the filter is dried to constant weight at 103-105 °C. The increase in weight over that of the pre-weighed filter represents the TSS content. The filtrate from this procedure may be used for TDS determination. The filter from this procedure may also be used for VSS analysis.

2.4 **Total Volatile Solids (TVS):** The residue obtained from the determination of total solids is ignited at 550 °C in a muffle furnace. The loss of weight on ignition is reported as mg/L volatile solids.

2.5 **Volatile Suspended Solids (VSS):** The residue obtained from the determination of total suspended solids is ignited at 550 °C in a muffle furnace. The loss of weight on ignition is reported as mg/L volatile suspended solids.

3.0 Definitions

3.1 **Total Solids (TS):** The term applied to the residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at 103-105 °C. Total Solids includes "total suspended solids," the portion of solids retained by a filter, and "total dissolved solids," the portion that passes through the filter.

3.2 **Total Dissolved Solids (TDS):** Those solids capable of passing through a glass fiber filter and dried to constant weight at 180 °C. TDS is also referred to as filterable residue. The reporting limit is 10 mg/L.

3.3 **Total Suspended Solids (TSS):** Those solids which are retained by a glass fiber filter and dried to constant weight at 103-105 °C. TSS is also referred to as non-filterable residue.

3.4 **Total Volatile Solids (TVS):** The portion of total solids which is lost on ignition at 550 °C.

3.5 **Volatile Suspended Solids (VSS):** The portion of suspended solids which is lost on ignition at 550 °C.

3.6 **Aliquot:** A representative portion of a sample.

3.7 **Reagent Water:** Deionized water which is free of the analyte(s) of interest.

4.0 Interferences

4.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All these materials must be routinely demonstrated to be free from interferences under the conditions of analysis by running method blanks.

4.2 Non-homogeneous samples may give erroneous results. Samples should be mixed as thoroughly as possible before removing an aliquot for analysis.

4.3 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result. The presence and removal of these artifacts should be noted on the benchsheet in the TestAmerica LIMS (TALS).

4.4 Samples containing large amounts of solids may filter slowly. Prolonged filtration times resulting from filter clogging may produce high TSS results due to increased colloidal materials captured on the clogged filter.

4.5 Oil and grease in the samples will cause unreliable results due to difficulty in drying to constant weight. Floating oil and grease, if present, should be included in the sample and dispersed by vigorous shaking.

4.6 Filter material, pre-washing, post-washing, and drying temperatures are specified because these variables have been shown to affect the results.

4.7 The temperature at which the residue is dried has an important bearing on the results because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating.

4.8 Each sample requires close attention to desiccation after drying. Open the desiccator as little as possible to prevent moist air from entering. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

4.9 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride, and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.

4.10 Samples containing high concentrations of bicarbonate may require careful and possibly prolonged drying to ensure that all the bicarbonate is converted to carbonate.

4.11 Too much residue in the drying vessel will crust over, entrapping water that will not be driven off during drying. Total residue should be limited to about 200 mg.

4.12 Some samples may have fine suspended solids which will pass through the glass fiber filter causing high TDS results.

4.13 Aluminum pans should not be used for TS or TDS analyses. Components in some samples may react to form aluminum compounds, causing unreliable results.

4.14 For samples high in dissolved solids, thoroughly wash the filter to ensure removal of dissolved material prior to TSS determination.

4.15 The volatile solids tests are subject to many errors due to the loss of water of crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics and decomposition of mineral salts during combustion. The results should not be considered an accurate measure of organic carbon in the sample.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use.

It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

Eye protection that satisfies ANSI Z87.1 (as per the Environmental Health and Safety Manual), laboratory coat, and nitrile or latex gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.4 Primary Materials Used

There are no materials used in this method that have a serious or significant hazard rating. A complete list of materials used in the method can be found in the reagents and standards section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

6.0 Equipment and Supplies

6.1 Analytical balance capable of weighing to 0.0001 g. The balance calibration is checked each day of use with three Class 1 weights that bracket the range of use. Details for this procedure are covered in SOP DV-QA-0014.

6.2 Vacuum filtration apparatus.

6.3 Vacuum pump equipped with moisture trap.

6.4 Glass fiber filter disks, 47 mm, without organic binder (Gelman Type A/E) or equivalent. The laboratory currently uses pre-washed and pre-weighed filters purchased from an outside vendor for TSS and TVSS. If these pre-prepared filters are not available, filters can be prepared as stated below (Section 6.4.2).

6.4.1 Verification of pre-weighed filters

6.4.1.1 Pre-weighed filters are verified to ensure accuracy of values. For each lot number, seven filters are selected for comparison.

6.4.1.2 A verification spreadsheet is used to record the verification of the pre-weighed filters. This spreadsheet can be found at R:\\QA\Edit\FORMS\Wet Chemistry\Pre-weighed filter verification spreadsheet.

6.4.1.3 The pre-weighed dish numbers are entered in the “Dish Number” section and values given by the vendor are entered into the “Vendor Weights” section of the spreadsheet.

6.4.1.4 The filters are weighed on an analytical balance. Observed values must not differ from vendor reported values by more than 0.0005 grams.

The finished spreadsheet is saved as a new file within the Wet Chemistry folder on the public server. The completed files can be found at:

G:\\Wetchem\Hidden\Data\Forms\TDSTSS\Filter Lot Verification\2014

6.4.2 Preparation of Glass Fiber Filter Disk for TSS/VSS

NOTE: This procedure is only used if pre-prepared filters are not available.

6.4.2.1 Place the glass fiber filter disks, one at a time, on the membrane filter apparatus with wrinkled surface up.

6.4.2.2 While vacuum is applied, wash the disk with three successive (approximately) 20 mL volumes of distilled water.

6.4.2.3 Remove all traces of water by continuing to apply vacuum after water has passed through and discard washings.

6.4.2.4 Remove filter from membrane filter apparatus and place in a labeled, aluminum weighing dish and dry in an oven at 103-105 °C for one hour.

6.4.2.5 Remove the weighing dish from the oven and place in a desiccator and cool to room temperature.

6.4.2.6 Weigh the cooled filter and aluminum weighing dish to the nearest 0.0001 g using an analytical balance. Record the weight and the dish identification number on the benchsheet.

6.5 Glass beakers, minimum 150 mL volume, must be thoroughly cleaned, rinsed with de-ionized water and baked at 180 ± 2 °C for TDS at least one hour before use. Transfer to a desiccator and allow them to cool completely before use.

NOTE: Glass beakers must not be used for procedures requiring a muffle furnace. In that case, porcelain dishes, pre-dried and weighed, must be used.

6.6 Ceramic bowls, minimum 150 mL volume, must be thoroughly cleaned, rinsed with de-ionized water and baked in the muffle Furnace at 550°C for TS and TVS at least one hour before use. Transfer to a desiccator and allow them to cool completely before use.

6.7 Desiccators providing sufficient space for storage of in process samples separate from filters and evaporating dishes.

6.8 Desiccant containing a color indicator of moisture concentration or an instrumental indicator.

6.9 Drying ovens set at 103-105 °C and 180 ± 2 °C. Separate ovens should be maintained at appropriate temperatures if possible.

6.10 Muffle furnace (550 °C ± 50 °C).

6.11 Thermometers, NIST traceable.

6.12 Conductivity meter and associated apparatus.

6.13 Graduated cylinders, assorted sizes.

6.14 Volumetric flasks, Class A, assorted sizes.

6.15 Aluminum weighing dishes large enough to hold a 47 mm filter.

6.16 Forceps for handling filters.

6.17 Crucible tongs.

6.18 Zetex gloves or other gloves capable of providing protection at 550 °C.

6.19 Computer Software and Hardware

Please refer to the master list of documents, software and hardware located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

7.0 Reagents and Standards

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water must be produced by a Millipore DI system or equivalent (see also Section 10.9.3).

7.3 TDS/TS LCS solution 500 mg/L (TDS LCS):

Place 500.0 mg of sodium chloride into a 1000 mL volumetric flask and dilute to volume with deionized water. Mix well. Prepare fresh every three months. Alternatively, a commercially available LCS solution may be used.

NOTE: The LCS solution is not applicable for TS determination in solid samples.

7.4 TSS LCS solution 100 mg/L (TSS Daily STD):

Commercially available reference materials are used for the TSS LCS. Prepare according to manufacturer instructions.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Method	Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
TS	Water	HDPE	100 mL	Cool, $\leq 6^{o}C$	7 Days	40 CFR Part 136.3
TDS	Water	HDPE	100 mL	Cool, $\leq 6^{o}C$	7 Days	40 CFR Part 136.3
TSS	Water	HDPE	100 mL	Cool, $\leq 6^{o}C$	7 Days	40 CFR Part 136.3
TVS	Water	HDPE	100 mL	Cool, $\leq 6^{o}C$	7 Days	40 CFR Part 136.3
VSS	Water	HDPE	100 mL	Cool, $\leq 6^{o}C$	7 Days	40 CFR Part 136.3

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the TALS Method Comments to determine which specific QC requirements to apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Assurance Program.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs. This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated. Any deviation or exceptions from QSM 5.0 requirements must have prior approval in the project requirements.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in TALS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. See QC Policy DV-QA-003P for further details.

9.3 Method Blank

A method blank is required with every batch of 20 or fewer samples. The blank is deionized water taken through the procedure like a sample.

Acceptance Criteria: The general requirement is that the method blank result must be less than ½ the reporting limit or one-tenth of the concentration found in the associated samples (for samples with concentrations above the RL). Note that some agencies (e.g., South Carolina) require that the blank must be less than the MDL – see special requirements in TALS to determine which criterion applies.

Corrective Action: If the method blank exceeds allowable levels, all associated samples must be reanalyzed

9.4 Laboratory Control Sample (LCS)

One LCS is required with each analytical batch. The process of establishing control limits is described in more detail in QC Policy DV-QA-003P. The LCS solution is not applicable for TS determination in solid samples.

NOTE 1: The LCS solution is not applicable for TS determination in solid samples.

NOTE 2: The LCS/LCSD is not prepared for the determination of Total Volatile Solids. It is not possible to adequately represent the volatiles that may be present in the samples.

Acceptance Criteria: Historical control limits are based on three standard deviations of past results, and must be 80-120% or tighter.

Corrective Action: If the LCS exceeds allowable levels, all associated samples must be reanalyzed.

9.5 Duplicate Sample Analysis

A sample duplicate is required with each analytical batch with a minimum of one duplicate for every set of 10 or fewer samples (e.g. one to ten samples, one duplicate, eleven to twenty samples, two duplicates). The process of establishing control limits is described in more detail in QC Policy DV-QA-003P.

Acceptance Criteria: The relative percent difference (RPD) must be within 10% for TS, TSS and TDS and 20% for TVS and Percent Solids. The control limits only apply to samples with results greater than 5 times the RL. The process of establishing control limits is described in more detail in the QC Policy DV-QA-003P.

Corrective Action: If the RPD exceeds the acceptance limit the sample should be reanalyzed.

NOTE: Method precision is assessed using the sample duplicate. It is not feasible to spike a sample for the determination of solids so the Matrix Spike/Matrix Spike Duplicate is not analyzed by this procedure.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 Proper sample identification is extremely important in any analytical procedure. Labeling of evaporating dishes and filters holders must be done in a manner to ensure connection with the proper sample.

10.4 If possible, analyze all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.

10.5 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result. The presence/removal of these artifacts should be noted on the benchsheet.

10.6 If samples are visibly oily, this should be noted on the benchsheet.

10.7 If there is limited sample volume or high solids content, smaller amounts of sample may need to be processed than detailed in the following sections. This occurrence must be noted on the benchsheet and reporting limits must be adjusted appropriately.

10.8 When aliquoting samples Class A or wide-bore pipettes are to be used.

NOTE: Disposable narrow-bore pipette tips may be used when modified by removing the tip. If a modified tip is used the pipette must be calibrated with a modified tip prior to aliquoting samples.

10.9 Calibration

NOTE: Calibration of a balance for use in a gravimetric test is a verification, not a determination of the relationship between concentration and response, therefore, use of an ICV, CCV or internal standard is not applicable to this procedure.

10.9.1 Proper balance operation will be verified daily or prior to sample analysis by following SOP DV-QA-0014.

10.9.2 Oven temperature must be checked daily and recorded on the bench sheet.

10.9.3 Conductivity for the TDS method blank must be monitored and recorded in the raw data. The maximum permissible conductivity is 1.0 µmhos/cm (at 25 °C). If the conductivity reading on the method blank exceeds this level, do not use the water for these procedures and notify the supervisor immediately**.**

10.10 Sample Preparation

10.10.1 Total Solids

10.10.1.1 If only total solids are to be measured, heat clean dish to 103-105 °C for one hour. If total volatile solids are to be measured in addition to total solids, ignite the clean evaporating dish at 550 °C for one hour in a muffle furnace.

10.10.1.2 Remove the dish from the muffle furnace using tongs and heat resistant gloves.

10.10.1.3 Cool and store dish in desiccator until dish reaches room temperature or until needed.

10.10.1.4 Weigh the dish immediately before use to the nearest 0.0001 g. Record the weight in the TALS benchsheet.

10.10.2 Total Dissolved Solids

10.10.2.1 If only total dissolved solids are to be measured, heat clean beakers to 180 ± 2 °C for one hour.

10.10.2.2 Heat resistant gloves and tongs must be used when removing items from the muffle furnace.

10.10.2.3 Store and cool dish in desiccator until dish reaches room temperature or until needed.

NOTE: Analyst must transfer the dish with gloves or tongs to prevent added weight due to oil from fingerprints.

10.10.2.4 Weigh the dish immediately before use to the nearest 0.0001 g. Record the weight in the TALS benchsheet.

10.10.3 Total Suspended Solids

10.10.3.1 The pre-washed and pre-weighed filters come in aluminum pans that have scan bars that are associated with an ID and weight of each filter. These IDs are scanned into TALS. See Section 6.4 for additional details.

10.11 Sample Analysis

10.11.1 Total Solids

10.11.1.1 A volume of 100 mL is used for aqueous samples, but sample volume should be chosen in order to have an aliquot of sample sufficient to contain a residue of at least 2.5 mg but less than 200 mg.

10.11.1.2 If a solid matrix is analyzed, the nominal sample size is 25 g. The procedure is carried out in the same manner with duplicate samples and a method blank for the batch QC. The result is provided as a percentage. See Section 11.5.6

10.11.1.3 If the sample is known to contain > 2000 mg/L dissolved solids, a smaller volume should be used. Prescreening should be performed using a conductivity meter to determine the required sample volume or dilution. Dilution should be the smallest dilution sufficient to bring the approximate conductivity to less than 2000 µmho/cm. See WI-DV-0075 for details.

10.11.1.4 Invert and shake the sample vigorously, then quickly aliquot the sample (See Note). Prepare one sample duplicate for every 10 samples in the batch. If more than 10 samples are in the batch there will be two duplicate pairs in the batch.

NOTE: It is important to pour out the sample immediately after shaking so that the solids do not have time to settle.

10.11.1.5 Transfer the measured aliquot of well-mixed sample to the pre-weighed, labeled dish (Section 10.10.1.) For aqueous samples, record the volume of sample to the nearest mL on

the benchsheet. For soil samples, weigh the dish and sample and record the weight on the benchsheet.

10.11.1.6 For the MB, for aqueous samples measure 100 mL of reagent water and pour it into the dish. For soil samples weigh 25 g of reagent grade water into a pre-weighed dish. Prepare one method blank per batch.

10.11.1.7 For the LCS, measure 100 mL of the LCS Solution (Section 7.3) and pour into the dish. Prepare at least one LCS per batch.

NOTE: The LCS solution is not applicable for TS determination in solid samples.

10.11.1.8 Place the tray of samples into a 103-105°C drying oven for at least one hour after all liquid is evaporated.

10.11.1.9 Record the date, time, and oven temperature on the benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.11.1.10 Remove the tray of weighing dishes from the oven using heat-resistant gloves. Place in a desiccator and cool to room temperature.

NOTE: Replace desiccant when needed based on change in indicator color.

10.11.1.11 Weigh the dish to the nearest 0.0001 g. Record the weight on the TALS benchsheet.

10.11.1.12 Return the samples to the oven for another hour, cool in a desiccator, and reweigh. Repeat the drying, cooling, desiccating, and weighing cycle until a constant weight is obtained or weight difference is ≤ 0.5 mg. If a constant weight is not achieved in three drying cycles, prepare an NCM.

NOTE: When weighing dried sample, be alert to change in weight due to air exposure and/or sample degradation.

10.11.1.13 If total volatile solids are to be determined, treat the residue according to Section 10.11.4.

10.11.1.14 Calculate results according to the equation provided in Section 11.5.1. Use the final weight achieved for calculating TS.

10.11.2 Total Dissolved Solids

10.11.2.1 The conductance of each sample may be used to determine the appropriate sample volume to process. See WI-DV-0075 for details.

NOTE: TDS is typically 55-90% of the conductance result. The exact relationship depends on the compounds present in the samples and may not hold for very high concentrations or samples containing non-ionic species or samples with conductance greater than 10,000 µmho/cm or less than 50 µmho/cm.

10.11.2.2 If the sample has a conductance less than 2,000 µmhos/cm, 100 mL should be used. See WI-DV-0075 for details.

10.11.2.3 If the conductance is > 2,000 µmhos/cm, the smallest dilution that would bring the conductance to less than 2,000 µmhos/cm should be used. See Attachment 3 (DV-WI-0075) for details.

10.11.2.4 A smaller amount should be filtered if the sample is high in TSS or is otherwise slow to filter. Filter 25 mL at a time until filtration slows. Record on the benchsheet the reason that a smaller volume had to be used and any sample observations.

10.11.2.5 Record the volume of sample used (to the nearest mL) on the benchsheet.

10.11.2.6 Thoroughly rinse the entire filtration apparatus with reagent water (discard the rinsing) before filtering each sample.

10.11.2.7 Assemble the filtering apparatus, place a glass fiber filter in the apparatus, pre-wet the filter using reagent water, and begin suction.

NOTE: If the sample also requires TSS, use the pre-weighed filters or prepare filters and refer to Section 10.10.3 for additional guidance.

10.11.2.8 Invert and shake the sample vigorously, then quickly aliquot the sample (See Note 1). Transfer 100 mL or a larger volume to yield between 2.5 mg and 200 mg dried residue to the funnel by means of a graduated cylinder. Decrease the sample volume if more than 10 minutes are required to complete filtration.

NOTE 1: It is important to pour out the sample immediately after shaking so that the solids do not have time to settle.

NOTE 2: Multiple filters may be used if performing only TDS analysis.

10.11.2.9 Prepare one sample in duplicate for every 10 samples in the batch. If more than 10 samples are in the batch there will be two duplicate pairs in the batch.

10.11.2.10 For the method blank, process 100 mL of reagent water as the sample.

10.11.2.11 For the LCS, process 100 mL of the LCS Solution. Refer to Section 7.3 for instructions on how to prepare the LCS.

10.11.2.12 Filter the sample through the glass fiber filter.

10.11.2.13 Rinse the graduated cylinder, funnel walls, and filter with three 10 mL portions of reagent water and allow for complete drainage between washings. Continue to apply vacuum until the filter is completely dried.

NOTE: There will be a change in the tone of the vacuum pump once the sample is completely drained. This indicates that air is now being pulled through the filter. Wait 30 seconds after the change in tone and then transfer the filtrate.

10.11.2.14 Transfer the filtrate (including the washings) to a pre-weighed evaporating dish on a tray (See Section 10.10.2). Rinse the receiving flask with 10-25 mL of reagent water and transfer washings into the dish to ensure complete transfer of the sample.

10.11.2.15 Dry the sample in an oven for at least one hour after all liquid is evaporated at 180 $\pm$ 2 °C.

10.11.2.16 Record the date, time, and oven temperature on the TALS benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.11.2.17 Use heat resistant gloves to remove the tray of samples from the oven. Place in a desiccator and cool to room temperature.

NOTE: Replace desiccant when needed based on change in indicator color.

10.11.2.18 Weigh the dish to the nearest 0.0001 g. Record the combined weight of the dried residue and the dish on the TALS benchsheet.

NOTE: If the sample residue is over 200 mg (0.2 g) the sample needs to be re-analyzed at a dilution or an NCM needs to be written.

10.11.2.19 Return the samples to the oven for another hour, cool in a desiccator, and reweigh. Repeat the drying, cooling, desiccating and weighing cycle until a constant weight is obtained or weight difference is < 0.0005 g. If a constant weight is not achieved in four drying cycles, prepare an NCM.

10.11.2.20 Calculate results according to the equation in Section 11.5.2. Use the final weight achieved for calculating TDS.

10.11.3 Total Suspended Solids

10.11.3.1 Assemble the filtering apparatus, place the pre-weighed glass fiber filter in the apparatus (see Section 10.10.3), pre-wet the filter using reagent water and begin suction.

NOTE: Handle the filters only with forceps.

10.11.3.2 Selection of Sample Volume

10.11.3.2.1 For a 47 mm diameter filter, measure sufficient sample to yield between 10 mg and 200 mg of dried residue. Generally 250 mL of sample is used. Some clients or agencies (e.g. South Carolina) require increasing sample volume up to 1 L to achieve a minimum residue of between 2.5 mg and 200 mg.

NOTE: If the sample appears high in TSS, start with a smaller sample volume.

10.11.3.2.2 Because it can be difficult in some samples to determine the amount of TSS present visually, record on the benchsheet all observations on samples for which the entire volume could not be filtered due to slowing of filtration.

10.11.3.2.3 If during filtration of this initial volume, the filtration rate drops rapidly or if filtration time exceeds 5-10 minutes, a smaller volume of sample should be processed.

10.11.3.3 Invert and shake the sample vigorously, then quickly aliquot the sample (See Note 1). A smaller amount should be filtered if the sample is high in TSS or is otherwise slow to

filter. Filter 25 mL at a time until filtration slows. Record the volume of sample filtered (to the nearest mL) on the benchsheet.

NOTE 1: It is important to pour out the sample immediately after shaking so that the solids do not have time to settle.

NOTE 2: If Total Dissolved Solids (TDS) is also required, the filtrate may be used. Refer to Section 10.11.2 for additional guidance.

10.11.3.4 Remove all traces of water by continuing to apply vacuum after the sample has passed through.

10.11.3.5 With suction on, rinse the graduated cylinder, filter, suspended solids residue, and filter funnel wall with three 10 mL portions of reagent water allowing complete drainage between washings.

10.11.3.6 Remove all traces of water by continuing to apply vacuum until the filter is completely dry.

NOTE: There will be a change in tone of the vacuum pump once the sample is completely drained. This indicates that air is now being pulled through the filter. Wait 30 seconds after the change in tone and then transfer the filter.

10.11.3.7 Carefully remove the filter from the filter support and transfer to an aluminum weighing dish. If the filter is torn or damaged during this process, the sample must be reanalyzed. Take care to keep the filter face-up during the transfer so that the residue does not fall off.

10.11.3.8 Dry the filter at least one hour at 103-105 °C.

10.11.3.9 Prepare one sample in duplicate for every 10 samples in the batch. If more than 10 samples are in the batch there will be two duplicate pairs in the batch.

10.11.3.10 For the MB, measure 250 mL of reagent water and pour into the dish. Prepare one method blank per batch.

10.11.3.11 For the LCS, measure 250 mL of the LCS Solution (Section 7.3) and pour into the dish. Prepare at least one LCS per batch.

10.11.3.12 Record the date, time, and oven temperature on the TALS benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.11.3.13 Use heat resistant gloves to remove the tray of dishes from the oven and place in a desiccator to cool.

10.11.3.14 Cool the samples in a desiccator (minimum of 1 hour) weigh (to the nearest 0.0001 g), and record the weight on the benchsheet.

NOTE: Replace desiccant when needed based on change in indicator color.

10.11.3.15 Return the samples to the oven for another hour, cool in a desiccator (until samples are at room temperature), and reweigh. Repeat the drying, cooling, desiccating, and weighing cycle until a constant weight is obtained or weight difference is < 0.0005 g. If a constant weight is not achieved in three drying cycles, prepare a Nonconformance Memo.

10.11.3.16 If volatile suspended solids are to be determined, treat the residue according to Section 10.11.5.

10.11.3.17 Calculate the results using the formula given in Section 11.5.3. Use the final weight achieved for calculating TSS.

10.11.4 Total Volatile Solids

10.11.4.1 Heat the muffle furnace up to temperature (550 ± 50 °C).

10.11.4.2 Place evaporating dish containing the Total Solids (Section 10.11.1) residue in the muffle furnace to ignite the residue. Include any sample duplicate pairs and the method blank from the Total Solids protocol. Fill out a placement chart (Attachment 4) to track the sample positions in the furnace. Attach the completed chart to the Analytical Batch in TALS. The chart can be found at:

R:\\QA\Edit\FORMS\Wet Chemistry\VSS-TVS Placement Chart

NOTE: Determination of Total Volatile Solids uses the residue from the **same** sample aliquot used to determine Total Solids.

10.11.4.3 Record the date, time, and oven temperature on the TALS benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.11.4.4 Typically, one hour ignition is required for 200 mg of residue. However, more than one sample and/or heavier residues may necessitate longer ignition times.

10.11.4.5 Using tongs and heat resistant gloves, remove the weighing dish from the muffle furnace.

10.11.4.6 Let dish cool partially in air until most of the heat has dissipated before transferring to a desiccator for final cooling.

NOTE: Replace desiccant when needed based on change in indicator color.

10.11.4.7 Return the samples to the muffle furnace for another cycle repeating steps 10.11.4.2 – 10.11.4.6 until a constant weight is obtained or weight difference is less than 0.0005 g. If a constant weight is not achieved in three drying cycles, prepare a Nonconformance Memo.

10.11.4.8 Calculate the results using the formula given in Section 11.5.4. Use the final weight achieved for calculating VS.

10.11.5 Volatile Suspended Solids

10.11.5.1 Heat muffle furnace up to temperature (550 ± 50 °C).

10.11.5.2 Place the weighing dish with the glass fiber filter disk containing the Total Suspended Solids residue (Section 10.11.3) in the muffle furnace to ignite the residue. Include the method blank and any sample duplicate pairs from the TSS protocol. Fill out a placement chart (Attachment 4) to track the sample positions in the furnace. Attach the completed chart to the Analytical Batch in TALS. The chart can be found at:

R:\QA\Edit\FORMS\Wet Chemistry\VSS-TVS Placement Chart

NOTE: Determination of Volatile Suspended Solids uses the residue from the **same** sample aliquot used to determine Total Dissolved Solids.

10.11.5.3 Record the date, time, and oven temperature on the TALS benchsheet when the samples are initially placed in the oven and again when they are removed from the oven.

10.11.5.4 Typically, one hour ignition (± 20 minutes) is required for 200 mg of residue. However, more than one sample and/or heavier residues may necessitate longer ignition times.

10.11.5.5 Using tongs and heat resistant gloves, remove the weighing dish from the muffle furnace.

10.11.5.6 Place the dishes into a desiccator for final cooling to room temperature.

NOTE: Replace desiccant when needed based on change in indicator color.

10.11.5.7 Return the samples to the muffle furnace and repeat steps 10.11.5.3 – 10.11.5.6 until a constant weight is obtained or weight difference is less than 0.0005 g. If a constant weight is not achieved in three drying cycles, prepare an NCM.

10.11.5.8 Calculate the results using the formula given in Section 11.5.5. Use the final weight achieved for calculating VSS.

11.0 Calculations / Data Reduction

11.1 If multiple weighing cycles are required, the final sample weight is used for calculating solids content. All calculations are performed in TALS.

11.2 Conversion equation

All samples are weighed in grams but reported in milligrams. Use the following equation before computing further calculations:

Weight in grams X 1000 mg/g = Weight in milligrams *Equation 1*

11.3 Accuracy

$$\%\ \mathrm{Recovery} = \frac{Observed\ \ Concentration}{Known\ \ Concentration} \times 100 \qquad \textit{Equation 2}$$

11.4 Precision (RPD)

$$\%\ RPD = \frac{\left|Orig\ .sample\ value - dup.\ sample\ vaule\right|}{(Orig\ .sample\ value + dup.\ sample\ vaule)/2} \times 100 \qquad \textit{Equation 3}$$

11.5 Concentration

11.5.1 Total Solids

$$\mathrm{Total\ Solids,\ mg/L} = \frac{(\mathrm{A - B}) \times 1000}{\mathrm{C}} \qquad \textit{Equation 4}$$

Where: A = weight of dried residue + dish (mg)
B = weight of dish (mg)
C = volume of sample (mL)

11.5.2 Total Dissolved Solids

$$\text{Total Dissolved Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$ *Equation 5*

Where: A = weight of dried residue + dish (mg)
B = weight of dish (mg)
C = volume of sample (mL)

11.5.3 Total Suspended Solids

$$\text{Total Suspended Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$ *Equation 6*

Where: A = weight of filter + residue (mg)
B = weight of filter (mg)
C = volume of sample filtered (mL)

11.5.4 Volatile Solids

$$\text{Volatile Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$ *Equation 7*

Where: A = weight of residue + dish before ignition (mg)
B = weight of residue + dish after ignition (mg)
C = volume of sample (mL)

11.5.5 Volatile Suspended Solids

$$\text{Volatile Suspended Solids, mg/L} = \frac{(A - B) \times 1000}{C}$$ *Equation 8*

Where: A = weight of residue + filter before ignition (mg)
B = weight of residue + filter after ignition (mg)
C = volume of sample (mL)

11.5.6 Solid Matrix Reported as a Percentage

$$\%Solids = \frac{A - B}{C} \times 100$$ *Equation 9*

Where: A = weight of sample + dish after drying (g)
B = weight of dish (g)
C = initial sample weight (g)

NOTE: The holding time listed in Method 2540A does not apply to solid samples. If the measurement is made after the method holding time has passed, the H flag in TALS is removed manually. The H flag **would** apply to any water sample analyzed for Total Solids after the method holding time was passed.

11.6 The initial (first-level) data review is performed by the analyst and a second-level review is performed by the area supervisor or designee. Both reviews are documented on a Data Review Checklist. See SOP DV-QA-0020 for a copy of the checklist and for more detail on the review process.

11.7 Reporting

11.7.1 Reporting units are mg/L for water samples or % for solid samples.

11.7.2 If smaller or larger sample volumes are processed than are specified in the method, the reporting limit is adjusted appropriately in TALS. The data may require flagging.

11.7.3 All associated data are entered or uploaded into TALS as required.

NOTE: Unless special instructions indicate otherwise, samples less than the reporting limit are reported as ND.

11.7.4 When performing total solids on a solid matrix report the sample as a percentage and “back out” any H flags.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

12.1.1 The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory’s MDL policy in DV-QA-005P. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency.

NOTE: The volume used for the MDL must be the same volume as the MB and LCS.

12.1.2 For this procedure, MDLs are determined for TDS and TSS but not TS and TVS.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of capability (IDOC) on the instrument they will be using for analysis prior to testing samples. Ongoing

proficiency must be demonstrated annually. IDOCs and ongoing proficiency demonstrations are conducted as follows.

12.2.1 Four aliquots of the LCS are analyzed using the same procedures used to analyze samples, including sample preparation for TDS and TSS

12.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.2.4 TS and TVS demonstrations of capability are performed using a purchased "QC sample" of an unknown concentration to the analyst. The final result must be within the acceptance limits of the "QC sample" in order to be considered acceptable.

12.2.5 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

NOTE: In the absence of an LCS, the RPD of duplicate sample analyses are assessed.

12.3 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

13.0 Pollution Control

Prescreening is performed to determine the required sample volume or dilution in order to minimize laboratory waste. In addition, standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents to be disposed.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Corporate Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Plan."

14.2 The following waste streams are produce when this method is carried out:

14.2.1 Expired Chemicals/Reagents/Standards – Contact Waste Coordinator

14.2.2 Acidic sample waste – Waste Stream F

14.2.3 Filter and filter residue – Nonhazardous waste

14.2.4 Solid soil waste – Waste Stream S

NOTE: Radioactive and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Waste Coordinator for proper management of radioactive or potentially radioactive waste generated from this procedure.

15.0 References / Cross-References

15.1 Standard Methods for the Examination of Water and Wastewater, 20th Edition.

15.1.1 2450A – 1997, Introduction

15.1.2 2540B – 1997, Total Solids Dried at 103-105^{o}C

15.1.3 2540C – 1997, Total Dissolved Solids Dried at 180^{o}C

15.1.4 2540D – 1997, Total Suspended Solids Dried at 103-105^{o}C

15.2 Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1979: Method 160.4.

16.0 Method Modifications:

16.1 The source methods use an acceptance criteria of 5% of the average of the duplicate weights. This is equivalent to a 10% RPD for an average weight of 200 mg. This procedure uses a 10% RPD for all duplicates that exceed 5 times the RL rather than having to calculate the acceptance window by sample duplicate pair.

16.2 The source methods use a magnetic stirrer to homogenize the samples. This procedure uses mixing by shaking and the requirement to immediately remove the sample aliquot to gain a representative sample.

16.3 Method 2540B states to start the evaporation of the sample at approximately 2 ^{o}C below boiling. This procedure uses beakers rather than evaporating dishes which minimize concern for spattering. The oven is maintained at 103-105 ^{o}C for the entire drying process.

16.4 Methods 2540C and 2540D state to “continue suction for about 3 min after filtration is complete”. The laboratory waits 30 seconds after all fluid is drained through the filter between samples.

16.5 The source methods state to repeat, drying, cooling, desiccating and weighing cycle “until a constant weight is obtained or until the weight change is less than 4% of previous weight or 0.5 mg, whichever is less.” The laboratory utilizes the <0.5 mg weight change as a final measure because the calculated concentration of 0.5 mg weight would equal 5 mg/L (2 mg/L for method 2540D) which is less than the laboratory RL.

17.0 Attachments

Attachment 1: Example TDS/TS/TSS Benchsheet
Attachment 2: Example VSS/VDS/VS Benchsheet
Attachment 3: Example VSS-TVS Muffle Furnace Placement Chart

18.0 Revision History

- Revision 11, dated 30 June 2015
  - Added Section 10.8 and note regarding the use of wide-bore pipettes
  - Updated Section 10.11.2.13 to reflect the use of three 10 mL rinses

- Revision 10, dated 31 March 2015
  - Updated section 10.10.3.11 to reflect the use of 250 mL of LCS standard
  - Added Note to section 12.1.1
  - Updated section 10.10.2.9 to reflect 4 drying cycles for constant weight
  - Removed attachment 3 and revised sections to refer directly to DV-WI-0075 without having it embedded in the SOP

- Revision 9, dated 30 November 2014
  - Language changes throughout
  - Changed LIMS to TALS
  - Changed MSDS to SDS
  - Changed all measured weights to g instead of mg
  - Created a new spreadsheet for pre-weighed filter verifications
  - Removed **NOTE** from Section 5.4
  - Updated section 6.4.1 to reflect current practices
  - Added current section 6.6
  - Added LCS note to sections 7.3, 9.4 and 10.10.1.7
  - Provided detail concerning the frequency of sample duplicates to section 9.5.
  - Added aliquotting note to sections 10.10.1.4,10.10.2.3 and 10.10.3.3
  - Updated sections 10.10.1.5 and 10.10.1.6 to reflect current practices
  - Added the use of a placement chart to sections 10.10.4.2 and 10.10.6.2
  - Deleted all references and section on Volatile Dissolved Solids (no longer performed)
  - Added section 11.7.4
  - Added Attachment 4 Example VSS-TVSS Muffle Furnace Placement Chart

- Revision 8, dated 31 January 2014
  - Added detail to sections 7.3 and 7.4 concerning standard information.
  - Reordered the steps in section 10.10.1 to match the current procedure.
  - Changed the minimum residue amount to 2.5 mg in sections 10.10.1.1, 10.10.2.3, and 10.10.3.2.1.
  - Added “Invert and shake the sample vigorously, then quickly aliquot the sample. It is important to pour out the sample immediately after shaking so that the solids do not have time to settle” to sections 10.10.1.5 & 10.10.2.3.
  - Added “notes” to sections 10.10.2.13 and 10.10.3.6.
  - Changed sections 10.10.2.5 and 10.10.2.6 to reflect a maximum conductivity of 2,000 umhos/cm.
  - Changed section 10.10.2.13 to reflect rinsing with one 10 mL portion of reagent water followed by two 5 mL portions.

  - Added clarification to section 12.2.1 in regards to TDS and TSS DOC.
  - Added section 12.2.4 – requirements for TS and TVS DOC
  - Added Method modifications 16.4 and 16.5
  - Added Attachment 3 WI-DV-0075 TDS-TS Dilutions based on Sample Conductivity

- Revision 7, dated 22 April 2013
  - Added table of reporting limits to Section 1 and removed RLs from definitions in Section 3
  - Revised Sections 2.6, 10.10.4.2, 10.10.5.2, and 10.10.6.2 to clarify volatiles procedures.
  - Added note to Section 11.5.7

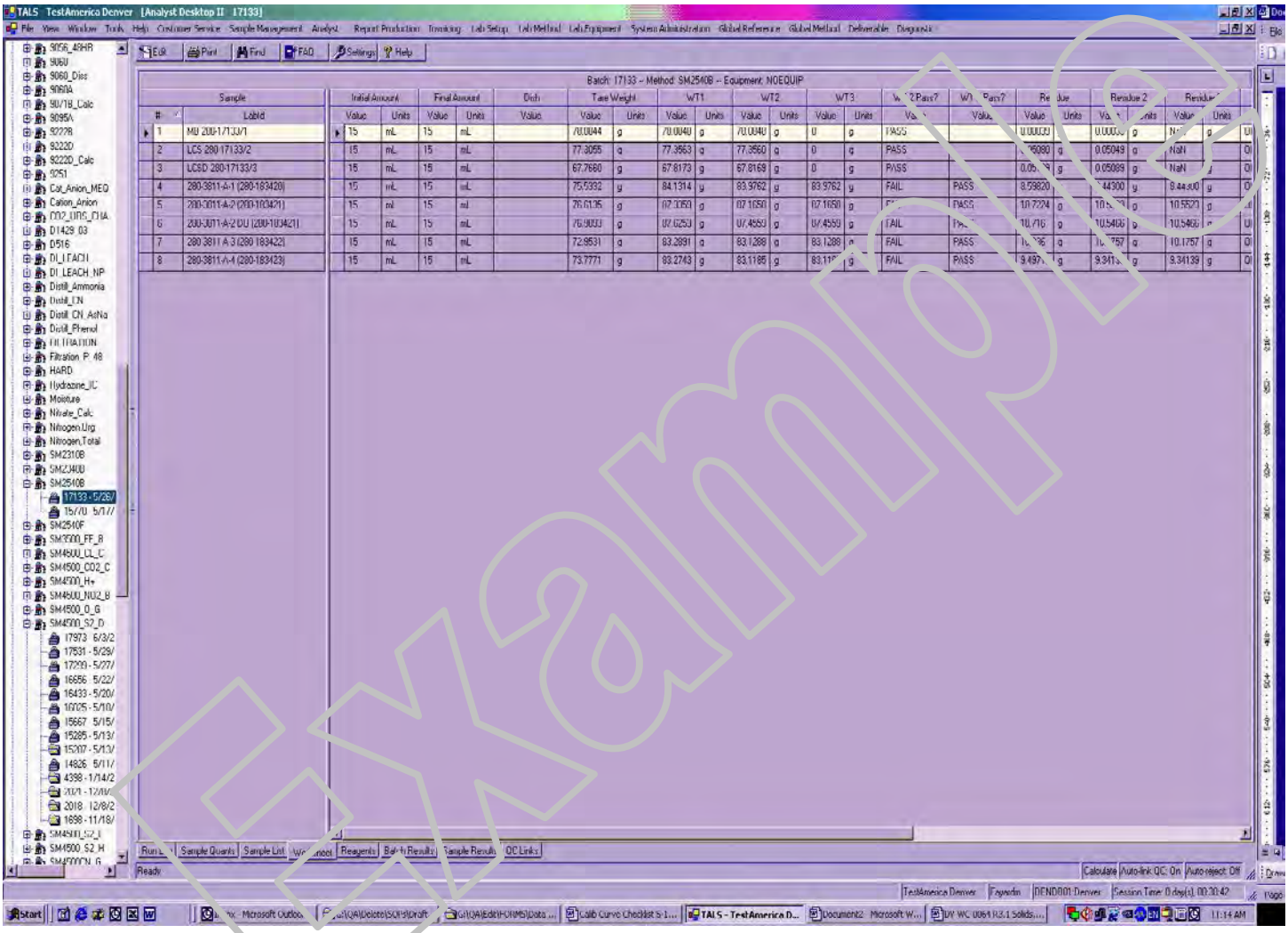
- Revision 6, dated 7 December 2012
  - Added application of matrix to solid samples to Sections 1 and 10.10.1.3.
  - Revised sections 7.3 and 7.4 to reflect current practice.
  - Revised Section 9 for consistency with current practice
  - Added statements to Sections 9.4, 9.5, 10.8 and 12.1 regarding absence of required QC elements per EPA MUR 2012
  - Added note to Section 12.2 regarding DOC for non-spiked parameters.
  - Revised section 10.8.3 for clarification.
  - Added information regarding analysis of QC samples in Sections 10.10.1, 10.10.2, 10.10.3 and 10.10.4
  - Revised sections 10.10.1.2 and 10.10.8.2 to identify nominal sample volume to use.
  - Revised reference to use of final weight for calculation throughout section 10.
  - Revised Section 10.10.2.10 to reflect current practice.
  - Added calculation for % solids for solid matrices (Section 11.5.7)
  - Removed Attachment 3 and added section 11.6
  - Added Sections 16.1-16.3
  - Source method review
  - Editorial and formatting changes throughout

- Revision 5.2, dated 30 November 2011
  - Annual technical review.
  - Corrected grammatical and formatting errors.
  - Added reporting limits for all analysis in Section 3.0
  - Clarified process for working with oily samples in Section 4.5
  - Clarified process of tracking materials in Section 4.6
  - Clarified the use of pre-weighed and washed filters for use with TSS and TVSS.
  - Added Section 6.18 – Computer Software and Hardware.
  - Added Section 10.1.4
  - Removed references to EAP methods 160.1, 160.2, and 160.3

- *Earlier revision histories have been archived and are available upon request.*

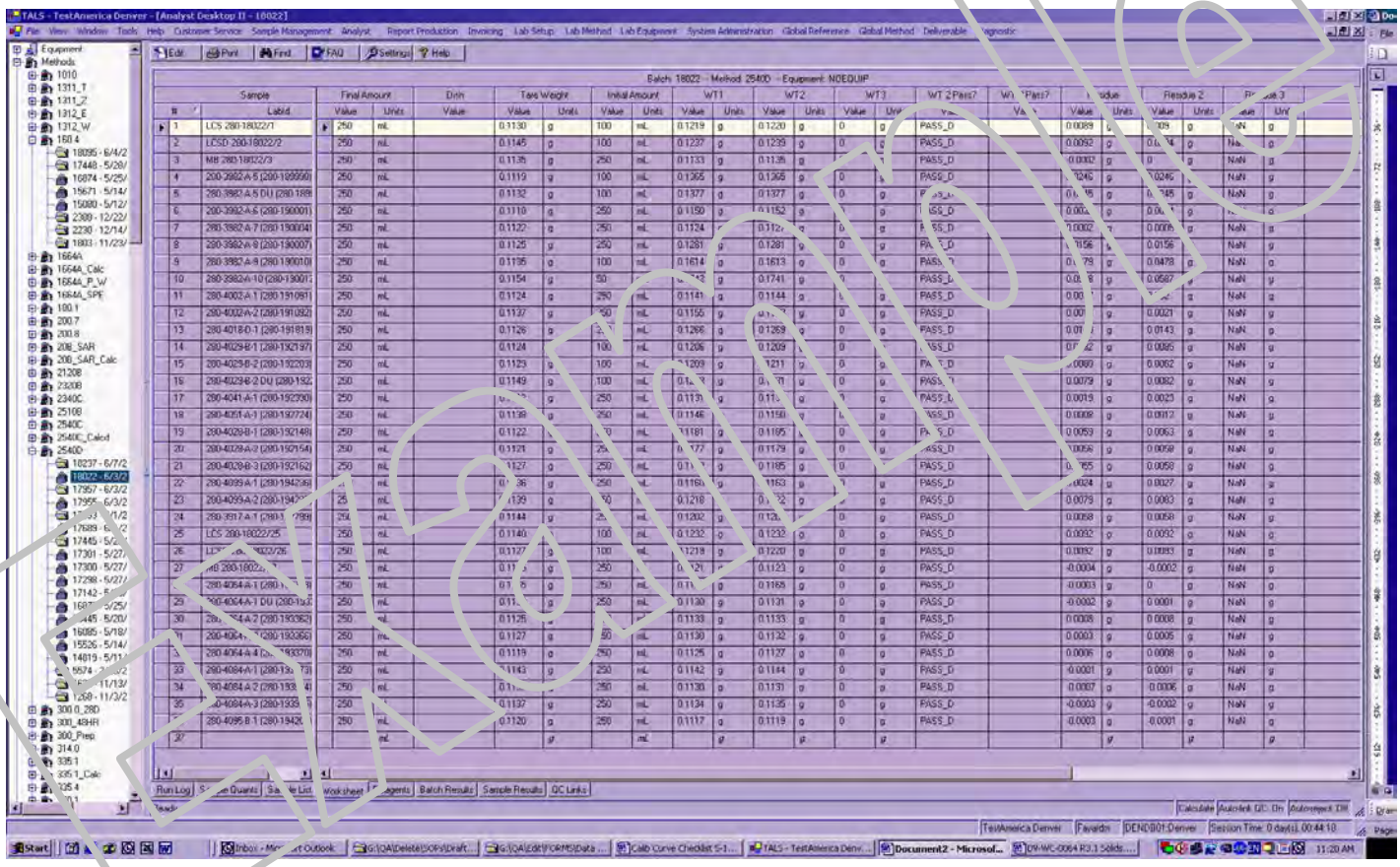
Attachment 1.

Example TDS/TS/TSS Benchsheet



Attachment 2.

Example VSS/VS/VDS Benchsheet



Attachment 3.

Example VSS-TVS Muffle Furnace Placement Chart

VSS-TVS Muffle Furnace Placement Chart

TestAmerica

TestAmerica Denver

Method 160.4

Dish ID Sample #	Dish ID Sample #	Dish ID Sample #
Dish ID Sample #	Dish ID Sample #	Dish ID Sample #
Dish ID Sample #	Dish ID Sample #	Dish ID Sample #
Dish ID Sample #	Dish ID Sample #	Dish ID Sample #

Left front Right Front

VSS/TVS E-Muffle 550 ℃

Analyst:
Date:

NOTE: All sections of the placement chart must be filled out. Empty positions should be marked with an NA

Revision 3, 11/03/2014
\\tafs\Lab2\Denver\Admin\QA\Edit\FORMS\Wet Chemistry\VSS-TVS Placement Chart_Rev3

1 of 1

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Electronic Copy Only -

Title: Hardness by Calculation [SM 2340B]

Approvals (Signature/Date):

Doug Gomer 7/31/15
Doug Gomer Date
Technical Specialist

Adam W Alban 31 July 15
Adam Alban Date
Health & Safety Manager / Coordinator

Margaret S. Sleevi 7/31/15
Margaret S. Sleevi Date
Quality Assurance Manager

L. S. L. 7/31/15
William S. Cicero Date
Laboratory Director

Facility Distribution No. _____ **Distributed To: _____**

1.0 Scope and Application

1.1 This method is applicable to the determination of total and dissolved hardness. The reporting limit is 1.3 mg/L.

1.2 This method is suitable for drinking, surface and saline waters, domestic and industrial waste.

1.3 The dynamic range will depend on the range of the instrument used for the analysis of calcium and magnesium. This range may be extended by dilution.

2.0 Summary of Method

The sample is analyzed for calcium and magnesium using an appropriate method (e.g., ICP). Hardness is calculated from the values for these metals.

3.0 Definitions

Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and Policy DV-QA-003P, *Quality Control Program*, for definitions of general analytical and QA/QC terms.

4.0 Interferences

Consult the appropriate ICP-AES analytical SOP for calcium and magnesium analysis.

5.0 Safety

5.1 There are no specific safety hazards associated with this SOP.

5.2 During the course of performing this procedure it may be necessary to go into laboratory areas to consult with appropriate staff members, therefore employees performing this procedure must be familiar with the Environmental Health & Safety Manual, Radiation Safety Manual and take appropriate precautions and wear appropriate attire and safety glasses.

6.0 Equipment and Supplies

6.1 Consult the appropriate ICP-AES SOP for analytical requirements.

6.2 Computer Software and Hardware

Please refer to the master list of documents and software located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

7.0 Reagents and Standards

7.1 Consult the appropriate ICP-AES SOP for descriptions of the relevant reagents and standards.

7.2 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.0 Sample Collection, Preservation, Shipment and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Water	HDPE	50 mL	HNO_3, pH < 2	180 Days	40 CFR Part 136.3

[1] Inclusive of digestion and analysis.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the TestAmerica LIMS (TALS) Method Comments to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver Policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver Policy DV-QA-024P, *QA/QC Requirements for Federal Programs*.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in TALS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 This SOP describes a calculation based on the determination of calcium and magnesium by ICP detailed in the appropriate ICP-AES SOPs. The requirements for the QC Elements described in the 2012 Method Update Rule to 40 CFR Part

136 are described in these SOPs.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 Data Entry

10.3.1 Run Backlog

10.3.1.1 In TALS, under the Sample Management menu, choose Backlog Report.

10.3.1.2 Select the Met_Calcs Backlog.

10.3.1.3 Hit Run.

10.3.2 Sort the Backlog by Ready status.

10.3.3 Create Analytical Batches by selecting the method in Analyst Desktop, right-clicking, and selecting create new batch from scratch.

10.3.4 Open the new batch and create a method blank.

10.3.5 Enter the appropriate Sample IDs

NOTE: If the sample data does not automatically pull into the analytical batch, it will be necessary to find the sample results and hand-enter the data according to the following steps.

10.3.6 Find the necessary Ca and Mg data by searching for the Job number under PM Desktop.

10.3.7 Make sure that the results are appropriate for the hardness calculation (i.e., total vs dissolved).

10.3.8 After the data have been entered into the batch, open the batch information window within the analytical batch and select 1 or 0 as directed to enable calculations within the batch.

10.3.9 Change the sample status to first-level reviewed.

11.0 Calculations / Data Reduction

11.1 Calculations

$$Hardness = (2.497 \times Ca) + (4.118 \times Mg) \qquad \text{Equation 1}$$

Hardness = Hardness, mg/L as $CaCO_3$.
Ca = Calcium concentration, mg/L
Mg = Magnesium concentration, mg/L

11.2 Results are reported as mg/L as $CaCO_3$.

11.3 The data for the determinative method (Method 6010B or 6010C) undergoes two levels of review. The calcium and magnesium results are then automatically transferred within TALS to the Hardness by Calculation method and TALS calculates the hardness value. The second level reviewer checks the completeness of this action.

12.0 Method Performance

Method performance requirements are listed in the SOP for calcium and magnesium determination.

13.0 Pollution Control

The generation of paper waste is reduced by making use of computer resources.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, *Waste Management and Pollution Prevention*, of the Environmental Health and Safety Manual, and DV-HS-001P, *Waste Management Program*.

14.2 The following waste streams are produced when this method is carried out:

Normal office waste, including paper waste, may be disposed of in the office area trash containers.

15.0 References / Cross-References

15.1 Method 2340B-1997, Hardness by Calculation, “Standard Methods for the Examination of Water and Wastewater,” 20th Edition.

15.2 SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

15.2.1 Method 3005A, Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy, Revision 1, July 1992.

15.2.2 Method 3010A, Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy, Revision 1, July 1992.

15.2.3 Method 6010B, Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 2, December 1996.

15.2.4 Method 6010C, Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 3, Update IV, February 2007.

16.0 Method Modifications:

N/A

17.0 Attachments

N/A

18.0 Revision History

- Revision 4, dated 31 July 2015
  - Annual review
  - Minor formatting throughout
  - Added procedure for entering data into TALS

- Revision 3, dated 31 July 2014
  - Revised section 9.2 to reference analytical method SOPs for 2012 MUR requirements
  - Annual review

- Revision 2, dated 31 July 2013
  - Revised section 3.0 to reflect current practice
  - Revised section 9.2 to address 2012 MUR requirements
  - Annual Review

- Revision 1.4, dated 27 July 2012
  - Updated sections 9.1, 10.1, and 10.2 to reflect current practice
  - Revised Section 11.3
  - Added references for source methods for sample prep and the determinative methods from which the data are obtained for the calculation described in this SOP.
  - Source method review (Hardness by Calculation)
  - Formatting and editorial changes throughout

- Revision 1.3, dated 29 July 2011
  - Annual Technical Review.
  - Added Section 6.1

- Added additional information to Section 7.
- Updated Section 9 to current practices.
- Updated the RL listed in Section 1.1
- Updated Section 10.1 to reflect current practices.
- Updated references
- Removed Attachment 1.

- Revision 1.2, dated 08 July 2010
  - Annual Technical Review.

- Revision 1.1, dated 17 July 2009
  - Annual Technical Review.
  - Updated SOP references throughout SOP.
  - Added updated Checklist to Attachment 2.

- Revision 1, dated 14 July 2008
  - Integration for TestAmerica and STL operations.
  - Updated formatting.
  - Updated method references.
  - Technical review performed.

- Revision 0.1, dated 22 November 2006
  - For this minor revision, the technical content of this SOP was not reviewed or updated. The purpose of this minor revision is to incorporate the Safety Bulletin information to ensure compliance with STL Corporate requirements. In addition, Section 9.1 was revised to reference Policy QA-024 for specific QC requirements for federal programs, any existing interim changes were incorporated, and formatting was updated consistent with Policy QA-001.

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Title: Manual and Automated pH [SM 4500-H+ B, SW 9040 B & C]

Approvals (Signature/Date):

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Roxanne Sullivan Date
Technical Specialist

Adam W Allan 13 Jan 15
Adam Alban Date
Health & Safety Manager / Coordinator

Margaret S. Sleevi 1/13/15
Margaret S. Sleevi Date
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William S. Cicero Date
Laboratory Director

Facility Distribution No. _____ **Distributed To:** _____

1.0 Scope and Application

1.1 This is an electrometric procedure for measuring pH in aqueous samples. This method is applicable to the analysis of drinking, surface, and saline waters, and acid rain. It also applies to multiphase wastes where the aqueous phase constitutes at least 20% of the total volume of the waste. Corrosivity of concentrated acids and bases cannot be measured by this procedure.

1.2 Liquid samples which are not miscible with water or solids must be analyzed by DV-WC-0001, Soil and Waste pH.

1.3 A detection limit (MDL) for pH has not been defined, however, for reporting purposes this laboratory uses 0.1 pH units as the RL and MDL.

1.4 This method is applicable to all ranges of pH.

2.0 Summary of Method

The pH meter, glass electrode, and reference electrode (or single combination electrode) are standardized using five reference buffer solutions of known pH bracketing the pH expected to be found in the sample. The sample measurement is made by immersing the electrodes into the test solution and taking a reading from the meter.

3.0 Definitions

pH - At a given temperature, the intensity of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. Because of ionic interactions in all but very dilute solutions, it is necessary to use the "activity" of an ion and not its molar concentration. The use of the term pH assumes that the activity of the hydrogen ion is being considered. The approximate *equivalence* to molarity can be presumed only in very dilute solutions. A logarithmic scale is used to accommodate the wide range of ionic activities.

4.0 Interferences

4.1 The pH response of most glass electrodes is imperfect at both ends of the scale. The indicated pH value of highly alkaline solutions, as measured with the glass electrode, will be too low. The indicated pH value of salts and strong acids having a pH less than 1, will often be higher than the true pH value. Interferences can be minimized by the selection of the proper electrodes for these conditions. For example, sodium may interfere at pH > 10, and is controlled by using a "low sodium error" electrode.

4.2 Coatings of oil and particulate matter may impair electrode response.

4.3 Temperature variations will change the pH of the samples and also affect electrode response. Electronic temperature correction may be used to correct for electrode response.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety

Manual, Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

Eye protection that satisfies ANSI Z87.1 (as per the Corporate Environmental Health and Safety Manual), laboratory coat, and nitrile or latex gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.4 Primary Materials Used

There are no materials used in this method that have a serious or significant hazard rating. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS (formerly known as MSDS) for each material before using it for the first time or when there are major changes to the SDS.

6.0 Equipment and Supplies

6.1 Instrumentation

6.1.1 Manual pH

6.1.1.1 pH meter including temperature compensation ability.

6.1.1.2 Glass electrode with reference electrode--a calomel, silver-silver chloride or other reference electrode of constant potential may be used; or use a combination electrode that incorporates both measuring and reference functions.

6.1.1.3 Magnetic stirrer and Teflon-coated stir bars.

6.1.2 Automated pH

6.1.2.1 Man-Tech Autotitrator (AT3), consisting of:

- Burivar I/2 Buret Module
- Titrasip Titration Module
- PC-Tis Interface Module
- PC running PC-Titrate software

6.2 Supplies

6.2.1 Tubes to fit autosampler. These must be thoroughly rinsed to remove all

traces of salt if reused.

6.2.2 Pipette calibrated to 5 mL, and disposable tips.

6.2.3 Disposable beakers.

6.2.4 Miscellaneous laboratory apparatus and glassware.

6.3 Computer Software and Hardware

Please refer to the master list of documents, software and hardware located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

7.0 Reagents and Standards

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

NOTE: TALS reagent codes are given in parentheses.

7.2 **pH Buffers, 2, 4, 7,10, and 12:** These buffers should be obtained commercially and traceable to NIST standards. Other buffers can be used as appropriate to bracket the range of each sample. (TALS Reagent codes: pH 2.0 Buffer, pH 4.0 Buffer, pH 7.0 Buffer, pH 10 Buffer, pH 12 Buffer)

7.3 **ICV Buffer Solution (pH 7.0 ICV):** A pH 7 buffer solution from a second source provider, obtained commercially and traceable to NIST standards.

7.4 **Laboratory Control Sample (LCS) Solution (pH 7.0 Buffer):** The LCS solution must be certified for pH and is commercially available. The pH 7 buffer from Section 7.2 is normally used as the LCS.

7.5 **3 M Potassium Chloride:** This solution is purchased from Thermo.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation[1]	Holding Time[2]	Reference
Water	Glass or plastic	100 mL	None	None	SW-846
Water	Glass or plastic	100 mL	None	Analyze within 15 minutes	40 CFR Part 136.3

[1] 40 CFR Part 136.3 and SW-846 indicate no preservation is required for pH. It is intended by both programs that the samples be analyzed in the field. TestAmerica Denver typically refrigerates these samples because the aliquot tested is taken from a sample container that is used for other tests that do require refrigeration.

[2] pH is intended to be a field measurement. The laboratory attempts to measure pH as soon as possible upon receipt.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS Method Comments to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Assurance Program.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs. This procedure meets all requirements for DoD QSM 5.0 unless otherwise specified.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in the LIMS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 **Sample QC** - The following quality control samples are prepared with each batch of samples.

9.2.1 Laboratory Control Sample (LCS):

One LCS is required with each batch of samples processed not to exceed 20 samples.

Acceptance Criteria: The LCS must be within ± 0.05 pH units of the true value. Note: This limit is presented in TALS as 99-101% based on the use of the pH 7 buffer.

Corrective Action: If the LCS is not within the control limits, rerun all associated samples.

9.2.2 Duplicate Samples:

One duplicate sample must be analyzed for each water sample not to exceed 20 samples.

Acceptance Criteria: The two results should agree within ± 0.10 pH units.

Corrective Action: If the difference is greater than ± 0.10 repeat the analysis. If the difference still exceeds the control limit the data will be flagged as outside of the limit.

9.2.3 Method blanks and matrix spikes are not applicable to pH.

9.3 Instrument QC

9.3.1 Initial Calibration Verification

Record the expected pH, manufacturer, and lot number of the verification buffer used for a second source pH 7.0 buffer solution.

Acceptance Criteria: The ICV buffer must read within ± 0.05 pH units of the true value.

Corrective Action: If this criterion is not met, the problem should be identified, corrected, and the meter recalibrated.

9.3.2 Continuing Calibration Verification

A pH 7.0 buffer check is required after every 10 or fewer samples and at the end of the run. The CCV is the same pH 7 buffer solution used in the initial calibration.

Acceptance Criteria: The CCV pH buffer checks must be within ± 0.05 units of the true value.

Corrective Action: If the pH 7.0 buffer check is outside of the control limits, rerun all samples since the last acceptable pH 7.0 buffer check.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP # DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 Manual Sample Analysis

10.3.1 Follow the operating instructions supplied by the manufacturer of the pH meter.

10.3.2 Record instrument ID, pH probe ID, thermometer probe ID, and reagent IDs in the batch record in TALS.

10.3.3 When using the Thermo Five Star pH meter, all results are to be temperature corrected to 25°C using the Automatic Temperature Compensation function available with the instrument.

NOTE: Methods 9040 B & C state "The sample temperatures must be within ± 2 ℃ of the calibrated buffers or temperat ure corrected." All samples are automatically corrected for temperature by the instrument.

10.3.4 Calibrate the pH meter using five buffers at pH 2.0, 4.0, 7.0, 10.0, and 12.0. The aliquots of buffers should be fresh for each day of use.

10.3.4.1 Record the expected pH, manufacturer, and lot number of the buffers used. See Attachment 1.

10.3.4.2 The reading of the buffer solutions must be within ± 0.05 pH units of the certified buffer solution values. If they are not, recalibrate.

10.3.4.3 Record the slope in the instrument logbook. The source methods do not provide criteria for acceptance of the slope. If there is a significant variation from previous values, maintenance may be required.

NOTE: Internal standard is not an appropriate calibration technique for the determination of pH.

10.3.5 Verify the calibration using a buffer solution (ICV). See Sections 7.3 and 9.3.1.

10.3.5.1 Record the pH, manufacturer, and lot number of the verification buffer used.

10.3.5.2 The reading of the buffer solution should be within ± 0.05 pH units of the true value. If this criteria is not met, the problem should be identified, corrected, and the meter recalibrated.

NOTE: Internal standard is not an appropriate calibration technique for the determination of pH.

10.3.6 Analyze one LCS and one sample duplicate per batch of 20 samples.

10.3.7 Pour enough sample into a beaker to cover the electrodes and place on the magnetic stirrer. Stirring should be fast enough to provide homogeneity and keep solids suspended, but should not disturb the air-water interface. Acid rain samples should not be stirred.

10.3.8 Immerse the electrodes in the sample and allow the reading to stabilize. The pH is recorded to the nearest 0.01 pH.

10.3.9 Repeat measurement on successive volumes of sample until the values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient.

10.3.10 The pH reading, temperature, and time are recorded directly in the LIMS by the analyst at the time of measurement.

NOTE: Methods 9040B & C require the sample temperature to be reported with each pH result. All sample temperatures are recorded on the instrument raw data. The LIMS reports the pH as pH adj. to 25℃ to account for the temperature correction performed by the instrument.

10.3.11 Rinse the electrodes with a stream of deionized water in between samples.

10.3.12 Rinse the magnetic stir bars with deionized water in between samples.

10.3.13 A CCV at pH 7.0 is analyzed every 10 or fewer samples (excluding the LCS and LCSD, if analyzed). See Section 9.3.2.

10.3.14 Follow the instructions supplied with the electrodes for storage after use. Record daily maintenance in the pH Calibration and Maintenance Log. See Attachment 1.

10.4 Automated Sample Analysis

10.4.1 The pH meter is calibrated each day of operation.

10.4.2 Be sure the reference electrode has been filled with 3 M potassium chloride.

10.4.3 Calibrate the pH meter using pH 2, 4, 7, 10, and 12 buffers.

10.4.3.1 The reading of the buffer solutions must be within ± 0.05 pH units of the certified buffer solution values. If they are not, recalibrate.

10.4.3.2 Fill the first seven tubes in the autosampler with the following order of samples: pH 2 buffer, pH 4 buffer, pH 7 buffer, pH 10 buffer, pH 12 buffer, and deionized water.

10.4.3.3 Click on the button "PH CALIBRATION" and follow the screens to calibrate.

10.4.4 When calibration has finished, go to titrator and choose "examine calibrations." Print the calibration if instrument states it is valid. If the calibration is not valid, recalibrate.

10.5 Click on the button "PH CALIBRATION" and follow the screens to calibrate.

10.5.1 Check the calibration using a buffer solution (ICV). See Sections 7.3 and 9.3.1.

10.5.1.1 Record the pH, manufacturer, and lot number of the verification buffer used.

10.5.1.2 The reading of the buffer solution should be within ± 0.05 pH units of the true value. If this criteria is not met, the problem should be identified, corrected, and the meter recalibrated.

NOTE: Internal standard is not an appropriate calibration technique for the determination of pH.

10.6 Troubleshooting & Maintenance

10.6.1 See Section 20 of the Denver Quality Assurance Manual for maintenance procedures.

10.6.2 Slow response or a wavering response is indicative of a dirty or oil-coated pH probe or that the probe is not properly connected to the meter. Samples high in dissolved CO_2 can cause the pH to change as the sample is stirred.

10.6.3 No temperature displayed may be a result of the temperature probe not being properly connected to the meter.

10.6.4 Using plastic disposable beakers and a magnetic stir plate and stir bar may generate static electricity that could affect stability. Turn off the stir plate, unplug and allow to sit for a few minutes.

11.0 Calculations / Data Reduction

11.1 For Manual pH, data are entered directly into the worksheet in TALS at the time of observation. There is no transcription of data.

11.2 For Automated pH, the data are recorded by the instrument and uploaded to TALS when the run is complete. There is no transcription of data.

11.3 The initial data review is performed by the analyst and a second-level review is performed by the area supervisor or designee. Both reviews are documented on a Data Review Checklist. See SOP DV-QA-0020 for a copy of the checklist and for more detail on the review process.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

There is no MDL study for pH. The laboratory reports samples to the nearest 0.1 pH units and uses this increment as the MDL for reporting purposes.

12.2 Demonstration of Capabilities

12.2.1 All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows"

12.2.1.1 Four aliquots of the QC check sample (LCS) are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.

12.2.1.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.2.1.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.2.1.4 Further details concerning demonstrations of proficiency are described in DV-QA-0024.

12.3 Training Requirements

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use, has the required experience, and has successfully analyzed initial demonstration samples (see SOP # DV-QA-0024 for details).

13.0 Pollution Control

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

13.2 This method does not contain any specific modifications that serve to prevent or minimize pollution.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Corporate Safety Manual, and HS-001, "Waste Management Program."

14.2 The following waste streams are produce when this method is carried out:

14.2.1 Expired Chemicals/Reagents/Standards – Contact Waste Coordinator

14.2.2 Acidic or neutral sample waste – Waste Stream F

14.2.3 Basic sample waste – Waste Stream E

NOTE: Radioactive, mixed waste and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Third Edition and all promulgated updates, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, January 2005.

15.1.1 Method 9040B, "pH Electrometric Measurement", Revision 2, January 1995.

15.1.2 Method 9040C, "pH Electrometric Measurement", Revision 3, November 2004.

15.2 "Standard Methods for the Examination of Water and Wastewater, online Edition; Clesceri, L.S.; Greenberg, A.E.; Eaton, A.D.; Editors; American Public Health Association, American Water Works Association, and Water Environment Federation.

15.2.1 Method 4500-H+ B-2000 or Method 4500--H+ B-2011

16.0 Method Modifications:

Item	Method	Modification
1	9040B 9040C SM 4500 H+ B	Temperature is not reported with the pH result. Sample pH is reported as pH adj. to 25°C.
2	9040B	Methods 9040B and 9040C specify use of glass beakers while SM

Item	Method	Modification
	9040C SM 4500 H+ B	recommends polyethylene. This procedure uses disposable plastic beakers.
3	SM 4500 H+ B	The Standard Methods method states buffer solutions be replaced every 4 weeks. This procedure uses commercially available buffer solutions and uses the manufacturer's expiration date.
4	9040B 9040C SM 4500 H+ B	The source documents do not require preservation of samples for pH as it is intended as a field measurement. The laboratory typically does refrigerate samples during transit and prior to analysis.

17.0 Attachments

Attachment 1: Example pH Calibration and Maintenance Log
Attachment 2: Example Autotitrator pH Calibration Report
Attachment 3: Example Benchsheet

18.0 Revision History

- Revision 10, dated 14 January 2015
  - Added procedure sections on use of autotitrator for pH determination and all related information regarding instrument throughout
  - Added requirement to document calibration slope for manual pH
  - Added example autotitration calibration report as new attachment 2
  - Revised Section 11.1 to address both manual data and autotitrator data
  - Renumbered attachments

- Revision 9, dated 31 July 2014
  - Updated table in Section 8 to include both SW846 and 40 CFR Part 136.3 and to reflect the requirements in each of these programs. Added footnote to table in Section 8 regarding preservation of samples.
  - Revised section 10.3.1.1 to remove requirement to record the calibration slope in the logbook. The assessment of the slope is not a method requirement and no acceptance criteria are provided in the methods.
  - Added Sections 10.5 and 10.6 for Maintenance and Troubleshooting.
  - Revised Section 11.1 to note that results are entered directly into TALS with no transcription.
  - Updated reference section to reflect requirements of 40 CFR Part 136.3.
  - Added method modification item 4 to address refrigeration of samples.
  - Updated logbook to remove Calibration Slope entry per Section 10.3.

- Revision 8, dated 31 January 2014
  - Removed section 9.4 and added 2012 MUR QC requirements to the appropriate sections
  - Added note to section 10.3 that IS is not appropriate for this method
  - Added section 10.4.10 to describe cleaning procedure for stir bars
  - Added statement to section 10.4.8 that data are entered directly into the LIMS
  - Added section 10.5 Maintenance
  - Added information to Sections 1.3 and 12.1 about MDL and RL used for reporting purposes

- Revision 7, dated 04 January 2013
  - Added section 9.4 for 2012 MUR QC requirements

- Revision 6, dated 27 July 2012
  - Revised Section 6 to identify replacement pH meter
  - Updated Section 7 to include second source ICV buffer at pH 7.0
  - Removed HCl and cleaning procedure for probe.
  - Revised Section 8 and added footnote
  - Moved procedural note in Section 4 to Section 10.4.5
  - Updated Sections 9.1, 10.1 and 10.2 to reflect current practice
  - Revised calibration procedure (Section 10)
  - Removed ASTM method reference and added SM 4500-H+ B-2000
  - Added Section 11.2 and removed Attachment
  - Updated Section 16
  - Added Attachments 1 and 2.
  - Source method review
  - Formatting and editorial changes throughout
- Revision 5.5, dated 30 December 2011
  - Annual Technical Review
- Revision 5.4, dated 17 January 2011
  - Annual Technical Review
  - Deleted Attachment 1
  - Updated Attachment 2 (now 1)
  - Added section 6.3, Computer Software and Hardware
- Revision 5.2, dated 26 August 2009
  - Added note to section 10.2.2
- Revision 5.1, dated 23 February 2009
  - Updated method references
  - Updated formatting and grammatical errors
- Revision 5, dated 25 January 2008
  - Integration for TestAmerica and STL operations.
  - Added pH 12 buffer throughout the SOP.
  - Updated the definition of pH in section 3.0.
  - Updated formatting.
  - Added attachments 1 and 2.
- Revision 4, dated 29 November 2005
  - Safety, Pollution Prevention, and Waste Management sections were updated.
  - Appendix I was removed.
  - Automatic Temperature Correction using the Orin Sensorlink Software was included.
- Revision 3, dated 22 August 2003
  - Bracketing requirements for sample results added.
  - Correction to the pH unit reading requirement in section 10.1
  - Removed flow chart
  - Formatting corrections
  - Addition of data review sheet
  - Detail added to QC sample of sample duplicates and batch duplicates.
  - Safety section updated to reference the Corporate Safety Manual.
  - Duplicate, LCS, CCV and ICV acceptance limit changed from <5% to +0.1 pH

units.

- Revision 2, dated 6 July 2001
  - The company name is changed from Quanterra to STL.
  - Initial calibration verification standard to be at a pH in middle of the working range of the calibration where this is possible.

- Revision 1, dated 18 August 1997
  - Added Appendix I: Flow Chart.

Attachment 1

Example pH Calibration and Maintenance Log

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Denver

Calibration and Maintenance Log

Wet Chemistry / pH Probe

Daily Maintenance	Day	Sat	Sun	Mon	Tue	Wed	Thu	Fri
(No maintenance required when instrument is not in use.)	**Date/Time:**							
	Analyst:							
1) Inspect the probe for scratches or cracks.								
2) Probe solution refilled.								
3) Store probe in storage solution.								
4) Wipe off apparatus and clean up any spills.								
Calibration Standards:	2.0 Buffer Lot #: Expiration Date:							
	4.0 Buffer Lot #: Expiration Date:							
	7.0 Buffer Lot #: Expiration Date:							
	10.0 Buffer Lot #: Expiration Date:							
	12.0 Buffer Lot #: Expiration Date:							
Calibration Slope:								

Additional Maintenance/Comments:

G:\QA\Edit\Forms\Wet Chemistry\pH Calibration and Maintenance Logbook
Rev. 2.0, 7/23/2012

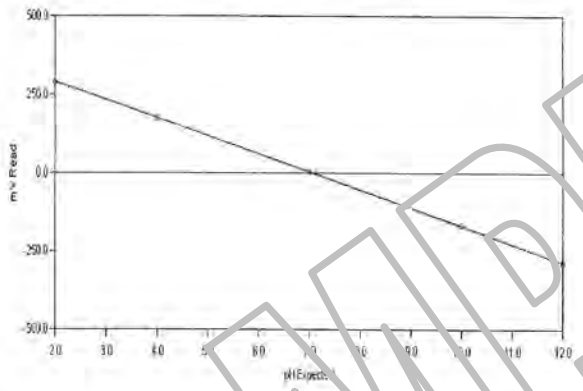
Attachment 2
Example Autotitrator pH Calibration Report

Report Date: 01/06/2015 : 10:10 AM

PC-TitratION PLUS

Calibration Report

Calibration Record # 749



Calibration Settings

Calibration ID	PH	Date	01/06/2015
Channel	1	Time	10:07 AM
Probe Type	pH	Temperature	293.74 K 20.59 C
Probe ID	PH ELECTRODE	Analysis Type	Single Line Fit

Calibration Results

Slope	-57.810	Corr Coef	1.0000
Intercept	3.074	Equation:	Y = (-57.810) X + (3.074)

Calibration Validity True Operator

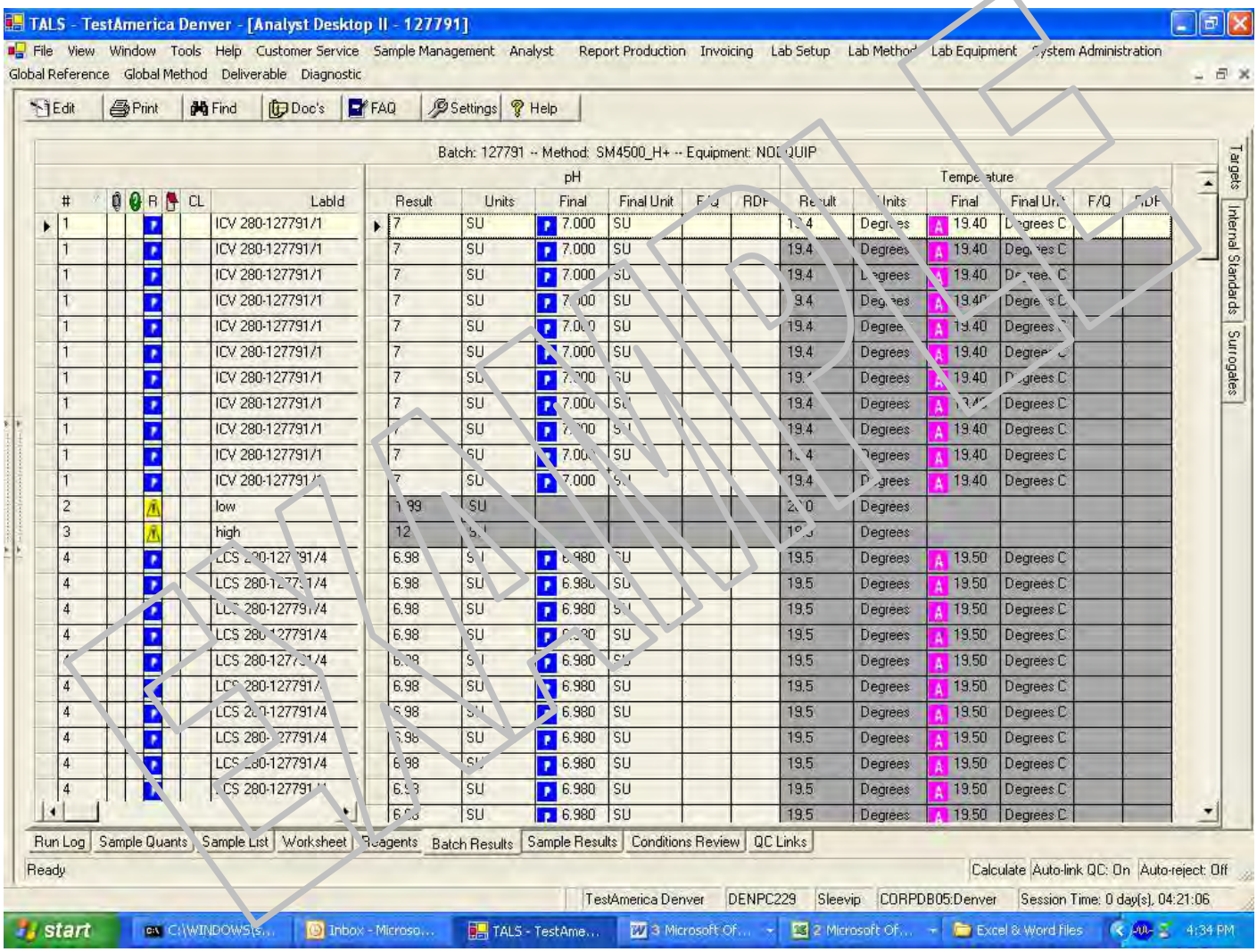
	Result	Minimum	Maximum
Slope	57.810	-65.00	-53.00
Intercept	3.074	-100.00	100.00
Correlation Coefficient	1.0000	0.99	1.00

Note: "True" means the calibration was within the specified ranges
"False" means the calibration was NOT within the specified ranges

Calibration Data	Standard	Reading
	2.00	292.23
	4.00	175.65
	7.00	3.17
	10.00	-167.72
	12.00	-287.96

Page: 1 of 1
PC-TitratION PLUS by Man-Tech Associates, Inc.
CALRPRT.SRW
Copyright Hinterland Software Ltd.

Attachment 3
Example Benchsheet



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Electronic Copy Only -

Title: Alkalinity by Automated Titration and Free Carbon Dioxide [SM2320B, SW9040B, SM 4500-H+B] [SM4500-CO_2 D]

Approvals (Signature/Date):

Roxanne Sullivan 1/15/15
Roxanne Sullivan Date
Technical Specialist

Adam W Alban 16 Jan 15
Adam Alban Date
Health & Safety Manager / Coordinator

Margaret S. Sleevi 1/26/15
Margaret S. Sleevi Date
Quality Assurance Manager

L R C 1/26/15
William S. Cicero Date
Laboratory Director

Facility Distribution No. _____ **Distributed To: _____**

1.0 Scope and Application

1.1 This procedure is to be used for the determination of alkalinity in water. The different forms of alkalinity (total, bicarbonate, carbonate, and hydroxide) can also be calculated. The procedure can be extended to determine alkalinity in soil following extraction with de-ionized water. (See SOP DV-WC-0036). The reporting limit for all forms of alkalinity is 5 mg/L in water and 100 mg/Kg in soil.

1.2 This method is applicable to all ranges likely to be encountered. As a practical matter, samples with an alkalinity greater than about 1200 mg/L as calcium carbonate require a reduced volume or stronger titrant in order to keep the titrant volume to a reasonable amount. Samples with an alkalinity greater than 1200 mg/L will be analyzed per SOP DV-WC-0085.

1.3 The concentration of Free Carbon Dioxide can be calculated from the Total Alkalinity results. The reporting limit for Free Carbon Dioxide is 5 mg/L.

2.0 Summary of Method

2.1 Samples are analyzed for pH and alkalinity simultaneously on an automated titrator as follows:

2.1.1 The pH is determined electrometrically with a glass electrode in combination with a reference electrode. The special glass used in the electrode develops a voltage across it that depends on the pH of the solution being analyzed. The voltage is measured and converted to pH by calibration against buffers of known pH.

2.1.2 Alkalinity is determined by titration of the sample with a standardized acid to specified endpoints (pH 8.3 and 4.5). Alkalinity is calculated from the volume of acid required to reach the endpoints and is traditionally reported as calcium carbonate. Samples for alkalinity should not be altered (i.e., filtered or diluted).

2.2 Free Carbon Dioxide is calculated using the sample pH and the bicarbonate alkalinity, which in turn is calculated from the sample pH and Total Alkalinity.

3.0 Definitions

3.1 **pH -** At a given temperature, the intensity of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. Because of the ionic interactions in all but very dilute solutions, it is necessary to use the “activity” of the hydrogen ion and not its molar concentration. The approximate equivalent to molarity can be presumed only in very dilute solutions. A logarithmic scale is used for pH in order to express a wide range of hydrogen ion activities. Neutral pH is 7.0 at 25 ^{o}C, while acidic pH’s are <7 and basic pHs are >7.

3.2 **Alkalinity –** A measure of the acid-neutralizing capacity of water.

3.3 Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and policy DV-QA-003P, "Quality Assurance Program," for definitions of general analytical and QA/QC terms.

4.0 Interferences

4.1 The pH response of most glass electrodes is imperfect at both ends of the scale. The indicated pH value of highly alkaline solutions, as measured with the glass electrode, will be too low. The indicated pH value of salts and strong acids having a pH less than 1, will often be higher than the true pH value. Interferences can be minimized by the selection of the proper electrodes for these conditions. For example, sodium may interfere at pH > 10, and is controlled by using a "low sodium error" electrode.

4.2 The pH electrode may exhibit slow or noisy response with high purity waters due to the lack of ionic strength.

4.3 Coatings of oil and particulate matter may impair electrode response.

NOTE: If the electrode becomes coated with oil, immerse in a mild detergent solution, rinse well with deionized water, and recalibrate. If this fails, try rinsing in 10% HCl.

4.4 Temperature variations will change the pH of the samples and also affect electrode response. Electronic temperature correction must be used to correct for electrode response.

4.5 Salts of weak organic and inorganic acids will contribute to alkalinity. If the alkalinity is intended to be a measure of carbonate and bicarbonate only, the presence of these substances will cause high results.

4.6 The pH 4.5 is the routine endpoint for total alkalinity. This assumes the normal carbon dioxide/bicarbonate/carbonate/hydroxide mass action interrelationships for natural waters. Other types of waters can have other interrelationships that might dictate the use of a different endpoint.

4.7 Samples not in equilibrium with the atmosphere may exhibit changes in pH and in the distribution of the various forms of alkalinity when exposed to the atmosphere. The sample containers should be filled completely and kept closed until just prior to the analysis. The analysis should be performed as soon as possible.

4.8 Particulates in the sample may affect the alkalinity results. This interference can cause an error in the ion balance calculation.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use.

It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.3.2 Exercise caution when using syringes with attached filter assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.

5.4 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3 (TWA)	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

6.1.1 Man-Tech Autotitator (AT3), consisting of:

- Burivar I/2 Buret Module
- Titrasip Titration Module
- PC-Tis Interface Module
- PC running PC-Titrate software

6.1.2 Radiometer Autotitrator (AT2), consisting of:

- SAC 80 Sample Changer
- TIT 85 Titrator
- ABU 80 Autoburette

6.1.3 Combination pH Electrode – Epoxy-covered glass, with temperature correction, Ross Sure-Flow or equivalent

6.2 Supplies

6.2.1 Tubes to fit autosampler. These must be thoroughly rinsed to remove all traces of salt if reused.

6.2.2 Pipette calibrated to 10.0 mL, and disposable tips.

6.2.3 Miscellaneous laboratory apparatus and glassware.

6.3 Computer Software and Hardware

Please refer to the master list of documents and software/hardware located on R:\QA\Read\Master List of Documents\Master List of Documents and Software/hardware.xls or current revision for the current software to be used for data processing.

7.0 Reagents and Standards

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 All of the standard materials are obtained from commercial sources, and must be NIST traceable. Either the calibration standards or the ICV must be obtained from an ISO Guide 34 approved vendor.

7.3 pH Buffers: 2, 4, 7,10 and 12.

7.4 Alkalinity Standards:

7.4.1 Sodium Carbonate solution (1 N)

This standard is purchased commercially.

7.4.2 Sodium Carbonate solution (200 mg/L as $CaCO_3$)

Pipette 4 mL of the 1 N Sodium Carbonate Solution into a 1 liter volumetric flask. Bring to volume with de-ionized water.

For the high range, pipette 5 mL of the 1 N Sodium Carbonate Solution into a 250 ml volumetric flask. Bring to volume with de-ionized water.

7.4.3 0.02 N Sulfuric Acid (Alkalinity Titrant)

Purchase from a commercially available source.

7.4.4 0.1 N Sulfuric Acid (Alkalinity Titrant – High Range)

Purchase from a commercially available source.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Method	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
2320B	HDPE	1 liter	Cool, $\leq 6^{o}C$	14 Days	40 CFR Part 136.3
9040B	HDPE	1 liter	None	Analyze Immediately	40 CFR Part 136.3

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS Method Comments to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Assurance Program.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in the LIMS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the

laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Sample QC - The following quality control samples are prepared with each batch of 20 samples.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 in 20 or fewer samples	< Reporting Limit
Laboratory Control Sample (LCS)[1]	1 in 20 or fewer samples	± 10% of the true value
Sample Duplicate - pH	1 in 20 or fewer samples[2]	≤0.05 units
Sample Duplicate - Alkalinity	1 in 20 or fewer samples	≤ 10% RSD

[1] MB is not possible for pH
[2] Some programs (e.g., South Carolina and North Carolina) require duplicates to be analyzed at a 10% frequency.

9.2.1 Method Blank (MB)

The MB consists of reagent water that is carried through the entire analytical procedure, including preparation and analysis. The MB is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The MB is prepared in the same manner as the samples using DI water for water samples.

Acceptance Criteria: The MB should not contain any analyte of interest at or above the reporting limit (RL).

Corrective Action: If the analyte level in the MB exceeds the reporting limit for the test, all associated samples are re-prepared and reanalyzed. If this is not possible due to limited sample quantity or other considerations, the corresponding sample data must be taken in consultation with the client and must be addressed in the project narrative.

If the analyte concentration is greater than the reporting limit (RL) in the samples associated with an unacceptable MB, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the project narrative.

If all samples associated with a blank greater than the RL are greater than 10 times the blank value, the samples may be reported with an NCM to qualify the high blank value.

9.2.2 Laboratory Control Sample (LCS)

One LCS is analyzed with each batch of 20 or fewer samples.

Fill a tube with the LCS solution (Section 7.4.2) and analyze the same as samples (Section 10). The true value of this standard is 200 mg/L.

Acceptance Criteria: The LCS should be between 90-110% of the expected value.

Corrective Action: If the LCS exceeds allowable levels, all associated samples must be reanalyzed.

9.2.3 Duplicate Samples

One duplicate sample must be recorded with each batch of samples processed not to exceed 20 samples. Some programs (e.g., South Carolina and North Carolina) require duplicates to be analyzed at a 10% frequency.

Acceptance Criteria: The relative percent difference (RPD) for the duplicate pair must be $\leq$10%.

Corrective Action: If the duplicate results are outside of these control limits, check instrument conditions and repeat the analysis. If still outside control limits and all of the calibration checks are in control, report the situation in a Nonconformance Memo so that the information can be included in the case narrative of the final report.

NOTE: A matrix spike/matrix spike duplicate pair is not analyzed for this method. It is not possible to spike a sample to be measured for alkalinity and calculate recovery in the same manner as other tests. Alkalinity is determined based on sample pH. pH is a logarithmic scale. Method precision is assessed with the sample duplicate analysis.

9.3 Instrument QC

9.3.1 Initial Check and Continuing Calibration Verification

9.3.1.1 The 200 mg/L standard (Section 7.4.2) is used for the Alkalinity Initial check and CCV.

9.3.1.2 Calibration verification standards are to be analyzed initially (Initial Check) and after ten samples and at the end of the run (CCV).

Acceptance Criteria The Initial check and the CCV should be between 90-110% of the expected value.

Corrective Action: If the verifications exceed allowable levels, all associated samples must be reanalyzed.

9.3.1.3 A calibration blank is run for the alkalinity after each calibration check standard (initial and continuing). The calibration blank must be <RL or all samples must be reanalyzed.

9.3.1.4 A calibration blank is not appropriate for pH analysis.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP # DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 Sample Preparation

Allow the sample to come to room temperature before analyzing.

10.4 Calibration

10.4.1 Initial Calibration for pH

10.4.1.1 This calibration procedure is applicable to both Instrument AT2 and Instrument AT3.

10.4.1.2 The pH meter is calibrated each day of operation.

10.4.1.3 Be sure that the reference electrode has been filled with 3 M potassium chloride.

10.4.1.4 Calibrate the pH meter using pH 2, 4, 7, 10, and 12.

10.4.1.4.1 Fill the first six tubes in the autosampler with the following order of samples: pH 2 buffer, pH 4 buffer, pH 7 buffer, pH 10 buffer, pH 12 buffer, and deionized water.

10.4.1.4.2 Click on the button “PH CALIBRATION” and follow the screens to calibrate.

10.4.1.4.3 When calibration has finished, go to titrator and choose "examine calibrations." Print the calibration if instrument states it is valid. If the calibration is not valid, recalibrate.

10.4.1.4.4 Open up "documents" and select the bottom option (Alk-new) to update the buffers and standards. Update the information and print this out.

NOTE: Internal standard is not an appropriate technique for titration.

10.5 Sample Analysis

10.5.1 Be sure the titrant reservoir for 0.02 N sulfuric acid is at least half full. Be sure that there are no air bubbles in the line. Fill deionized water container used for rinses to the top.

10.5.2 Click on the button "Conductivity – pH – Alkalinity". Click load template and load the appropriate template. Add the sample IDs to the schedule and save the template.

10.5.3 Begin to load the autosampler as indicated by the schedule, using approximately 40 mL in each tube. Click the button "start" when ready to begin analysis.

10.5.4 The titrator has been programmed to deliver a maximum volume of 25 mL titrant. Samples requiring more than this should be reanalyzed using a smaller aliquot or using the high level method.

10.5.5 Calculate the results according to the calculation section below.

NOTE: Low level alkalinity (<20 mg/L) is performed by the autotitrator checking measurements every 0.3 pH units. If the sample pH is < 4.5 the alkalinity is reported as ND.

10.5.6 High Range Samples

10.5.6.1 If the sample pH is greater than 4.5 with an alkalinity result of zero than the high range alkalinity method needs to be performed. Using the automated method, repeat the analysis as described in Sections 10.5.1 – 10.5.5 using the 0.1 N H_2SO_4 titrant in the reservoir.

10.5.6.2 If the high range alkalinity method has a total alkalinity result that is zero with a pH greater than 4.5; the sample should be run using the manual titration method described in SOP DV-WC-0085.

10.6 Troubleshooting / Maintenance

10.6.1 For Auto-titrators

10.6.1.1 Verify titration cell is draining completely

10.6.1.2 Insure absence of air bubble in burette.

10.6.1.3 Purge burette if air bubble are observed

10.6.1.4 Verify lines in titration cell are at correct position.

10.6.1.5 Correct positions are marked on dispenser tips.

10.6.1.6 Verify pump is working

10.6.1.7 Verify potassium chloride volume is full in pH meter.

10.6.2 Verify volumes and reagent amounts in TALS.

10.6.3 Verify validity of standards and reagents.

10.6.4 Verify standards and intermediates are the correct concentration and reagents are not expired.

10.6.5 Verify pipettes and burettes are reading correct volumes.

10.6.6 Insure pH meter calibration and QC standards are accurate.

10.6.7 Check interferences for contributing factors.

10.6.8 Verify TALS calculations.

11.0 Calculations / Data Reduction

11.1 Standardization of Alkalinity Titrant

$$N_{ACID} = \frac{N_{BASE} \times V_{BASE}}{V_{ACID}} \qquad \textit{Equation 1}$$

Where:

N_{ACID} = Normality of titrant
N_{BASE} = Normality of Sodium Carbonate
V_{BASE} = Volume of Sodium Carbonate titrated, mL
V_{ACID} = Volume of titrant needed for titration, mL

11.2 Calculate the RPD for the sample and sample duplicate as follows:

$$RPD(\%) = 100 \times \left[\frac{S - SD}{\frac{S + SD}{2}} \right]$$ *Equation 2*

11.3 Accuracy

ICV / CCV, LCS % Recovery

$$\%\ \mathrm{Recovery} = \frac{observed\ concentration}{known\ concentration} \times 100\%$$ *Equation 3*

MS % Recovery

$$MS\ \%\ \mathrm{Recovery} = \frac{(spiked\ sample\ conc.) - (unspiked\ sample\ conc.)}{spike\ concentration} \times 100\%$$ *Equation 4*

11.4 For calculation of Free Carbon Dioxide, pH values and alkalinity results are recorded directly from the titrator printout into the CO2 benchseet (Attachment 1).

11.5 All forms of alkalinity results are uploaded directly from the instrument into TALS (Attachment 2).

11.6 Three values for alkalinity will be printed if the pH is greater than 8.3. Record the values at pH 8.3 and 4.5 on the bench sheet. The third value is the difference and is ignored. Note that some results will be printed in scientific notation; be careful to check this when recording results.

11.7 If the pH is less than 8.3, only one value will be printed (at pH 4.5). Record this value on the bench sheet. P alkalinity is ND on these samples.

11.8 Calculation of Alkalinity

11.8.1 Potentiometric titration to end-point pH:

$$Alkalinity, mg/L\ CaCO_3 = \frac{A\ x\ N\ x\ 50{,}000}{mL\ sample}$$ *Equation 2*

Where:
A = mL standard acid used.
N = Normality of standard acid.

11.8.2 Potentiometric titration of low alkalinity:

$$Total\ Alkalinity, mg/L\ CaCO_3 = \frac{(2B - C)\ x\ N\ x\ 50{,}000}{mL\ sample} \qquad \textit{Equation 3}$$

Where:
B = Volume of titrant to first recorded pH, in mL.
C = Total volume of titrant added to reach a pH level 0.3 units lower.
N = Normality of acid.

11.9 Calculate the individual forms of alkalinity as follows:

Result of Titration	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Alkalinity
P = ND	ND	ND	T
P < T/2	ND	2P	T - 2P
P = T/2	ND	2P	ND
P > T/2	2P - T	2(T - P)	ND
P = T	T	ND	ND

Where:
T = Total Alkalinity = Alkalinity at pH 4.5
P = Phenolphthalein Alkalinity = Alkalinity at pH 8.3

11.10 Record the values for Total, Bicarbonate, Carbonate, and Hydroxide Alkalinity.

11.11 Calculate Free Carbon Dioxide using the following formulas:

$$mg\ CO_2\ /L = 2.0 \times B \times 10^{(6-pH)} \qquad \textit{Equation 4}$$

Where:

B = Bicarbonate alkalinity = HCO_3^- as mg $CaCO_3$/L

$$B = HCO_3^-\ \text{as mg}\ CaCO_3/L\ = \frac{T - 5.0 \times 10^{(pH-10)}}{1 - 0.94 \times 10^{(pH-10)}} \qquad \textit{Equation 5}$$

T = Total alkalinity, mg $CaCO_3$/L

11.12 Reporting

11.12.1 Alkalinity results less than 5 mg/L are reported as ND. All forms of alkalinity are reported in mg/L as Calcium Carbonate.

11.12.2 For LCS, Dup, and CCV results, results are only reported for tALK. All other analytes must be manually rejected in TALS.

11.12.3 Report case narratives for South Carolina must include date and time of collection.

11.12.4 The initial data review is performed by the analyst, and a second-level review is performed by the area supervisor or designee. Both reviews are documented on a Data Review Checklist. See SOP DV-QA-0020 for a copy of the checklist and for more detail on the review process.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

12.1.1 The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL policy in DV-QA-005P. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency.

12.2 Demonstration of Capabilities

12.2.1 All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows."

12.2.1.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.

12.2.1.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.2.1.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.2.1.4 Further details concerning demonstrations of proficiency are described in SOP# DV-QA-0024.

12.3 Training Requirements

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use, has the required

experience, and has successfully analyzed initial demonstration samples (see SOP # DV-QA-0024 for details).

13.0 Pollution Control

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability).

13.2 Standards and reagents are prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

14.2 The following waste streams are produced when this method is carried out:

14.2.1 Expired Chemicals/Reagents/Standards – Contact Waste Coordinator

14.2.2 Titrated sample waste – Aqueous Acidic - Waste Stream F

NOTE: Radioactive, mixed waste and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 pH:

15.1.1 Method 9040B, "pH Electrometric Measurement", Test Methods for Evaluating Solid Waste, EPA SW-846 Third Edition, 1/95.

15.1.2 Method 4500-H+ B-, pH Value, "Standard Methods for the Examination of Water and Wastewater," 20th Edition, 1998.

15.2 Alkalinity:

15.2.1 Method 2320A-1997, Alkalinity – Introduction, "Standard Methods for the Examination of Water and Wastewater," 20th Edition, 1998.

15.2.2 Method 2320B-1997, Alkalinity – Titration Method, "Standard Methods for the Examination of Water and Wastewater," 20th Edition, 1998.

15.3 Free Carbon Dioxide:

15.3.1 Method 4500-CO_2 A-1997, Introduction, "Standard Methods for the Examination of Water and Wastewater," 20th Edition, 1998.

15.3.2 Method 4500-CO_2 D-1997, Carbon Dioxide and Forms of Alkalinity by Calculation, "Standard Methods for the Examination of Water and Wastewater," 20th Edition, 1998.

16.0 Method Modifications:

Item	Method	Modification
1	SM 2320B	The method requires an initial verification of the sulfuric acid titrant. The laboratory purchases the titrant from a commercial source and therefore does not perform additional verification.

17.0 Attachments

Attachment 1: Example Spreadsheet for Calculation of Free Carbon Dioxide
Attachment 2: Example Alkalinity Batch Results uploaded into TALS

18.0 Revision History

- Revision 9, dated 31 January 2015
  - Annual Technical Review
  - Corrected note in section 9.2, changed acidity to alkalinity.
  - Revised section 10.4.1 to a single calibration procedure applicable to both instruments..
  - Removed section 10.4.1.3.4 and 10.4.1.3.8 to reflect current practices.
  - Added section 10.6 troubleshooting and maintenance section
  - Added section 11.2 RPD calculation
  - Added section 11.3 Accuracy calculation
  - Added section 11.12.2

- Revision 8, dated 31 January 2014
  - Added instrument IDs to Sections 6.1.1 and 6.1.2
  - Added requirement for ISO Guide 34 approved vendor
  - Added buffers to 7.3
  - Added High range standard to 7.4.2
  - Added Section 9.2.1 – 9.2.3.
  - Revised Section 9.3
  - Added buffers and AT3 calibration to 10.4.13
  - Added calibration acceptance criteria to sections 10.4.1.3.3 and 10.4.1.3.8.
  - Changed wording of 10.5.6.2
  - Added Section 11.3
  - Added Attachment 2

- Revision 7, dated 7 December 2012
  - Added Free Carbon Dioxide (Sections 1.3, 11.8, 15.3 and Attachment 1)
  - Added soil matrix
  - Added calculation for alkalinity based on titration to end-point pH (Section

11.5.1)
  - Added statements for MUR 2012 QC Elements (Sections 9.2, 10.4)
  - Revised sections 9.1, 10.1, 10.2 to reflect current practice
  - Added section 7.4.4
  - Added Sections 10.5.6 and 10.5.7 to describe high level procedure and use of manual titration method.
  - Source method review
  - Formatting and editorial changes throughout

- Revision 6.3, dated 30 November 2011
  - Annual Technical Review
  - Removed all references to EPA method 310.1
  - Corrected grammatical and formatting error.
  - Added Section 9.1
  - Deleted reference to using the pH 7.0 buffer for the CCV in Section 9.3
  - Updated Attachment 1.

- Revision 6.2, dated 19 November 2010
  - Added reagent quality requirements to section 7.0

- Revision 6.1, dated 03 May 2010
  - Added section 6.3
  - Annual Review

- Revision 6, dated 27 March 2009
  - Deleted the Conductivity method from SOP
  - Updated other SOP references and formatting
  - Deleted Attachment 2 – Data Review Checklist for Direct Measurements.
  - Added references toDV-WC-0085 (manual titration) for high alkalinity samples.
- Revision 5, dated 30 January 2008
  - Integration for TestAmerica and STL operations.
  - Updated formatting
  - Removed references to EPA method 305.1
- Revision 4.1, dated 20 November 2006
  - For this minor revision, the technical content of this SOP was not reviewed or updated. The purpose of this minor revision is to incorporate the Safety Bulletin information to ensure compliance with STL Corporate requirements. In addition, Section 9.1 was revised to reference Policy QA-024 for specific QC requirements for federal programs, any existing interim changes were incorporated, and formatting was updated consistent with Policy QA-001.
- Revision 4, dated 17 September 2002
  - Company name changed from Quanterra to STL Denver.
  - Definitions for conductivity and alkalinity were added to Section 3.
  - Details about the instrumentation were added to Section 6.
  - The pH meter is calibrated with 3 buffers, including a pH 7 buffer.
  - Details about the standards were added in section 7.
  - The old SOP made reference to LCS. Instead, this SOP refers to these solutions as calibration verification standards in Section 10.4

- The high conductivity curve option was removed because current instrumentation does not allow adjustment of the cell constant.
- The low level alkalinity option in the old SOP was redundant because all analyses use the 0.02N sulfuric acid, the low-level titrant.

Attachment 1.

Example Spreadsheet for Calculation of Free Carbon Dioxide

Laboratory Bench Sheet
Free CO_2, Total, BiCarb, Carbonate,Hydroxide Alkalinity
Revision 8 - March 30, 2012

TestAmerica - Denver

Analyst:	Joe Analyst	SOP Information	
Date:	3/28/2012	Number:	DV-WC-0025
Batch #:	999999	Revision:	6.3

Cup #:	Sample ID	Vol mL	FREE CO2	pH	Alkalinities (mg/L) at pH 8.3	at pH 4.5	OH-	CO3=	HCO3-	Total	CHAAP CO2
1	BLANK	20	0.15	7.080	0.00	0.88	ND	ND	0.88	0.88	0.39
2	LPR5K	20	177.10	5.960	0.00	80.76	ND	ND	80.76	80.76	35.53
3	LPR5K	20	182.62	5.900	0.00	72.53	ND	ND	72.53	72.53	31.91
4	LPR58	20	31.84	7.390	0.00	390.83	ND	ND	390.83	390.83	171.97
5	LPR59	20	267.94	6.480	0.00	404.59	ND	ND	404.59	404.59	178.02
6	LPR60	20	19.26	7.630	0.00	410.75	ND	ND	410.75	410.75	180.73
7	LPR61	20	211.95	6.540	0.00	367.45	ND	ND	367.45	367.45	161.68
8	LPR62	20	236.55	6.700	0.00	592.79	ND	ND	592.79	592.79	260.83
9	LPR63	20	226.65	6.710	0.00	581.19	ND	ND	581.19	581.19	255.72
10	LPR64	20	455.66	6.650	0.00	1017.69	ND	ND	1017.69	1017.69	447.77
11	LPR65	20	193.77	6.400	0.00	243.36	ND	ND	243.36	243.36	107.08
12	LPR66	20	720.07	8.2[illegible]	0.00	597.51	ND	ND	597.51	597.51	262.90
13	LPR67	20	543.69	[illegible].340	0.00	594.73	ND	ND	594.73	594.73	261.68
14	LPR68	20	1.13	[illegible].650	0.00	2.52	ND	ND	2.52	2.52	1.11
15	LPR69	20	249.79	7.[illegible]70	0.00	1467.41	ND	ND	1467.41	1467.41	645.66
16	LPR70	20	18.80	7.69[illegible]	0.00	406.50	ND	ND	406.50	406.50	178.86
17	LPR71	20	13.98	7.800	0.00	441.15	ND	ND	441.15	441.15	194.11
18	LPR72	20	42.23	7.[illegible]60	0.00	608.17	ND	ND	608.97	608.17	267.95
19	LPR73	20	ND	11.[illegible]10	599.91	643.42	576.41	67.02	ND	643.42	283.10
20	LPR74	20	3.80	7.170	0.00	730.68	ND	ND	730.68	730.68	321.50
21	LPR75	20	24.[illegible]	7.520	0.00	405.09	ND	ND	405.09	405.09	178.24
22	LPR76	20	17.83	7.650	0.00	416.14	ND	ND	416.14	416.14	183.10
23	LPR77	20	3.80	8[illegible]0	0.00	144.26	ND	ND	144.26	144.26	63.47
24	LPR78	20	18.62	[illegible]660	0.00	425.56	ND	ND	425.56	425.56	187.25
25	LPR79	20	23.78	7.540	0.00	412.30	ND	ND	412.30	412.30	181.41
26	LPR80	20	[illegible]41	6.93[illegible]	0.00	1.74	ND	ND	1.74	1.74	0.77
27	LPR81	20	0.[illegible]2	7.1[illegible]0	0.00	1.74	ND	ND	1.74	1.74	0.77
28	LPR82	20	13.25	[illegible].770	0.00	390.25	ND	ND	390.25	390.25	171.71
29	LPR83	20	26.[illegible]5	7.560	0.00	502.80	ND	ND	502.80	502.80	221.23
30	LPR84	20	80.[illegible]4	7.39	0.00	740.60	ND	ND	740.60	740.60	325.86
31	LPR85	20	ND	11.700	313.38	350.10	276.66	73.44	ND	350.10	154.04
32	LPR86	20	11.59	7.84	0.00	400.94	ND	ND	400.94	400.94	176.41
33	LPR[illegible]87	20	23.84	7.57	0.00	442.85	ND	ND	442.85	442.85	194.85
34		20									
35		20									
36		20									

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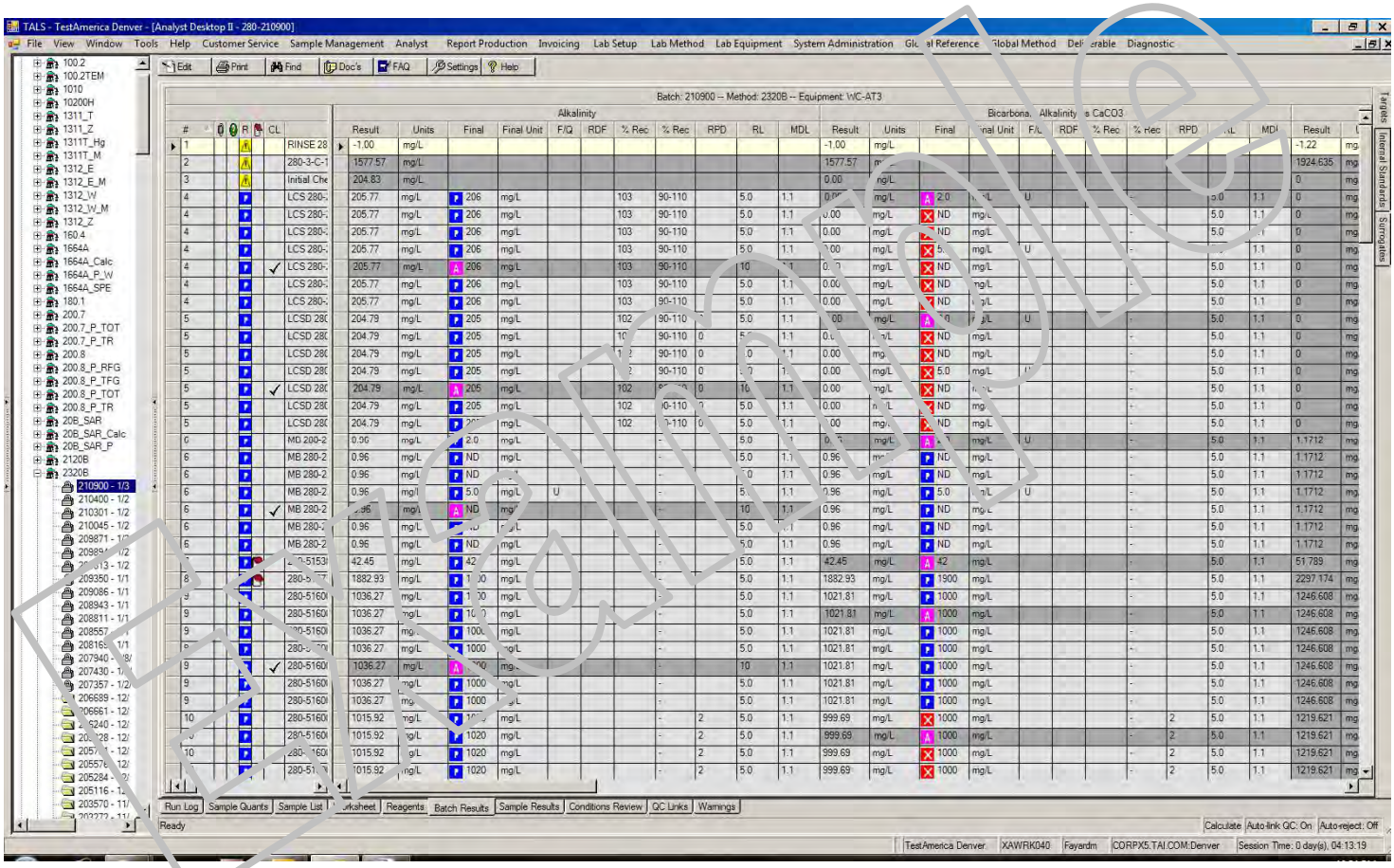
Page 1 of 1

Attachment 2.

Example Alkalinity Batch Results uploaded into TALS



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Inductively Coupled Plasma Mass Spectrometry for Trace Element Analysis by SW-846 Method 6020A

Approvals (Signature/Date):

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1.0 Scope and Application

1.1 This procedure describes multi-elemental analysis by inductively coupled plasma-mass spectrometry (ICP-MS) based on EPA Method 6020A.

1.2 Method 6020A lists twenty-three elements approved for analysis by ICP-MS (Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Ag, Na, Tl, V, and Zn). This procedure has been developed for twenty elements and additional elements may be included provided that the method performance criteria presented in Sections 9 and 12 are met. However, project approval may be required from the controlling agencies for compliance testing beyond the elements included in the promulgated methods.

1.3 The procedure is applicable to the analysis of acid digested waters, sediments, sludges and soils. Standard reporting limits are listed in Attachment 1 for water and soil. The preliminary acid digestion for aqueous samples is described in SOP DV-IP-0014, and the digestion procedure for solids is given in SOP DV-IP-0015.

2.0 Summary of Method

2.1 Aqueous digestates are nebulized into a spray chamber where a stream of argon carries the sample aerosol through the quartz torch and injects it into a radiofrequency (RF) plasma. There the sample is decomposed and desolvated.

2.2 The ions produced are entrained in the plasma gas and by means of a water-cooled, differentially pumped interface, introduced into a high-vacuum chamber that houses a quadrapole mass spectrometer capable of providing a mass resolution better than or equal to 0.9 amu (see Section 3) peak width at 10% of the peak height. The ions are sorted according to their mass-to-charge ratio and measured with a channel electron multiplier.

2.3 A collision/reaction cell utilizing He and (optionally) H_2 gases is used to remove molecular interferences. As the ion beam passes through the cell chamber, a diffuse cloud of He or H_2 gas is injected into its path. Collisions between the ions and the atoms in the gas deflect and remove interferences. See Section 4.2.3 for more information.

2.4 Interferences must be assessed and valid corrections applied, or the data flagged to indicate problems. Interference corrections must include compensation for background ions contributed by the plasma gas, reagents, and the constituents of the sample matrix. Recommended elemental equations, which correct for many of these interferences, are listed in Attachment 2. Interference equations may vary or be unnecessary depending on the instrument setup and choice of collision/reaction gas.

2.5 Use of the internal standard technique is required to compensate for suppressions and enhancements caused by sample matrices. Internal standard assignments are listed in Attachment 4.

3.0 Definitions

3.1 Atomic Mass Unit (amu) – Obsolete term replaced by "unified atomic mass unit (u)" or "dalton (Da)", which denotes a small unit of mass that is used to express atomic and molecular masses. It is defined to be 1/12 of the mass of one atom of carbon-12.

3.2 Batch – The batch is a set of up to 20 samples of the same or similar matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches are defined at the sample preparation stage. See Policy DV-QA-003P for further details.

3.3 Dissolved Metals - Those elements which pass through a 0.45-µm membrane filter (sample is acidified after filtration).

3.4 Total Metals - The concentration determined on an unfiltered sample following vigorous acid digestion.

3.5 Total Recoverable Metals - The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acids.

3.6 Instrument Detection Limit (IDL) - See Section 12.3.

3.7 Sensitivity - The slope of the analytical curve (i.e., the functional relationship between raw instrument signal and the concentration).

3.8 Tuning Solution - This is a multi-element solution containing analytes which are representative of the entire mass range capable of being scanned by the instrument. It is used to optimize the sensitivity of the instrument and to verify the mass resolution meets method criteria.

3.9 Initial Calibration Verification / Quality Control Standard (ICV) - A multi-element standard of known concentrations prepared to verify instrument calibration. This solution must be an independent standard prepared near the mid-point of the calibration curve, and at a concentration other than that used for instrument calibration.

3.10 Continuing Calibration Verification (CCV) - A multi-element standard of known concentrations prepared to monitor and verify the instrument daily continuing performance.

3.11 Interference Check Standard (ICS) - A solution containing both interfering and analyte elements of known concentration that is used to correction factors.

3.12 Laboratory Control Sample / Laboratory Fortified Blank (LCS/LFB) - A multi-element standard of known concentrations that is carried through the entire sample preparation and analysis procedure. This solution is used to verify the accuracy of the sample preparation.

3.13 Reagent Blank - High purity (> 18 megohm-cm) water containing the same acid matrix as the calibration standards that is carried through the entire digestion

process.

3.14 **Calibration Blank -** High purity (> 18 megohm- cm) water acidified with the same acid concentrations present in the standards and samples. Also referred to as the Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB).

3.15 **Method Detection Limit (MDL) -** The minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

3.16 **Low Level ICV (LLICV) / Continuing Calibration Verification (LLCCV) -** A multi-element standard of known concentrations prepared to monitor and verify the instrument performance at the reporting limit (RL).

3.17 Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and Policy DV-QA-003P, *Quality Control Program*, for definitions of general analytical and QA/QC terms.

4.0 Interferences

4.1 Elemental Isobaric Interferences

Elemental isobaric interferences in the ICPMS are caused by isotopes of different elements forming ions with the same nominal mass-to-charge ratio (m/z). Most interferences of this type are corrected for by the instrument software and by the careful selection of isotopes for analysis.

4.2 Isobaric Molecular Interferences

4.2.1 Polyatomic interferences are derived from the plasma gas, reagents or sample matrix. Isobaric molecular interferences are caused by ions consisting of more than one atom or charge. Attachment 3 lists isobaric interferences which might possibly affect required analytes. These molecular interferences are minimized by use of the collision cell utilizing He and/or H_2 gases. When these interferences cannot be avoided by the use of another isotope with sufficient natural abundance, corrections must be applied and the data flagged to indicate the presence of interferences.

4.2.2 Chloride in samples can produce low recoveries for antimony and silver. If chloride interference is a concern, 1% HCl can be added during digestion, but calibration standards must be adjusted to include 1% HCl also. The use of hydrochloric and sulfuric acids should be minimized due to higher incidence of molecular-ion interferences with the presence of these acids. Excessive amounts of nitric acid can also lead to molecular interferences.

4.2.3 Collision cell interference removal works both by causing the interfering molecular ion to dissociate and by reducing the kinetic energy of the ion. The latter is termed Kinetic Energy Discrimination (KED), and is the

primary mechanism for interference removal. Polyatomic ions are larger than elemental ions and so collide with the helium atoms in the collision cell more frequently than the smaller elemental ions. Each collision reduces the energy of the ion, so the molecular ions lose energy more quickly. At the end of the collision cell a positive voltage plate prevents passage of the now low energy molecular ions. Thus, the interference is eliminated because the molecular ions do not reach the detector.

4.3 Doubly Charged Ion Interferences

Doubly charged elemental ion interferences are possible in cases where the second ionization potential of the element is significantly below the first ionization potential for argon (15.7 eV). If a doubly charged ion is formed, it will cause a response at half of its elemental mass, potentially causing interference. Most elements have high enough second ionization potentials that formation of doubly charged ions is not an issue. The percentage of doubly charged ions being formed in the plasma is monitored on a daily basis during the instrument tuning process.

4.4 Physical Interferences

4.4.1 Physical interferences are associated with the transport and nebulization process. Internal standards are used to compensate for these types of interferences.

4.4.2 Internal standards should be added at a level to give approximately 100,000 – 20,000,000 counts of raw signal intensity. The mass of the internal standard should ideally be within 50 amu of the mass of the measured analyte.

4.4.3 Matrix effects are monitored by comparing the internal standard intensity in the sample to the internal standard intensity of the calibration blank. When performing method 6020A, the internal standard recoveries in samples can not fall below 70% of the intensity of the calibration standard. If they fall outside this window, a five-fold dilution (1:4) is performed on the sample to correct for matrix effects and the sample is reanalyzed.

4.4.4 Memory effects or carry-over can occur when there are large relative concentration differences between samples and/or standards which are analyzed sequentially. The rinse period between samples must be long enough to eliminate significant memory interference.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use.

It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile or latex gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.3.2 The ICP-MS plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma. The RF Generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.4 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material[1]	Hazards	Exposure Limit[2]	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

6.1.1 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) capable of providing resolution less than or equal to 0.9 amu at 10% peak height and 1.0 amu at 5% peak height in the mass range from 6-253 with a data system that allows corrections for isobaric interferences and the application of the internal standard technique. The ICP-MS must be equipped with a collision cell for the removal of molecular interferences.

6.1.2 A four-channel peristaltic pump.

6.1.3 Autosampler with autosampler tubes.

6.1.4 Appropriate water cooling device.

6.2 Supplies

6.2.1 Argon gas: High purity grade (99.99%).

6.2.2 Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.2.3 Class A volumetric flasks.

6.3 Computer Software and Hardware

Please refer to the master list of documents and software located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

7.0 Reagents and Standards

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All standards must be entered into the TestAmerica LIMS (TALS) Reagent Module. Reagents that are not used for calculating results may either be recorded in the Reagent Module or may be entered into batch worksheets.

7.1 Storage and Shelf-Life

7.1.1 All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Standards stored at concentrations as received from the vendor and mid-level dilutions must be replaced prior to the expiration date assigned by the vendor. If no expiration date is provided, the stocks and mid-level standards may be stored for up to one year. They must be replaced sooner if verification from an independent source indicates a problem.

7.1.2 Working standards, i.e., all standards at concentrations ready to analyze on the ICP-MS (except tuning mixes, ICSA and ICSAB mixes, which are received at ready-to-use concentrations) are prepared fresh daily.

7.1.3 For more information on standard storage and shelf-life, see SOP DV-QA-0015.

7.2 Standards

Detailed instructions regarding the preparation of standards and reagents are given in this section. Alternate procedures are allowed as necessary to accommodate volume requirements as long as final concentrations are maintained and an accurate description of the standard or reagent used is entered into the Reagent Module in TALS.

7.2.1 Tuning Solution

The parent tuning solution is purchased as a custom multi-element mix. The elements and concentrations of the constituents are shown in Attachment 7. Prepare the working tuning Solution as detailed below.

7.2.1.1 Obtain a clean 1 L volumetric flask

7.2.1.2 Place 500 mL of reagent water and 10 mL of conc. HNO3 in the flask

7.2.1.3 Pipette 1mL of the Tuning Solution Stock into the flask

7.2.1.4 For the Agilent 7700 also add 50 µL of a 500 mg/L Mg solution and 30 µL of a 1000 mg/L Be solution.

7.2.1.5 Dilute to volume with reagent blank (See Section 7.3). Stopper and mix.

7.2.2 P/A factor solution

7.2.2.1 The Pulse/Analog (P/A) solution is used to monitor the correlation between the Pulse counting and Analog modes of the electron multiplier. The diluted solution must be prepared at different concentrations depending on the current instrument conditions. Multiple dilutions may be required to cover the required intensity range for all elements.

7.2.2.2 The P/A solution may be commercially purchased as a custom multi-element mix. See Attachment 7 for a list of the constituents and concentrations.

7.2.2.3 Prepare and use the P/A solution as recommended by the instrument manufacturer. The P/A solution should be analyzed daily.

7.2.3 Calibration Standard

Stock calibration standards are purchased as custom multi-element mixes or as single element solutions. Each day of analysis, the standards are diluted to working levels using reagent blank (see Section 7.3). The concentrations are given in Attachment 10. Prepare the Daily Working Calibration Standard as shown.

7.2.3.1 Daily Working Calibration Standard for Instruments 077 and 078 (ms 77 cal std)

7.2.3.1.1 Obtain a clean 100 mL volumetric flask.

7.2.3.1.2 Place 50 mL of reagent blank in the flask.

7.2.3.1.3 Pipette 0.5 mL of the MS CALSTD-1 stock standard into the flask.

7.2.3.1.4 Pipette 0.5 mL of the MS CALSTD-2 stock standard into the flask.

7.2.3.1.5 Pipette 0.5 mL of the MS CALSTD-3 stock standard into the flask.

7.2.3.1.6 Pipette 0.5 mL of the MS BRC CALSTD stock standard into the flask.

7.2.3.1.7 Pipette 0.5 mL of a 20 mg/L Zr standard into the flask.

7.2.3.1.8 Dilute to volume with reagent blank. Stopper and mix.

7.2.3.2 Daily Working Calibration Standard for Instrument 024 (MS CAL DAILY)

7.2.3.2.1 Obtain a clean 100 mL volumetric flask.

7.2.3.2.2 Place 50 mL of reagent blank in the flask.

7.2.3.2.3 Pipette 0.5 mL of the MS CALSTD-1 stock standard into the flask.

7.2.3.2.4 Pipette 0.5 mL of the MS CALSTD-2 stock standard into the flask.

7.2.3.2.5 Pipette 0.5 mL of the MS CALSTD-3 stock standard into the flask.

7.2.3.2.6 Pipette 0.5 mL of a 20 mg/L W standard into the flask.

7.2.3.2.7 Dilute to volume with reagent blank. Stopper and mix.

7.2.4 Initial Calibration Verification (ICV) Standard

The ICV stock is from a source different than the source for the calibration standards. Each day of analysis, the ICV standards are prepared in reagent blank to the concentrations shown in Attachment 10. Prepare the ICV as shown below:

7.2.4.1 Initial Calibration Verification Standard for Instruments 077 and 078 (MS 77 ICV)

7.2.4.1.1 Obtain a clean 50 mL volumetric flask.

7.2.4.1.2 Place 25 mL of reagent blank in the flask.

7.2.4.1.3 Pipette 0.1 mL of the MS ICV StockA Standard into the flask.

7.2.4.1.4 Pipette 0.1 mL of the MS ICV StockB Standard into the flask.

7.2.4.1.5 Pipette 0.1 mL of the MS ICV Alt HP Standard into the flask.

7.2.4.1.6 Pipette 0.1 mL of the MS ICV BRC HP Standard into the flask.

7.2.4.1.7 Dilute to volume with reagent blank. Stopper and mix.

7.2.4.2 Initial Calibration Verification Standard for Instrument 024 (MS ICV)

7.2.4.2.1 Obtain a clean 50 mL volumetric flask.

7.2.4.2.2 Place 25 mL of reagent blank in the flask.

7.2.4.2.3 Pipette 0.1 mL of the MS ICV StockA Standard into the flask.

7.2.4.2.4 Pipette 0.1 mL of the MS ICV StockB Standard into the flask.

7.2.4.2.5 Pipette 0.1 mL of the MS ICV Alt HP Standard into the flask.

7.2.4.2.6 Dilute to volume with reagent blank. Stopper and mix.

7.2.5 Continuing Calibration Verification (CCV) Standard

The CCV is prepared from the same source as the calibration standards. The CCV standards are prepared fresh each day of analysis in reagent blank. The concentration is shown in Attachment 10.

7.2.5.1 Continuing Calibration Verification for Instruments 077 and 078 (ms 77 ccv)

7.2.5.1.1 Obtain a clean 100 mL volumetric flask.

7.2.5.1.2 Place 50 mL of the Daily Working Calibration Standard in the flask.

7.2.5.1.3 Dilute to volume with reagent blank. Stopper and mix.

7.2.5.2 Continuing Calibration Verification for Instrument 024 (MS CCV)

7.2.5.2.1 Obtain a clean 100 mL volumetric flask.

7.2.5.2.2 Place 50 mL of reagent blank in the flask.

7.2.5.2.3 Pipette 0.25 mL of the MS CALSTD-1 stock standard into the flask.

7.2.5.2.4 Pipette 0.25 mL of the MS CALSTD-2 stock standard into the flask.

7.2.5.2.5 Pipette 0.25 mL of the MS CALSTD-3 stock standard into the flask.

7.2.5.2.6 Pipette 0.25 mL of a 20 mg/L W standard into the flask.

7.2.5.2.7 Dilute to volume with reagent blank. Stopper and mix.

7.2.6 Reporting Limit (RL) Standards

The reporting limit standards are prepared fresh daily from the same stock as the calibration standards using the reagent blank. The analyte concentrations must be less than or equal to the respective reporting limits. Multiple solutions may be required in order to satisfy all of the project and client specific reporting limits. Alternate reporting limit concentrations may be used as necessary to meet client requirements as long as an accurate description of the standard used is entered into the Reagents module in TALS. Prepare the Reporting Limit Standard for the Agilent 7700 as detailed below.

7.2.6.1 RL Standard for Instruments 077 and 078 (ms 77 RL)

7.2.6.1.1 Obtain a clean 50 mL volumetric flask.

7.2.6.1.2 Place 30 mL of reagent blank in the flask.

7.2.6.1.3 Pipette 0.5 mL of the ms 77 cal std solution into the flask.

7.2.6.1.4 Dilute to volume with reagent blank. Stopper and mix.

7.2.6.2 RL Standard for Instrument 024 (MS RL STD)

7.2.6.2.1 Obtain a clean 10 mL autosampler tube.

7.2.6.2.2 Place 5 mL of reagent blank in the flask.

7.2.6.2.3 Pipette 0.1 mL of the MS CAL DAILY standard into the flask.

7.2.6.2.4 Pipette 0.09 mL of a mixed 1 mg/L Sn and Zn standard into the flask.

7.2.6.2.5 Dilute to volume with reagent blank and mix well.

7.2.7 Daily Linear Range Standard

The Linear Range standard is prepared from the same stock as the calibration standards using reagent blank.

7.2.7.1 Daily Linear Range Standard for Instruments 077 and 078 (MS 77 LR STD)

7.2.7.1.1 Obtain a clean 500 mL volumetric flask.

7.2.7.1.2 Place 50 mL of reagent blank in the flask.

7.2.7.1.3 Pipette 1.0 mL of a 1,000 mg/L As standard into the flask.

7.2.7.1.4 Pipette 2.5 mL of a 1,000 mg/L Ba standard into the flask.

7.2.7.1.5 Pipette 1.0 mL of a 1,000 mg/L Be standard into the flask.

7.2.7.1.6 Pipette 1.0 mL of a 1,000 mg/L Cd standard into the flask.

7.2.7.1.7 Pipette 1.0 mL of a 1,000 mg/L Co standard into the flask.

7.2.7.1.8 Pipette 2.5 mL of a 1,000 mg/L Cr standard into the flask.

7.2.7.1.9 Pipette 2.5 mL of a 1,000 mg/L Cu standard into the flask.

7.2.7.1.10 Pipette 5.0 mL of a 1,000 mg/L Mn standard into the flask.

7.2.7.1.11 Pipette 1.0 mL of a 1,000 mg/L Mo standard into the flask.

7.2.7.1.12 Pipette 2.5 mL of a 1,000 mg/L Ni standard into the flask.

7.2.7.1.13 Pipette 2.5 mL of a 1,000 mg/L Pb standard into the flask.

7.2.7.1.14 Pipette 0.5 mL of a 1,000 mg/L Sb standard into the flask.

7.2.7.1.15 Pipette 1.0 mL of a 1,000 mg/L Se standard into the flask.

7.2.7.1.16 Pipette 1.0 mL of a 1,000 mg/L Sn standard into the flask.

7.2.7.1.17 Pipette 0.5 mL of a 1,000 mg/L Tl standard into the flask.

7.2.7.1.18 Pipette 1.0 mL of a 1,000 mg/L U standard into the flask.

7.2.7.1.19 Pipette 1.0 mL of a 1,000 mg/L V standard into the flask.

7.2.7.1.20 Pipette 2.5 mL of a 1,000 mg/L Zn standard into the flask.

7.2.7.1.21 Pipette 0.05 mL of a 10,000 mg/L Th standard into the flask.

7.2.7.1.22 Dilute to volume with reagent blank. Stopper and mix.

7.2.7.2 Daily Linear Range Standard for Instrument 024 (MS LR STD)

7.2.7.2.1 Obtain a clean 10 mL autosampler tube.

7.2.7.2.2 Place 5 mL of reagent blank in the flask.

7.2.7.2.3 Pipette 0.5 mL of the MS CALSTD-1 stock standard into the flask.

7.2.7.2.4 Pipette 0.5 mL of the MS CALSTD-2 stock standard into the flask.

7.2.7.2.5 Pipette 0.5 mL of a 20 mg/L W standard into the flask.

7.2.7.2.6 Dilute to volume with reagent blank and mix well.

7.2.8 Internal Standard (IS) Solution (77 I.S. / MS I.S. INT)

The internal standard solution is added continuously by peristaltic pump through a mixing tee. The concentrations and components are specified in Attachment 4. Prepare the IS solution as follows:

7.2.8.1 Obtain a clean 250 mL volumetric flask.

7.2.8.2 Place 100 mL of reagent blank in the flask.

7.2.8.3 Pipette 1.2 mL of the 1,000 mg/L Ge Standard into the flask.

7.2.8.4 Pipette 0.4 mL of the 1,000 mg/L Ho Standard into the flask.

7.2.8.5 Pipette 0.4 mL of the 1,000 mg/L In Standard into the flask.

7.2.8.6 Pipette 0.75 mL of the 1,000 mg/L Sc Standard into the flask.

7.2.8.7 Pipette 1.5 mL of the 1,000 mg/L ^{6}Li Standard into the flask.

7.2.8.8 Dilute to volume with the appropriate reagent blank. Stopper and mix.

7.2.9 Interference Check Standard Solutions (ICSA / ICSAB)

The interference check standard solution (ICSA) and the spiked interference check standard solution (ICSAB) are prepared as follows:

7.2.9.1 ICSA Standard (ms 77 icsa / MS ICSA)

7.2.9.1.1 Obtain a clean 100 mL volumetric flask.

7.2.9.1.2 Place 50 mL of reagent blank in the flask.

7.2.9.1.3 Pipette 10.0 mL of the MS ICSA STOCK standard into the flask.

7.2.9.1.4 Dilute to volume with the appropriate reagent blank. Stopper and mix.

7.2.9.2 ICSAB Standard (MS 77 ICSAB / MS ICSAB)

7.2.9.2.1 Obtain a clean 100 mL volumetric flask.

7.2.9.2.2 Place 50 mL of reagent blank in the flask.

7.2.9.2.3 Pipette 0.5 mL of the MS CALSTD-1 stock standard into the flask.

7.2.9.2.4 Pipette 0.5 mL of the MS CALSTD-2 stock standard into the flask.

7.2.9.2.5 Pipette 0.5 mL of the MS CALSTD-3 stock standard into the flask.

7.2.9.2.6 For the Agilent 7700 instruments pipette 0.5 mL of the MS BRC CALSTD stock standard into the flask.

7.2.9.2.7 For the Agilent 7500 instrument pipette 0.5 mL of a 20 mg/L W standard into the flask.

7.2.9.2.8 Pipette 10.0 mL of the MS ICSA STOCK standard into the flask.

7.2.9.2.9 Dilute to volume with the appropriate reagent blank. Stopper and mix.

7.2.10 Low Level Initial Calibration Verification and Low-Level Continuing Verifications (ms 77 LLCCV / MS LCCV)

The low level ICV / low level CCV solution is prepared from the same source as the calibration standards. The low level standard is prepared fresh each day of analysis in reagent blank. The concentration is shown in Attachment 10. Prepare the low level standard solution as follows:

7.2.10.1 Obtain a clean 100 mL volumetric flask.

7.2.10.2 Place 50 mL of reagent blank in the flask.

7.2.10.3 Pipette 1.0 mL of the MS LLCCV1 stock standard into the flask.

7.2.10.4 Pipette 1.0 mL of the MS LLCCV 2A stock standard into the flask.

7.2.10.5 Dilute to volume with the appropriate reagent blank. Stopper and mix.

7.3 Reagents

7.3.1 Reagent Water - ASTM Type I or equivalent for the elements of interest, generated using an ion-exchange water polishing system capable of achieving 18.0 megohm-cm.

7.3.2 Reagent Blank - Agilent 7500, 5% HNO3 - Carefully dilute 50 mL of concentrated HNO_3 in 1.0 L of reagent water. This solution is used to dilute samples and it is used for the initial and continuing calibration blanks.

7.3.3 Reagent Blank - Agilent 7700, 2% HNO3/0.5% HCl – Carefully dilute 40 mL of concentrated HNO3 and 10 mL of HCl in 2.0 L of reagent water. This solution is used to dilute samples and it is used for the initial and continuing calibration blanks.

7.3.4 Reagent Blank - Agilent 7700, 5% HNO3/5% HCL (Zr only) – Carefully dilute 100 ml of concentrated HNO_3 and 100 ml if HCL in 2.0 L of reagent water. This solution is used to dilute samples and it is used for calibration blanks.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation[1]	Holding Time[2]	Reference
Water[3]	HDPE	50 mLs	HNO_3, pH < 2	180 Days	SW-846
Soil	Glass	4 oz	Cool $\leq$ 6°C[4]	180 Days	SW-846

[1]SW-846 specifies a holding time but does not specify a preservation for solid samples for total metals. TAL-Denver refrigerates these samples.

[2]Samples must be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Holding Times are calculated from the date the sample was collected.

[3]Water samples collected for dissolved elements are filtered immediately on-site by the sampler before adding preservative.

[4]Although ICP analysis of soil does not require refrigeration of the samples, mercury analysis does require refrigeration. Samples which will be used to aliquot for both analyses must be refrigerated.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the

TALS Method Comments to determine specific QC requirements that apply. Quality control requirements are summarized in Attachment 9.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver Policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver Policy DV-QA-024P, *QA/QC Requirements for Federal Programs*. This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in TALS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Method Blank (MB)

For aqueous and soil samples, the method blank consists of reagent water that has been processed in the same manner as the samples. For soil samples analyzed under the AFCEE and DoD QAPPs, the method blank consists of <1 mm glass beads that have been processed in the same manner as the samples. One method blank must be processed with each preparation batch.

Acceptance Criteria: Method blank results are acceptable if the concentration for each analyte of interest is less than ½ the reporting limit (RL). For DoD QSM 5.0 the control limit is less than ½ LOQ. In the absence of project specific reporting limits, if the blank is less than 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater, then the method blank is considered acceptable.

Corrective Action: If the method blank does not meet the acceptance criteria, the source of contamination should be investigated to determine if the problem can be minimized or eliminated.

Samples associated with the contaminated blank shall be reprocessed for analysis or, under the following circumstances, may be reported as qualified (qualifier flags or narrative comments):

- The same analyte was not detected in the associated samples;
- The method blank concentration is less than 1/10 of the measured concentration of any sample in the batch;
- The method blank concentration is less than 1/10 the specified regulatory limit; or
- The analyte is a common laboratory contaminant (e.g., copper, zinc, iron, or lead) less than 2 times the RL. Note that some programs do not recognize common lab contaminants or have a more stringent criterion (e.g., DoD QSM 5.0 allows common laboratory contaminants up to the RL).

If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative and the client must be notified.

9.3 Laboratory Control Sample (LCS)

The LCS consists of reagent water that is spiked with the analytes of interest at the project specific action level or, when lacking specific action levels, at approximately the mid-point of the calibration range (summarized in Attachment 10). For soil samples analyzed under the AFCEE and DoD QAPPs, the LCS consists of <1 mm glass beads that have been spiked with the analytes of interest and processed in the same manner as the samples. One LCS must be processed for each preparation batch.

Acceptance Criteria: LCS control limits are based on three standard deviations of past laboratory results or program specific requirements. These limits must not exceed 80-120%. The control limits are maintained in TALS. For DoD QSM 5.0 the laboratory must use QSM Appendix C Limits for batch control if project limits are not specified.

Corrective Action: If the LCS recovery falls outside of the control limits for any analyte, that analyte is judged to be out of control. All associated samples must be reanalyzed One possible exception is a recovery for a given element above the upper control limit with no detection for the same element in the samples. If project requirements allow this exception, the data may be accepted with qualifiers, an NCM must be generated, and the failure narrated in the final report.

9.4 Matrix Spike / Matrix Spike Duplicate (MS / MSD)

The MS is prepared by taking a second aliquot of a selected sample and spiking it with the analytes of interest at the same level as the LCS (summarized in Attachment 10). An MSD is prepared by taking a third aliquot of the selected sample and spiking it with the analytes of interest at the same level as the LCS (summarized in Attachment 10). The MS and MSD are processed in the same manner as the samples. One MS/MSD pair must be processed for each preparation batch. Some programs (e.g., AFCEE) require that matrix spikes can be performed only on project samples, and that the samples to be used are identified on the chain of custody form. The spike concentration should be the same level as the LCS.

Acceptance Criteria: Control limits are based on historical data or project specific requirements. Historical control limits are based on three standard deviations of past laboratory results. These limits are not to exceed 75-125% recovery, and 20% relative percent difference (RPD). The control limits are maintained in TALS. For DoD QSM 5.0 the laboratory must use QSM Appendix C limits for batch control if project limits are not specified.

Corrective Action: If MS/MSD results do not meet the acceptance criteria and all other quality control criteria have been met, then matrix interference is suspected. Failed matrix spikes are flagged automatically, and are discussed in the final report case narrative. For DoD QSM 5.0 a “J” flag is applied to the parent sample if the acceptance criteria is not met. In addition, a serial dilution and PDS must be run.

NOTE: This method does not require a sample duplicate. Precision is measured using the MS/MSD. Use of the MS/MSD is preferred as not all samples will contain measurable concentrations of the target analytes. Samples that have target analytes at low concentrations or non-detectable levels do not provide useful precision data. When an MS/MSD is not available, an LCS and LCSD will be used to measure precision.

9.5 Interference Check Solutions (ICSA/ICSAB)

The interference check solution is prepared with known concentrations of interfering elements so a determination may be made as to the magnitude of the interference on analytes of interest as well as a test of any software corrections. The required elements and their concentrations are listed in Attachment 5. The interference check solutions must be analyzed at the beginning of every analytical run and once every 12 hours thereafter. The results of solution "A" and solution "AB" should be monitored for possible interferences.

Acceptance Criteria: The results for the trace elements (B portion) must be ±20% of the expected value. In addition, the internal standard recoveries for both the ICSA and AB must be within 70-150%. Some programs have control limits for

the non-spiked elements in the ICSA. Please check the client specific requirements. For DoD QSM 5.0 the ICSA for non-spiked elements is controlled to less than the absolute value of the LOD unless they are a verified impurity.

Corrective Action: If the ICSAB results exceed the 20% limit or the ICSA is out for DoD QSM 5.0, then the analysis sequence must be terminated. For DoD QSM 5.0 if the ICSA is outside of the control limits for the non-spiked elements the sequence must also be terminated. The problem must be investigated and fixed. The ICSA and all affected samples must be re-analyzed.

NOTE: It may not be possible to obtain absolutely clean ICSA/ICSAB standards. If contamination can be confirmed by another method (e.g., ICPAES), acceptance criteria will be applied at that level and the data accepted.

9.6 Internal Standards Evaluation for Samples

The IS recovery in samples can not fall below 70% or be above 150% of the intensity of the calibration blank. If sample IS recoveries fall outside of these criteria, a five-fold (1:4) dilution must be performed, the dilution analyzed, and the same acceptance criteria applied. For DoD QSM 5.0 the internal standard for samples is controlled to 30-120%.

9.7 Serial Dilution

One serial five-fold dilution should be analyzed per preparation batch. If the analyte concentration is within the linear range of the instrument and sufficiently high (minimally, a factor of 10 above the MDL in the diluted sample), the serial dilution must agree to within 10% of the original analysis. If not, an interference effect is suspected, which must be described in an anomaly report and included in the final report narrative. Samples identified as blanks should not be used for serial dilution. For DoD QSM 5.0 the serial dilution is evaluated if the parent sample concentration is greater than 50x the LOQ prior to dilution. If the acceptance criteria are not met then the parent sample is flagged “J”.

9.8 Post-Digestion Spike Addition (PDS)

A PDS is performed for each batch. An analytical spike added to a portion of a prepared sample, or its dilution, should be recovered to within 80 - 120% of the known value. If the PDS fails to meet this criterion, matrix interference should be suspected. Typically the concentration of the PDS is 200 µg/L for each element except silver which is spiked at 50 µg/L. For DoD QSM 5.0 if the parent sample concentration is less than 50x the LOQ prior to dilution then the PDS must recover within 80-120%. If the recovery is outside of the control limits for a given element then the parent sample is flagged “J”.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any unauthorized deviations from this procedure identified after the work has been completed must also be documented in an NCM, with a cause and corrective action described.

10.3 Instrument Maintenance

See Section 20 in the QAM

10.4 Instrument Troubleshooting

See Attachment 11

10.5 Sample Preparation

Solid and aqueous samples must be digested prior to analysis by the appropriate method (see SOPs DV-IP-0014 and DV-IP-0015).

10.6 Calibration

10.6.1 Instrument Start Up

Set up the instrument according to manufacturer's operating instructions. Allow the instrument to become thermally stable for at least 30 minutes before tuning. It is recommended that the instrument be flushed with the ICSA solution to help condition the cones and improve stability. Allow the instrument time to rinse completely before tuning the instrument.

10.6.2 Oxide\Doubly Charge Performance Check

With the sample probe in the Tune solution verify that the oxides and doubly charged ions are less the 3% by running the Tune report.

10.6.3 Instrument Tuning / Mass Calibration

Tune the instrument with a solution containing elements representing all of the mass regions of interest. The relative standard deviations must be less than 5% after running the tuning solution a minimum of 5 times. Mass calibration and resolution checks using the tuning solution must be completed at the beginning of every day. If either of the following

conditions fails the instrument setup must be re-evaluated and the solution rerun.

Mass Calibration Check – The mass calibration results must be within 0.1 amu from the true value. If this criterion is not met, the mass calibration must be adjusted before running samples.

Mass Resolution Check - The resolution must be verified to be less than 0.9 amu full width at 10% peak height.

10.6.4 Initial Calibration

The ICP-MS is calibrated each day of operation using a blank and a single standard (see Section 7.2.3). At least three integrations are employed. The validity of the calibration is determined by the subsequent calibration verifications, which are performed at concentrations as described in the next sections.

10.6.5 Low-Level Initial Calibration Verification (LLICV/ICVL)

A low-level ICV standard at or below the reporting limit (see Section 7.2.10) is analyzed after the initial calibration. This is a standard obtained from the same vendor used for calibration.

Acceptance Criteria: The ICVL recovery must be within 70-130%. The ICVL can be reanalyzed, but two consecutive successful results must be obtained or corrective action is taken.

Corrective Action: If the ICVL results are outside of the acceptance limits, investigate the accuracy of the standards, correct as necessary, and recalibrate.

10.6.6 Mid-Level Second-Source Initial Calibration Verification (ICV)

A 40 µg/L ICV standard (see Section 7.2.4) is analyzed immediately after the initial calibration. This is a standard obtained from a different vendor than the standard used for calibration.

Acceptance Criteria: The ICV recovery must be within 90-110%. The ICV can be reanalyzed, but two consecutive successful results must be obtained or corrective action is taken.

Corrective Action: If the ICV results are outside of the acceptance limits, investigate the accuracy of the standards, correct as necessary, and recalibrate.

10.6.7 Calibration Blank

An initial calibration blank (ICB) is analyzed after the ICV. Continuing calibration blanks (CCBs) are analyzed after each continuing calibration verification. The appropriate reagent blank is used for the blanks.

Acceptance Criteria: Absolute values for the calibration blanks must be less than ½ the standard RL. Common lab contaminants such as sodium must be less than the RL. In addition, the internal standard recoveries must be within 70-150% of the associated calibration blank. Client specific requirements take precedence. DoD QSM 5.0 requires control of blanks to a concentration less than or equal to the LOD.

Corrective Action: If the calibration blank exceeds acceptance limits, then the possibility of instrument contamination should be examined, particularly the possibility of carry-over from high level samples. The blank can be reanalyzed, and if successful, analysis can continue. However, samples tested after high-level samples should be retested. If the reanalysis is not successful, then the analysis should be terminated. After the problem is corrected, recalibrate and reanalyze all samples tested since the last acceptable CCB.

10.6.8 Reporting Limit (RL/CRI) Verification Standard

Because the ICP-MS calibration does not include multiple calibration levels, an independent standard is analyzed after the ICV to monitor the lab's ability to produce reliable results at RL-level concentrations. The RL verification standard (see Section 7.2.6) is analyzed after the daily ICB.

Acceptance Criteria: For standard projects, the results should be within 50% of the expected value. Some programs may require tighter controls. For DoD QSM 5.0 the control limits are 80-120%.

Corrective Action: If the RL verification fails to meet acceptance limits, data for the associated samples must be assessed. For example, if the results are high, consider blank contamination, and if the results are low, consider MDL verifications. At a minimum, sample results must be qualified in the final report. For DoD QSM 5.0, if the low-level standard does not meet the limits when spiked at

the required project RL, the run sequence must be terminated.

10.6.9 Lower Limit of Quantitation Check (LLQC)

The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits and on an as needed basis to demonstrate the desired detection capability. The difference between the LLQC and the RL is that this standard is carried through the entire preparation and analytical procedure.

Acceptance Criteria: LLQC is verified when all analytes are detected within ± 30% of their true value.

Corrective Action: If the LLQC fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.6.10 Low-Continuing Calibration Verification (LLCCV/CCVL) Standard

A low-level CCV standard is analyzed after every set of ten samples and at the end of the analytical sequence.

Acceptance Criteria: The CCVL recovery must be within 70-130%. In addition, the IS recovery must be within method limits. If CCVL results are not within these limits, the CCVL can be reanalyzed, but it must be successful twice in succession. If the calibration cannot be verified within these specified limits, the analysis of samples containing the affected analytes at similar concentrations cannot continue until the cause is determined and the CCVL standard successfully analyzed.

Corrective Action: If the CCVL fails acceptance criteria, then the analysis should be terminated. Recalibrate and reanalyze all samples tested since the last acceptable CCVL. If the associated samples are at levels greater than 10X the level of the CCVL the data may be considered acceptable but the failure must be documented with an NCM and addressed in the case narrative.

10.6.11 Continuing Calibration Verification (CCV) Standard

A 50 µg/L CCV standard (see Section 7.2.5) is analyzed after every set of ten samples or every 2 hours, whichever is most frequent, and at the end of the analytical sequence.

Acceptance Criteria: The CCV recovery must be within 90-110%. In addition, the IS recovery must be within 70-150%. If CCV results are not within these limits, the CCV can be reanalyzed, but it must be successful twice in succession or further corrective action must be taken.

Corrective Action: If the CCV fails acceptance criteria, then the analysis should be terminated. Recalibrate and reanalyze all samples tested since the last acceptable CCV.

10.7 Sample Analysis

10.7.1 Report the average of at least three integrations for all field and QC samples analyzed.

10.7.2 Flush the system with the rinse blank for at least 30 seconds between samples and standards during the analytical run.

10.7.3 All soil samples and associated QC samples are diluted 5X prior to analysis on the Agilent 7500. This dilution is performed in an effort to reduce the impact of matrix interference on the performance of the ICPMS. The reported method detection limit has been corrected for the 5X dilution. The dilution factor on the report will be a 1X unless a subsequent dilution is required.

10.7.4 Masses which would affect the data quality must be monitored during the analytical run to determine the potential effects of matrix on a given element. See Attachment 3 for examples.

10.7.5 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte. Dod QSM 5.0 requires that samples be diluted and reanalyzed if they are above the daily linear range check standard. No analyte may be reported from an analysis of a diluted sample in which the analyte concentration is less than 5 times the RL. (The sample should be diluted to the approximate midrange of the analytical curve.)

10.7.6 The analytical run sequence should be performed as follows to meet all quality control criteria:

Instrument initialization / Warm-Up
Tune instrument
Perform mass calibration
Perform resolution check
Validate tuning criteria
Calibration blank
Calibration standard
ICV
ICB
LLICV
RL verification standard

LLQC(as needed)
ICSA
ICSAB
LRA
CCV
CCB
LLCCV
10 Samples (which can include all sample types)
CCV
CCB
LLCCV
Reslope
CCV
CCB
LLCCV

11.0 Calculations / Data Reduction

11.1 Detailed calibration equations can be found in the corporate Policy CA-Q-P-003, *Calibration Curves and the Selection of Calibration Points*, and under the public folder, *Arizona Calibration Training*.

11.2 ICV percent recoveries are calculated according to the equation:

$$\%R = \left(\frac{\text{ICV Found Value}}{\text{ICV True Value}} \right) \times 100\%$$

11.3 CCV percent recoveries are calculated according to the equation:

$$\%R = \left(\frac{\text{CCV Found Value}}{\text{CCV True Value}} \right) \times 100\%$$

11.4 Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = \left(\frac{\text{SSR - SR}}{\text{SA}} \right) \times 100\%$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

NOTE: When the sample concentration is less than the detection limit, use SR = 0 for the purpose of calculating %R.

11.5 The relative percent difference (RPD) between sample duplicates is calculated according to the following equation:

$$RPD = \left[\frac{DU1 - DU2}{\frac{1}{2}(DU1 + DU2)} \right] \times 100$$

Where:

DU1 = Sample result

DU2 = Sample duplicate result

11.6 The final concentration for an aqueous sample is calculated as follows:

$$\text{Result } (\mu\text{g/L}) = \frac{C \times V1 \times D}{V2}$$

Where:

C = Concentration from instrument readout, ppb

D = Instrument dilution factor

V1 = Final volume in liters after sample preparation

V2 = Initial volume of sample digested in liters

11.7 The concentration determined in digested solid samples when reported on a dry weight basis is as follows:

$$\text{Result } (\mu\text{g/kg}) = \frac{C \times V \times D}{W \times S}$$

Where:

C = Concentration from instrument readout, ppb

D = Instrument dilution factor

V = Final volume in liters after sample preparation

W = Weight, in g, of wet sample digested

S = Percent solids/100

11.8 Sample data are reviewed by the analyst (Level 1 data review) and documented on the data review checklist (See SOP DV-QA-0020). The data package is then submitted for level 2 review by another analyst or data reviewer. Second level review is documented on the same checklist initiated by the analyst. The data review process is explained in SOP DV-QA-0020.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. An initial method detection limit study is performed in

accordance with Policy DV-QA-005P. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency. For DoD, AFCEE, and DOE projects, an MDL verification is performed quarterly.

12.2 MDL Verification (MDLV)

Calculated MDLs from the annual studies are subject to quarterly verification by analyzing an MDLV standard.

12.2.1 Prepare an MDLV standard at 2-4 times the calculated MDL concentration.

12.2.2 Analyze the MDLV standard immediately after each MDL study and quarterly thereafter. This standard is subject to the entire preparation and analysis process.

12.2.3 The calculated MDL is verified if the MDLV standard is detected, nominally signal to noise ratio > 3, under routine instrument conditions.

12.2.4 If the first MDLV is not detected, re-prepare the MDLV standard at twice the original concentration and analyze. The lowest concentration that produces a detectable signal will then be reported as the MDL.

12.3 Instrument Detection Limit Study

Instrument detection limit (IDL) studies are conducted quarterly for each instrument and each analyte used for analysis in accordance with Policy DV-QA-014.

12.3.1 Pour out seven undigested calibration blanks and run them on three non-consecutive days.

12.3.2 Calculate the standard deviation for each day. The final IDL concentration is the average of the three daily standard deviation values.

12.3.3 See Policy DV-QA-014P for a discussion of IDL studies and evaluation of IDL results.

12.4 Linear Dynamic Range (LDR)

12.4.1 The LDR must be determined initially (i.e., at initial setup) and then every three months for each analyte used on each instrument. The linear range is the concentration above which results cannot be reported without dilution of the sample.

12.4.2 The LDR must be determined from a linear calibration prepared in the normal manner using the normal operating procedures described in Sections 10 and 11.

12.4.3 The LDR is determined by analyzing successively higher standard concentrations of the analyte. A minimum of three standards are

required for the initial and on-going studies, and one of the levels must be at the upper end of the range. The highest concentration must be within 10% of the stated concentration.

12.4.4 The highest standard that meets this criterion defines the maximum concentration that can be reported for sample analysis without dilutions.

12.4.5 If the instrument is adjusted in any way that may affect the LDRs, new dynamic ranges must be determined. The LDR data must be documented and kept on file.

12.5 Linear Range Verification (LRA/LRC)

The LDRs should be verified whenever, in the judgment of the analyst, a change in the analytical performance caused by either a change in instrument hardware or operating conditions would dictate the necessity to re-establish them. Some programs (e.g., USACE) require verification of linear ranges in each analytical run. As described in Section 7.2.7, a lower concentration is used for the daily check than is used for the quarterly determination.

Acceptance Criteria: The result for this standard must be within 10% of the expected value.

Corrective Action: If the Linear Range Verification standard fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. Alternatively, results that do not exceed the level of the highest calibration standard may be accepted and reported.

12.6 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

12.6.1 Four aliquots of an LCS are analyzed using the same instrumental conditions and procedures used to analyze samples. The analyst must employ ICV's from four distinct analytical sequences. Using these four LCSs demonstrates the analyst's ability to optimize and calibrate the instrument and to prepare analytical solutions. Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.6.2 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the

need for the laboratory to evaluate the analytical procedure and take corrective action.

12.6.3 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

12.7 Training Requirements

12.7.1 The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

12.7.2 Each analyst performing the method must complete a demonstration of capability (DOC) by successfully preparing and/or analyzing four consecutive LCSs, or a blind performance evaluation (PE) sample, or other acceptable QC samples. The results of the DOC study are summarized in the NELAC format, as described in SOP DV-QA-0024. DOCs are approved by the Quality Assurance Manager and the Technical Director. DOC records are maintained by the QA staff in the central training files. Analysts who continue to perform the method must successfully complete a demonstration of capability annually.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, order chemicals based on quantity needed, and prepare reagents based on anticipated usage and reagent stability).

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in Section 13, *Waste Management and Pollution Prevention*, of the Corporate Environmental Health and Safety Manual, and DV-HS-001P, *Waste Management Program*.

14.2 The following waste streams are produce when this method is carried out:

14.2.1 **Aqueous Acidic (Metals) -** Corrosive - Waste Stream J

14.2.2 **Expired reagents and standards –** Contact the Waste Coordinator.

NOTE: Radioactive, mixed waste and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 Test Methods For Evaluating Solid Waste, EPA SW-846, Update IV, Method 6020A: "Inductively Coupled Argon Plasma - Mass Spectrometry", Revision 1, February 2007.

15.1.1 Method 6020: "Inductively Coupled Argon Plasma - Mass Spectrometry", Revision 0, September 1994.

15.1.2 Method 3005A, Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy, Revision 1, July 1992.

15.1.3 Method 3020A, Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy, Revision 1, July 1992.

15.1.4 Method 3050B, Acid Digestion of Sediments, Sludges and soils, Rev. 2, December 1996.

15.2 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 4.2, 10/20/2010

15.3 U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0.

15.4 Department of Defense Quality Systems Manual for Environmental Laboratories, Version 5, July 2013.

16.0 Method Modifications:

Item	Method	Modification
1	EPA 6020A	Commercially available standards are purchased and verified at the laboratory rather than being prepared from the solid material. These verification records are kept on file with QA.
2	EPA 6020A	Milli-Q or Nanopure water is substituted when reagent water is called for. This water is tested to be free of contaminants by conductivity (18megOhm) and by the analysis of blanks.
3	EPA 6020A	Corrective action for a PDS failure will be limited to flagging the PDS indicating the failed analyte and the recovery rather than diluting and reanalyzing the sample.
4	EPA 6020A	Internal standard recoveries are based on the intensities of the internal standards in the most recent calibration blank rather than the intensities of the internal standards in the initial calibration standard.

Item	Method	Modification
5	EPA 6020A	Method 6020A states that the dilution test is applicable if the matrix sample is at least 50x the reporting limit. TestAmerica uses the tighter limit of 50x the MDL.

17.0 Attachments

Attachment 1: Standard Reporting Limits for Water and Soil
Attachment 2: Recommended Elemental Equations
Attachment 3: Isobaric Molecular-Ion Interferences Which Could Affect the Analytes
Attachment 4: Internal Standards and Corresponding Metals
Attachment 5: Interference Check Sample Components and Concentrations
Attachment 6: Suggested Mass Choices
Attachment 7: Tuning Solution and P/A Solution
Attachment 8: Suggested Tuning and Response Factor Criteria
Attachment 9: Summary of Quality Control Requirements
Attachment 10: Calibration, Calibration Verification, and Spike Concentrations
Attachment 11: Troubleshooting

18.0 Revision History

Revision 5, Dated 30 April 2015

- Annual Review
- Language and formatting changes throughout
- Corrected tuning sample requirement from 4 replicates to five replicates
- Changed 12.4.2 to 12.5
- Added Section 2.1
- Added new Section 2.3 to describe reaction cell
- Added new Section 4.2.3
- Added batch definition
- Deleted Attachment 2
- Deleted Attachment 4
- Added new Attachment 1 standard reporting limits
- Section 4.3.2 enlarged expected IS intensities
- Integrated Sections 4.4 and 4.5 into 4.2
- Created new Section 4.3 Doubly charged ions
- Added new Section 6.2.3 volumetric flasks
- Section 7.2.1.4 corrected Mg addition to standard
- Section 7.2.2 replaced P/A section with same section from DV-MT-0025
- Added P/A section to Attachment 7
- Section 7.1.3 added reference to standards SOP
- Added all new standard prep information into Sections 7.2.3 – 7.2.9
- Section 9.3 changed spike level from midpoint of LR to midpoint of cal curve
- Added note to Section 9.4
- Changed timing of ICSA to beginning of analytical run and every 12 hours
- Changed concentration limits for SD in Section 9.7 to 50x MDL
- Added method modification 5 to address SD limit
- 10.6.7 added DoD 5.0 language to corrective action
- Removed Section 10.3

- 10.7.5 added DoD requirement to dilute above daily LR
- 11.5 Corrected RPD calculation
- 11.7 changed to dry weight correction
- 12.2.1 changed MDLV spike level to 2-4x MDL

Revision 2, dated 09 April 2014

- Annual review
- Updated Section 7.2 for standards to reference TALS for how to make
- Added Section 7.4.4 for 5%HNO3/5%HCL for Zirconium
- Added Section 10.4 for Maintenance
- Added Section 10.5 for Troubleshooting
- Updated Sections 9 and 10 to include requirements for DoD QSM 5.0
- Added reference to DoD QSM 5.0.

Revision 1, dated 15 July 2013

- Annual review
- Corrected formatting
- Added section 3.16
- Added reference to data review in section 10.7
- Added documentation information in section 11.8
- Added detail to note associated with section 14.2
- Updated reference in section 15.2
- Removed Attachment 13

Revision 0.3, dated 13 July 2012

- Revised standards preparation procedures in Section 7
- Added section 7.2.2
- Split acid diluent into two solutions depending upon instrument
- Updated standard mixes used to prepare standards; instrument specific mixes as needed
- Clarified requirements for preservation of soil samples for ICPMS only analysis, Section 8
- Revised list of common lab contaminants in method blank corrective action (Section 9.2)
- Added section 10.5.2: oxide/doubly charged performance check
- Updated Sections 9.2 and 10.5.7 to control method blanks and calibration blanks to ½ the RL
- Updated Sections 9.1, 10.1, 10.2 and 12.1 to reflect current practice.

Revision 0.2, dated 08 July 2011

- Added Section 4.4 on polyatomic interferences
- Added Instruments to Section 6.1
- Section 10.5.1 Added to condition cones with the ICSA solution
- Added Section 10.6.3 to reflect soil dilution practices
- Section 11.4 Corrected the RPD calculation
- Added section 11.1 referencing corporate SOP CA-Q-S-005 “Calibration Curves”
- Added section 12.2 “MDL Verification (MDLV)”
- Added Attachment 13 “ICP-MS Technical Data Review Checklist”

Revision 0.1, dated 18 June 2010

- Basic Annual Review

Revision 0, dated 19 June 2009

Attachment 1

Standard Reporting Limits for Water and Soil

Element Name	Element Symbol	Water (ug/L)	Soil (ug/Kg)
Aluminum	Al	30	5,000
Antimony	Sb	2.0	200
Arsenic	As	5.0	600
Barium	Ba	1.0	200
Beryllium	Be	1.0	100
Cadmium	Cd	1.0	100
Chromium	Cr	2.0	200
Cobalt	Co	1.0	100
Copper	Cu	2.0	250
Iron	Fe	50	5,000
Lead	Pb	1.0	150
Manganese	Mn	1.0	250
Molybdenum	Mo	2.0	200
Nickel	Ni	2.0	150
Selenium	Se	5.0	500
Silver	Ag	5.0	100
Thallium	Tl	1.0	100
Thorium	Th	5.0	200
Tin	Sn	10	2,500
Tungsten	W	5.0	500
Uranium	U	1.0	100
Vanadium	V	5.0	500
Zinc	Zn	10	1,000
Zirconium	Zr	0.5	---

Attachment 2

Recommended Elemental Equations

Element	Isobaric Correction	Mathematical Equation
Al	none	(1.0000)(27M)
Sb	none	(1.0000)(121M)
As	ArCl, Se	(1.0000)(75M) - (3.1278)(77M) + (1.0177)(78M)
Ba	none	(1.0000)(135M)
Be	none	(1.0000)(9M)
Cd	MoO, Sn	(1.0000)(114M) - (0.0268)(118M) - (1.0000)(135M)
Ca	none	(1.0000)(44M)
Cr	none	(1.0000)(52M)
Co	none	(1.0000)(59M)
Cu	none	(1.0000)(65M)
Fe	none	(1.0000)(57M)
Pb	none	(1.0000)(208M) + (1.0000)(207M) + (1.0000)(206M)
Mg	none	(1.0000)(25M)
Mn	none	(1.0000)(55M)
Ni	none	(1.0000)(60M)
K	none	(1.0000)(39M)
Se	Ar2	(1.0000)(78M) - (1.1869)(76M)
Ag	none	(1.0000)(107M)
Na	none	(1.0000)(23M)
Tl	none	(1.0000)(205M)
V	ClO, Cr	(1.0000)(51M) - (3.1081)(53M) + (0.3524)(52M)
Zn	none	(1.0000)(66M)
6Li	Li (natural)	(1.0000)(6M) - (0.0813)(7M)
Sc	none	(1.0000)(45M)
Y	none	(1.0000)(89M)
Rh	none	(1.0000)(103M)
In	Sn	(1.0000)(115M) - (0.0149)(118M)
Tb	none	(1.0000)(159M)
Ho	none	(1.0000)(165M)
Bi	none	(1.0000)(209M)

Where M = Total ion count rate at the specified mass.

Attachment 3

Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{121}Sb	PdO		AgN			AgC	
^{123}Sb	AgO		AgN	SrCl	ZrS	CdC	
^{75}As	CoO	NiOH	NiN	ArCl	CaS	CuC	
^{138}Ba	SnO	SbOH					
^{137}Ba	SbO	SnOH		MoCl			
^{136}Ba	SnO	SnOH				SnC	
^{135}Ba	SnO	SnOH		MoCl			
^{134}Ba	SnO	SnOH	SnN	MoCl		SnC	
^{132}Ba	SnO, CdO	InOH	SnN	MoCl	MoS	SnC	
^{130}Ba	CdO	CdOH	SnN, CdN	MoCl	MoS	SnC	
^{9}Be							
^{114}Cd	MoO	MoOH	MoN	SeCl	SeS		
^{112}Cd	MoO, ZrO	MoOH	MoN	AsCl, SeCl	SeS	MoC	
^{111}Cd	MoO	MoOH	MoN	GeCl			
^{110}Cd	MoO, ZrO		MoN, ZrN	GeCl, AsCl	SeS	MoC	
^{113}Cd	MoO	MoOH		SeCl, AsCl			
^{116}Cd	MoO						
^{106}Cd	ZrO		MoN, ZrN		GeS	MoC, ZrC	
^{108}Cd	MoO, ZrO	ZrOH	MoN, ZrN	GeCl	SeS, GeS	MoC, ZrC	
^{52}Cr	ArO	ClOH				ArC	
^{53}Cr	ClO	ArOH	KN	NCl, OCl		KC	
^{50}Cr	SO		ArN		SO	ArC	Mo^{++}
^{54}Cr		ClOH	ArN, CaN			CaC	
^{59}Cr	CaO	CaOH	ScN	MgCl	AlS	TiC	Sn^{++}
^{63}Cu	TiO, PO_2	TiOH	TiN	SiCl, MgCl	PS	VC	ArNa
^{65}Cu	TiO	TiOH	VN	SiCl	SS, SO_2H	CrC	
^{208}Pb							
^{206}Pb							
^{207}Pb							
^{204}Pb							
^{55}Mn	KO	ArOH	KN		NaS	CaC	Cd^{++}

Attachment 3 (cont.)
Isobaric Molecular-Ion Interferences Which Could Affect the Analytes

Analyte	Interferences						
	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{202}Hg	WO						
^{200}Hg	WO	WOH	WN				
^{199}Hg	WO	WOH					
^{201}Hg		WOH					
^{198}Hg	WO	TaOH	WN			WC	
^{204}Hg							
^{196}Hg			WN				
^{58}Ni	CaO	KOH	CaN	NaCl	MgS	TiC	Cd^{++}, Sn^{++}
^{60}Ni	CaO	CaOH	TiN	MgCl, NaCl	SiS	TiC	Sn^{++}
^{62}Ni	TiO	ScOH	TiN	AlCl, MgCl	SiS	TiC, CrC	Sn^{++}
^{61}Ni	SeO	CaOH	TiN	MgCl	SiS	TiC	
^{64}Ni	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{80}Se	ZnO	CuOH	ZnN	ScCl, CaCl	TiS	ZnC	
^{78}Se	NiO	NiOH	ZnN	CaCl, KCl	TiS	ZnC	
^{82}Se	ZnO	CuOH	ZnN	TiCl, ScCl	TiS, CrS		
^{76}Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
^{77}Se	NiO	CuN	CuN	CaCl, ArCl	ScS	CuC	
^{74}Se	NiO	NiN	NiN	ClCl, KCl	CaS	NiC	
^{107}Ag	ZrO	ZrOH		GeCl	AsS	MoC	
^{109}Ag		MoOH	MoN	GeCl	SeS	MoC	
^{205}Tl							
^{203}Tl		WOH					
^{51}V	ClO	SOH	ClN	ClO, ClN	FS	KC	
^{50}V	SO		ArN			ArC	Mo
^{64}Zn	TiO	TiOH	TiN, CrN	SiCl, AlCl	SS	CrC	
^{66}Zn	TiO	TiOH	CrN	PCl, SiCl	SS	FeC	
^{68}Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba^{++}
^{67}Zn	VO	TiOH, Cr	CrN	SCl	ClS	MnC	Ba^{++}
^{70}Zn	FeO	CrOH	GeN	ClCl	ArS	NiC	

NOTE: The information provided in this table does not indicate that all of the described interferences need to be tested. However, the table can be consulted for informational purposes if unusual samples are encountered.

Attachment 4
Internal Standards and Corresponding Metals

IS	ICP-MS 077/078	ICP-MS 024
^{6}Li	Be	Be
Sc	Na, Mg, Al, K, Ca	Na, Mg, Al, K, Ca
Ge	V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se	V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se
In	Mo, Ag, Cd, Sn, Sb, Ba	Mo, Ag, Cd, Sn, Sb, Ba
Ho	Tl, Pb, Th, U, W	Tl, Pb, Th, U, W

Attachment 5
Interference Check Sample Components and Concentrations

Interference Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	100.0	110.0
Ca	100.0	110.0
Fe	100.0	110.0
Mg	100.0	110.0
Na	100.0	110.0
P	100.0	100.0
K	100.0	110.0
S	100.0	100.0
C	200.0	200.0
Cl	1000.0	1000.0
Mo	2.0	2.1
Ti	2.0	2.0
As	0.0	0.1
Sb	0.0	0.1
Be	0.0	0.1
Ba	0.0	0.1
Cd	0.0	0.1
Cr	0.0	0.1
Co	0.0	0.1
Cu	0.0	0.1
Pb	0.0	0.1
Mn	0.0	0.1
Ni	0.0	0.1
Nb	0.0	0.2
Pd	0.0	0.1
Pt	0.0	0.1
Se	0.0	0.1
Tl	0.0	0.1
Th	0.0	0.1
Sn	0.0	0.1
Ag	0.0	0.1
U	0.0	0.1
V	0.0	0.1
W	0.0	0.1
Zn	0.0	0.1

Attachment 6
Suggested Mass Choices

Boldface masses indicate the masses which must have the most impact on data quality and the elemental equations used to collect the data. It is strongly recommended that elements other than those of interest be monitored to indicate other potential molecular interferences which could affect the data quality.

Mass	Element of Interest
"**27**"	Aluminum
121, "**123**"	Antimony
"75"	Arsenic
138, "137", 136, **135**, 134, 132, 130	Barium
"9"	Beryllium
114, 112, "111", 110, 113, 116, 106	Cadmium
42, 43, **44**, 46, 48	Calcium
"**52**", **53**, **50**, 54	Chromium
"**59**"	Cobalt
"**63**", **65**	Copper
56, **54**, **57**, 58	Iron
"**208**", "**207**", "**206**", 204	Lead
24, **25**, **26**	Magnesium
"**55**"	Manganese
58, "**60**", 62, **61**, 64	Nickel
93	Niobium
105	Palladium
195	Platinum
39	Potassium
80, **78**, "**82**", **76**, **77**, 74	Selenium
"**107**", **109**	Silver
23	Sodium
"**205**", 203	Thallium
232	Thorium
192	Tungsten
"**51**", **50**	Vanadium
64, "**66**", **68**, **67**, 70	Zinc
139	Lanthanum
118	Tin
238	Uranium
35, 37	Chlorine
98, 96, 92, **97**, 94, "95"	Molybdenum
72	Germanium (IS)
165	Holmium (IS)
115	Indium (IS)
6	Lithium (6+) (IS)
45	Scandium (IS)

Attachment 7: Tuning Solution and P/A Solution

A tuning solution containing elements representing all of the mass regions of interest must be analyzed. Below is a suggested solution covering a typical mass calibration range. Instrument manufacturer recommendations should be followed for tuning solutions.

The P/A solution is used to monitor the correlation between the Pulse and Analog parts of the electron multiplier. This solution is prepared at different concentrations depending on the current instrument conditions. The parent standard concentration is shown below.

Element	Tuning Concentration (µg/L)	P/A Concentration (mg/L)
Al		5
As		20
Ba	10	5
Be	10	20
Bi		5
Cd		20
Ce	10	
Co	10	5
Cr		5
Cu		5
Ge		10
In	10	5
Ir		5
^{6}Li		5
Li	10	
Lu		5
Mg	10	10
Mn		5
Mo		10
Na		5
Ni		10
Pb	10	10
Pd		10
Rh	10	
Ru		10
Sb		10
Sc		5
Sn		10
Sr		5
Tb		2.5
Th		50
Ti		50
Tl	10	50
U	10	50
V		50
Y	10	2.5
Zn		20

Attachment 8:

Suggested Tuning and Response Factor Criteria

Minimum Response from Tuning Solution:

Be	>1,000
Mg	>2,000
Rh	>20,000
Pb	>10,000
Li	>2,000
Co	>20,000
In	>1,000
Tl	>1,000

Suggested Mass Calibration:

Be	9.0122
Mg	23.98
Rh	102.91
Pb	207.98
Li	7.016
Co	58.9332
In	114.904
Tl	204.9744

Attachment 9:

Summary of Quality Control Requirements

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
LLQC	At the beginning of the run on an as needed basis	70 - 130% recovery. 6020A IS, 70-150% rec.	Terminate analysis; correct the problem; recalibrate.
LLICV	Beginning of every analytical run.	70 - 130% recovery. 6020A IS, 70-150% rec.	Terminate analysis; correct the problem; recalibrate.
ICV	Beginning of every analytical run.	90 - 110% recovery. 6020A IS, 70-150% rec.	Terminate analysis; correct the problem; recalibrate.
ICB/CB	Immediately after each ICV	The result is < ½ RL. 6020A IS, 70-150% rec.	Terminate analysis; correct the problem; recalibrate.
LLCCV	Beginning and end of run and every 10 samples OR every 2 hours, whichever is more frequent.	70 - 130% recovery. 6020A IS, 15070% rec.	See Section 10.6.10. Reanalyze twice in succession. If acceptable, continue. If unacceptable, terminate analysis; correct the problem recalibrate the instrument, reverify calibration and rerun all samples since the last acceptable CCV.
CCV	Beginning and end of run and every 10 samples OR every 2 hours, whichever is more frequent.	90 - 110% recovery. 6020a IS, 70-150% rec.	Reanalyze twice in succession. If acceptable, continue. If unacceptable, terminate analysis; correct the problem recalibrate the instrument, reverify calibration and rerun all samples since the last acceptable CCV.

Attachment 9: Summary of Quality Control Requirements (Continued)

QC Parameter	Frequency*	Acceptance Criteria	Corrective Action
CCB	Immediately following each CCV.	The result must be < ½ RL. 6020a IS, 70-150% rec.	Reanalyze once. If acceptable, continue. If unacceptable, terminate analysis; correct the problem recalibrate the instrument, reverify calibration and rerun all samples since the last acceptable CCB.
ICSA	Beginning and every 12 hours.	Monitor for possible interferences.	See Section 9.5
ICSAB	Immediately following each ICSA.	Monitor for possible interferences.	See Section 9.5
Method Blank	One per lot of 20 field samples or fewer.	The result must be < ½ RL. Sample results greater than 10x the blank concentration or samples for which the contaminant is < RL, do not require redigestion or reanalysis.	Re-run once. If > ½ RL, redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.2 for additional requirements.
Serial Dilution	One per batch of 20 field samples or fewer.	90 - 110% recovery	See Section 9.7 for additional requirements.
Post-Digestion Spike	One per batch of 20 field samples or fewer.	80-120% recovery	See Section 9.8.
Laboratory Control Sample	One per batch of 20 field samples or fewer.	Must be within laboratory control limits	See Section 9.3
Matrix Spike	One per lot of 20 field samples or fewer.	Must be within laboratory control limits	See Section 9.6 for additional requirements.

Attachment 10
Calibration, Calibration Verification, and Spike Concentrations

Element	Initial Calibration (µg/L)	ICV (µg/L)	CCV (µg/L)	LCS (µg/L)	MS/MSD (µg/L)	Post Digestion Spike (ug/L)
Aluminum	10000	40	50	400	400	20000
Antimony	100	40	50	40	40	200
Arsenic	100	40	50	40	40	200
Barium	100	40	50	40	40	200
Beryllium	100	40	50	40	40	200
Cadmium	100	40	50	40	40	200
Calcium	10000	4000	5000	--	--	--
Chromium	100	40	50	40	40	200
Cobalt	100	40	50	40	40	200
Copper	100	40	50	40	40	200
Iron	10000	4000	5000	400	400	20000
Lead	100	40	50	40	40	200
Magnesium	10000	4000	5000	--	--	--
Manganese	100	40	50	40	40	200
Molybdenum	100	40	50	40	40	200
Nickel	100	40	50	40	40	200
Selenium	100	40	50	40	40	200
Silver	100	40	50	40	40	50
Thallium	100	40	50	40	40	200
Thorium	100	40	50	40	40	--
Tin	100	40	50	40	40	200
Tungsten	100	40	50	40	40	200
Uranium	100	40	50	40	40	200
Vanadium	100	40	50	40	40	200
Zinc	100	40	50	40	40	200
Zirconium	100	40	50	40	40	--

This procedure has been developed for twenty elements. Additional elements may be included in the calibration solution at the above levels. Levels may be adjusted to meet specific regulatory or client programs.

Attachment 11

ICP-MS Troubleshooting Guide

Problem	Possible Cause/ Solution
High Calibration Blanks	Inspect historical blank data to determine root cause Inspect, clean or replace torch Inspect, clean or replace pump tubing or sample tubing Inspect, clean or replace nebulizer Remake blank solution Recalibrate instrument
Instrument Drift	Make sure instrument has warmed properly Condition cones to aid stability Reslope to correct for changing cone conditions during run Stop run, clean cones and start over with a new calibration
Erratic Readings, High RSDs	Check nebulizer pressure Check sample flow around the pump, adjust tension on pump tubing to ensure smooth flow Check for clogs in the uptake tubing, nebulizer, or valve Clean or replace nebulizer
Low Sensitivity	Clean cones Adjust lens voltages Remove and clean lens, remove and clean or replace reaction cell
Bad Tune: Bad Mass Cal	Adjust lens voltages, remove and clean lens
Bad Tune: High Oxides	Inspect, clean, or replace torch, nebulizer, and spray chamber

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ICP Analysis for Trace Elements by SW-846 Method 6010C

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Laboratory Director

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1.0 Scope and Application

1.1 This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICPAES). This procedure references Method 6010C for hazardous waste (RCRA) testing.

1.2 The elements that can be determined by this procedure are listed in Attachment 1, together with the routine reporting limits. Additional elements may be analyzed under Method 6010C provided that the method performance criteria presented in Section 12.0 are met.

1.3 The laboratory digests all water samples according to SOP DV-IP-0010.

1.4 Silver concentrations must be below 1.0 mg/L in aqueous sample digestates and 100 mg/kg in solid matrix sample digestates. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data. Samples with silver concentrations exceeding these levels must be re-prepared and reanalyzed using a smaller sample amount.

1.5 The digestion procedure for soil samples is described in SOP DV-IP-0015.

1.6 State or client specific requirements may take precedence over this SOP for water analyses. Review special instructions for each project before starting work.

2.0 Summary of Method

2.1 The laboratory uses simultaneous ICPAES instruments, with both axial and radial viewing configurations. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs.

2.2 Characteristic atomic-line emission spectra are produced by a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by a charge injection device (CID). The photo-currents from the charge injection device (CID) are processed and controlled by a computer system.

2.3 A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

2.4 Refer to the appropriate SOPs for details on sample preparation methods: DV-IP-0010 for aqueous samples and DV-IP-0015 for soil samples.

3.0 Definitions

3.1 **Dual View ICP** – an ICP equipped with both radial and axial viewing capabilities.

3.2 **Dissolved Metals -** Those elements which pass through a 0.45-μm membrane. (The sample is acidified after filtration).

3.3 **Potentially Dissolved Metals -** Potentially dissolved metals is the concentration of metals in solution after acidifying the sample with nitric acid to pH <2, holding at room temperature for 8 to 96 hours, and then filtering through a 0.45-μm membrane filter. This definition is based on the Colorado surface water regulations.

3.4 **Suspended Metals -** Those elements which are retained by a 0.45-μm membrane.

3.5 **Total Metals -** The concentration determined on an unfiltered sample following vigorous digestion.

3.6 **Total Recoverable Metals -** The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

3.7 **Reporting Limit (RL) -** The lowest concentration to which results are reported without qualification. Details concerning RLs are presented in Policy DV-QA-009P.

3.8 Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and Policy DV-QA-003P, *Quality Control Program*, for definitions of general analytical and QA/QC terms.

4.0 Interferences

4.1 Spectral, physical, and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by the following:

4.1.1 Overlap of a spectral line from another element.

4.1.2 Unresolved overlap of molecular band spectra.

4.1.3 Background contribution from continuous or recombination phenomena.

4.1.4 Stray light from the line emission of high concentration elements.

4.2 A background correction technique is used to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.3 **Spectral Interferences**

Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte signal. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes

low) concentration to be reported for the analyte. Inter-element corrections must be applied to the analyte to compensate for the effects of these unwanted emissions.

4.4 Physical Interferences

An internal standard (IS), yttrium or other suitable element, is added to all solutions to correct and monitor physical interferences. Use of a peristaltic pump and the mass flow controller also help to overcome physical interferences. Physical interferences are generally considered to be effects associated with sample transport, nebulization, and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If internal standard recoveries are not acceptable (see Section 9.11), then dilution of the sample may be necessary to overcome the interferences.

4.5 Chemical Interferences

Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not significant with the ICP technique, but if observed, can be minimized by buffering the sample, matrix matching, or standard addition procedures.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile or latex gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.3.2 The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma. The RF Generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

5.4 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material [(1)]	Hazards	Exposure Limit[(2)]	Signs and Symptoms of Exposure
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

6.1.1 Thermo Fischer ICP 6500E Trace Analyzers are currently used. Instruments with demonstrated equivalent performance can also be used

6.1.2 Radio Frequency Generator.

6.1.3 Argon gas supply, 99.99%

6.1.4 Coolflow or appropriate water-cooling device.

6.1.5 Peristaltic Pump.

6.1.6 Autosampler.

6.2 Supplies

6.2.1 Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.2.2 Class A volumetric flasks.

6.2.3 Autosampler tubes.

6.3 Computer Software and Hardware

Please refer to the master list of documents and software located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

7.0 Reagents and Standards

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. All standards used in calculations shall be entered into the TALS Reagent Module with all applicable information (e.g., components, concentrations, expiration, etc.).

7.2 Shelf-Life

7.2.1 Stock standards, standards as received from the vendor, expire on the date assigned by the vendor. If no date is assigned by the vendor, a one-year expiration will be assigned by the laboratory.

7.2.2 The expiration date of intermediate concentration standards or working standards cannot be later than the date assigned to any of the stock standards used to prepare the intermediate solution.

7.2.3 If visible deterioration is noted for any standard, it must be re-verified against a second-source. Any standard that does not verify must be replaced immediately.

7.3 Standards

7.3.1 Standards used for calibration and quality control purposes must be NIST traceable, where available. Multi-component custom blend standards must

be verified against a second-source standard before they are put into use (the only exception is standards purchased directly from NIST), as described in SOP DV-QA-0015.

7.3.2 Stock standards are purchased as custom multi-element mixes or as single-element solutions. All standards must be stored in FEP fluorocarbon, polyethylene, or polypropylene bottles. Silver standards must be protected from light. The preparation frequency is governed by the parent standard with the earliest expiration date unless specified otherwise in this SOP. Detailed instructions regarding the preparation of standards and reagents are given in this section. Alternate procedures are allowed as necessary to accommodate volume requirements as long as final concentrations are maintained and an accurate description of the standard or reagent used is entered into the Reagent Module in TALS.

7.3.3 Intermediate calibration and QC standards are prepared in water with hydrochloric and nitric acids in order to approximate the acidic matrix of the various digests analyzed. This is an important point. Even with the use of yttrium as an internal standard, deviations from these concentrations can cause physical effects, as discussed in Section 4.4 of this procedure.

7.4 Reagent Blank / Initial Calibration Blank (ICB) / Continuing Calibration Blank (CCB)

Fill a 20-liter carboy with about 18 liters of reagent water. Slowly add 1L of concentrated nitric acid and 1L concentrated hydrochloric acid. Adjust the total volume to 20L. Mix carefully. Record the acid lot number and other required information in the Blank Reagent Logbook stored in the metals prep area.

7.5 Stock ICSA and ICSAB Standards

The following standards are purchased from commercial sources:

Stock ICSA & ICSAB Standard	Elements	Concentration (mg/L)
Icp stk ICSA	Fe Al, Ca, Mg	2,000 5,000
ANALYTES B	Ba, Be, Co, Cr, Cu, Mn, V Ag, Cd, Ni, Pb, Zn	50 100
ICP ISAB STD1	Li, Mo, Sb, Sr As, B, P Se K, Na	100 200 500 5000

Stock ICSA & ICSAB Standard	Elements	Concentration (mg/L)
ICP ISAB STD2	Ti Sn	100 1,000
10000 Si	Si	10,000
10000 Th	Th	10,000
1000 Tl	Tl	1,000
1000 Zr	Zr	1,000
1000 S	S	1,000
1000 Bi	Bi	1,000

7.6 ICSA Working Standard (ICP ICSA)

A combined working ICSA standard is made in a 250-mL volumetric flask using the following volumes of the Stock ICSA and ICSAB Standards:

Stock Standard	Volume of Stock Added (mL)
ICSA Std	25

Adjust to volume (250 mL) using the reagent blank solution. This produces the final ICSA standard concentrations shown in Attachment 4.

7.7 ICSAB Working Standard

A combined working ICSAB standard is made in a 250-mL volumetric flask using the following volumes of the Stock ICSAB Standards:

Stock Standard	Volume of Stock Added (mL)
Icp stk ICSA	25
ANALYTES B	2.5
ICP ISAB STD1	2.5
ICP ISAB STD2	2.5
10000 Si	0.25
10000 Th	0.05
1000 Tl	2.5
1000 Zr	0.25
1000 S	0.25
1000 Bi	0.25

Adjust to volume (250 mL) using the reagent blank solution. This produces the final ICSAB standard concentrations shown in Attachment 4.

7.8 Calibration Check Standard (S1, S2)

The two calibration check standards are the same as the working ICAL standards (ICP ICAL1A and ICP ICAL2A) described in Section 7.12.

7.9 Laboratory Control Sample (LCS) Stock Standards

The LCS stock standards are purchased from commercial sources. The stocks are custom-made standards purchased at ready-to-use concentrations as follows:

LCS Stock Standards	Elements	Concentration (mg/L)
ICP SPK 3A	Ca, K, Mg, Na P Al, Ba, Bi, Se, Tl, U, As, Fe, Li, Sr, Th Co, Mn, Ni, Pb, V, Zn Cu Cr Cd Ag, Be	5,000 1,000 200 100 50 25 20 10 5
ICP SPK 2B	Sb, Zr B, Mo, Ti Sn Si (SiO_2) S	50 100 200 1,000 (2,140) 200

The soil and water LCSs are prepared according to the instructions in SOPs DV-IP-10 and DV-IP-0015. Final concentrations are shown in Attachment 2.

7.10 Matrix Spike / Matrix Spike Duplicate (MS/MSD)

The same LCS stock standards described in Section 7.8 are also used to prepare matrix spikes and matrix spike duplicates. Final concentrations are shown in Attachment 2.

7.11 Post Digestion Spike (PDS) Standards (Analyte Addition Spike Standards)

The custom standards tabulated below are purchased from a commercial source. Add 0.06 mL of each to 6 mL (100X) of digestate or dilution of digestate.

PDS Stock	Elements	Conc. (mg/L)
ICP PDS 1	Ag, Be, Cd, Co, Cr, Cu, Mn, Ni, Sr, V Ba, Li, Pb, As, Se, Th, Tl, Zn U Al, Fe P Ca, K, Mg, Na,	5.0 10 20 50 100 200 2,000
ICP PDS 2	Mo, Ti, Zr B, Sb, Sn Si (SiO_2)	5.0 10 500 (1,070)

7.12 Initial Calibration (ICAL) Standards

7.12.1 Stock Calibration Standards

The following stock solutions are purchased from commercial sources.

Stock Standard	Elements	Conc. (mg/L)
Icp cal std 2	Mo, Ti, Zr Sn Si (SiO_2)	100 200 1,000 (2,140)
Icp cal std 3	Ag, Al, B, Ba, Be, Cd, Co, Cr, Cu, Mn, Ni, Sr, V, Zn Li, P Fe Ca, Na Mg K	100 100 200 500 1,000 4,000 10,000
Al, Ca, Fe, Na, S, Th Stocks	Al, Ca, Fe, Na, S, Th	10,000
As, Pb, Sb, Se, Tl, U, Bi Stocks	As, Pb, Sb, Se, Tl, U, Bi	1,000

7.12.2 Working Initial Calibration Standard (ICP ICAL1A)

Add 5.0 mL each of Icp cal std 2 and Icp cal std 3 to a 500-mL volumetric flask partially filled with reagent blank solution. Add 1 mL of the As, Pb, Sb, Se, and Tl stocks. Dilute to the mark with reagent blank solution.

7.12.3 Working Initial Calibration Standard (ICP ICAL2A)

Add 10 mL of the Al and Fe and 50 mL of the Na 10,000 mg/L stock solutions; 1 mL of the Th and 20 mL of the U 1,000 mg/L stock solutions; 2ml of the 1,000 mg/l Bi solution and 1 mL of the 10,000 mg/L S solution to a 1,000-mL volumetric flask partially filled with reagent blank and dilute to the mark with reagent blank.

7.13 Initial Calibration Verification (ICV)

7.13.1 ICV Stock Standards

The following stock solutions are purchased from commercial sources:

Stock Standard	Elements	Conc. (mg/L)
Icp ICVL A	Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sr, V, Zn Se, Tl Ca, Na Mg K	25 25 50 200 1,000 2,000
Icp ICVL B	Ag, Mo, Sb, Ti, Zr Sn P, Si (SiO_2)	25 50 200 (428)
Icp ICVH	Al, Na Fe U Th	4,000 8,000 500 300
Bi, S Stocks	Bi, S	1,000

7.13.2 Working High Initial Calibration Verification (ICP ICVH)

Add 1.0 mL of the ICVH Stock, 0.05 ml Bi and 0.4 mL of the Sulfur to a 100 mL volumetric flask partially filled with reagent blank solution and dilute to the mark.

7.13.3 Working Initial Calibration Verification (ICP ICV)

Add 1.0 mL of each of the Icp ICVL A and Icp ICVL B stock solutions to a 100-mL volumetric flask partially filled with reagent blank solution and dilute to the mark.

7.14 Reporting Limit Standard (RLSTD)

7.14.1 RL Stock Standard

The following stock solutions are purchased from commercial sources:

Standard	Elements	Conc. (mg/L)
ICP RLSTD 1A	As, Sb, Se, Tl Pb	10 3.0
ICP RL STD 2A	Mo, Ti, Zr Sn Si (SiO2)	10 20 500 1,070
ICP RL STD3A	Ag, Cr, Cu, Li, Ni, Th, V, Zn, Al, B Ba, Cd, Co, Sr Be Ca, Mg Fe K, Na, P Mn U	10 100 5.0 1.0 200 30 1,000 3.0 60
100 mg/L S	S	100
100 mg/L Bi	Bi	100

7.14.2 Daily Reporting Limit Standard (ICP CRI)

Add 0.1 mL of each of ICP RLSTD 1A, ICP RL STD 2A, ICP RL STD 2A, 100 mg/L Bi and 100 mg/L S to a 100-mL volumetric flask partially filled with reagent blank and dilute to the mark. The Working RL standard must be prepared fresh each day.

7.15 High Continuing Calibration Verification (ICP CCVH)

Perform a 2x dilution of the working ICP ICAL2A solution (Section 7.11.3) with reagent blank solution.

7.16 Continuing Calibration Verification (ICP CCV)

Perform a 2x dilution of the working ICP ICAL1A solution (Section 7.11.2) with reagent blank solution.

7.17 Low Level ICV/Low Level CCV (ICP LLCCV)

The low level ICV/CCV verification stock standards are custom-made commercial standards as follows:

LLICV/LLCCV Stock Standard	Elements	Conc. (mg/L)
ICP LLCCV-1	K	300
	Na	100
	Ca, Mg	20
	Al, Bi, Fe	10
	U	6
	Ni	4
	Zn	2
	As, Cu, Se, Tl, Th	1.5
	Ba, Cr, Co, Li, Mn, Ag, Sr,	1
	V	1
	Pb	0.9
	Cd	0.5
	Be	0.1
ICP LLCCV-2	P	300
	Si	50
	B	10
	Sn	10
	Mo	2
	Zr	1.5
	Sb	1
	Ti	1

7.17.1 Low Level ICV \ Low Level CCV, Working Standards

RL Standard	Vol. of Stock Added (mL)
ICP-LLCCV-1	1
ICP-LLCCV-2	1

Adjust to volume (100 mL) using the reagent blank solution.

7.18 Reagents

7.18.1 Concentrated nitric acid (HNO3), trace metals grade or better.

7.18.2 Concentrated hydrochloric acid (HCl), trace metals grade or better.

7.18.3 Reagent water must be produced by a Millipore DI system or equivalent, with a minimum resistivity of 1.0 Mohm/cm at 25˚C.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client

requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation [1]	Holding Time [2]	Reference
Waters	HDPE	50 mLs	HNO_3, pH < 2; Cool ≤ 6°C	180 Days	40 CFR Part 136.3
Soils	Glass	3 grams	Cool ≤ 6 °C [3]	180 Days	N/A

[1] Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required for most programs. Preservation must be verified prior to analysis.

[2] Inclusive of digestion and analysis.

[3] Although ICP analysis of soil does not require refrigeration of the samples, mercury analysis does require refrigeration. Samples which will be used to aliquot volume for both analyses must be refrigerated.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the TALS Method Comments to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver Policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver Policy DV-QA-024P, *QA/QC Requirements for Federal Programs*. DoD QSM 5.0 QC Acceptance Criteria for ICP analyses are presented in Attachment 11. The criteria must be met unless otherwise documented in the project documents.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in TALS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. See Policy DV-QA-003P for further details.

9.3 Method Blank

The blank is de-ionized water taken through the procedure as if it were a sample. For soil samples analyzed under the AFCEE and DoD QAPPs, the method blank consists of <1 mm glass beads that have been processed in the same manner as the samples. A method blank is required with every batch of 20 or less samples.

Acceptance Criteria: The method blank must not contain any analyte of interest above ½ the reporting limit or above one-tenth of the concentration found in the associated samples (for samples with concentrations above the RL).

Corrective Action: If the method blank exceeds allowable levels, all associated samples must be redigested and reanalyzed. A possible exception is the situation in which the analyte is not detected in any of the associated samples, but this can only be done with client approval and it must be addressed in the final report case narrative.

9.4 Laboratory Control Sample (LCS)

The LCS is prepared as described in Section 7.8. One LCS is required with each analytical batch.

Acceptance Criteria: The recovery of the LCS must be within historical control limits. Historical control limits are based on three standard deviations of past results, and must be 80-120% or tighter. In the instance where the LCS recovery is greater than 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the report narrative. The process of establishing control limits is described in more detail in the Policy DV-QA-003P. The control limits are stored in TALS.

Corrective Action: If the LCS recovery falls outside of the established limits, all associated samples must be redigested and reanalyzed

9.5 Matrix Spike / Matrix Spike Duplicate (MS/MSD)

MS/MSDs are prepared as described in Section 0. One MS/MSD pair is required with each analytical batch. Note that some programs (e.g., North Carolina and South Carolina) require the MS/MSDs to be run at a 10% frequency. Some client specific data quality objectives (DQOs) may require the use of sample duplicates in

place of or in addition to MS/MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing on only the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Note that if client instructions on the chain of custody form tell the lab to use a field blank for the MS/MSD, this should be double-checked with the laboratory PM.

Acceptance Criteria: The recoveries for the MS and MSD must be within the historical control limits or the project-required control limits, whichever are appropriate. Historical control limits are based on three standard deviations of past results, and should be within the established project-specific method control limits, if they exist. The process of establishing control limits is described in more detail in Policy DV-QA-003P. The control limits are stored in the laboratory's LIMS system. Acceptance limits derived from historical data should be no wider than +/-25%.

Corrective Action: If MS/MSD recoveries fall outside of the established limits and the LCS is in control, the data will be flagged as outside of control limits. The failure will be documented by the PM in the case narrative to alert the client that a matrix affect may be present.

Acceptance Criteria: The relative percent difference (RPD) between the MS and MSD is evaluated to measure precision and must be less than or equal to the historical RPD control limit. Historical control limits are based on three standard deviations of past results, and must be no greater than 20%.

Corrective Action: If the RPD fails to meet precision limit and the recoveries pass, the control limits should be checked as this would be a very rare occurrence if the limits are set properly. If the LCS is in control, it indicates long-term precision, and precision failures within the batch may be due to sample non-homogeneity. MS/MSD results which fall established control limits must be addressed in the narrative.

NOTE: This method does not require a sample duplicate. Precision is measured using the MS/MSD. Use of the MS/MSD is preferred as not all samples will contain measurable concentrations of the target analytes. Samples that have target analytes at low concentrations or non-detectable levels do not provide useful precision data. When an MS/MSD is not available, an LCS and LCSD will be used to measure precision.

9.6 Serial Dilution Test

A dilution test is performed for each batch of samples. The purpose of this test is to ensure that neither positive nor negative interferences are biasing the analytical

results. The serial dilution test should be performed on the same sample used to perform the MS/MSD.

Acceptance Criteria: If the analyte concentration is sufficiently high (minimally, a factor of 50 times the MDL), an analysis of a 1:5 dilution (e.g., 1 mL of sample diluted to 5 mL with reagent blank solution) must agree within ± 10% of the original determination. For DoD QSM 5.0 the serial dilution is required if the MS or MSD fails and the parent concentration is greater than 50x the LOQ prior to dilution.

Corrective Action: If the two results do not agree within ± 10%, then a chemical or physical interference is suspected A qualifier flag is assigned to the data and the failure is addressed in the case narrative to alert the client that a matrix affect may be present. For DoD V 5 a J-flag is added to the parent sample for the specific analyte if the acceptance criteria are not met.

9.7 Post Digestion Spike (PDS)

Whenever the MS/MSD recoveries are unacceptable, a PDS spike must be performed. The PDS spike is prepared as described in Section 7.10. Some programs, e.g., AFCEE, require a PDS analysis whenever the serial dilution test fails. Other programs, e.g., DoD QSM, require a PDS to be included in every batch. Check project requirements. For these programs, the same sample that was used for the serial dilution test should be used for the PDS.

Acceptance Criteria: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 80-120% for Method 6010C. The spike addition should produce a minimum level of 10 times to a maximum of 100 times the lower limit of quantitation.

Corrective Action: If the spike is not recovered within the specified limits, a matrix effect is confirmed. For DoD QSM 5.0 a J-flag is added to the parent sample if the sample concentration is less than 50x the LOQ prior to dilution. Any failures are flagged and should be described in the report case narrative.

9.8 Method of Standard Additions (MSA)

This technique involves constructing a calibration curve in the sample matrix itself to compensate for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences that cause a baseline shift. Attachment 8 provides more guidance on performing MSA analyses.

9.9 Interference Check Analysis (ICSA / ICSAB)

The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Sections 7.4, 7.5, and 7.6 for the preparation of the ICSA and ICSAB solutions. Attachment 4 lists the final concentrations. All analytes are spiked into the ICSAB solution. The ICSA and ICSAB solutions are analyzed at the beginning of the run.

Acceptance Criteria: The ICSAB results for the all analytes must fall within 80-120% of the true value. If any ICSAB analyte result fails criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the samples rerun.

The absolute value of ICSA results for the non-interfering elements must be ≤ 2 x RL. The DoD and AFCEE programs have their own criteria based on the version used. For DoD QSM 5.0 the non-spiked analytes must be less than the absolute value of the LOD unless they are verified impurities.

Corrective action: If the ICSA results for the non-interfering elements do not meet these limits, the field sample data must be evaluated as follows: If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted. If the affected element was not required, then the sample data can be accepted. If the interfering elements are not present in the field sample at a concentration which would result in an absolute value > 2x RL, then the field sample data can be accepted. If the interfering element is present in the field sample at a level which would result in a false analyte signal > 2x RL, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the analyte signal in the ICSA. If the data do not meet the above conditions, then the IECs must be re-evaluated and corrected if necessary and the affected samples reanalyzed.

9.10 Monitoring Internal Standard Results

Yttrium is automatically added as an internal standard (IS) to every solution tested through use of a third pump channel and mixing coil. The analyst must monitor the response of the internal standard throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte).

Acceptance Criteria: If the internal standard counts fall within ±30% of the counts observed in the ICAL blank, then the data are acceptable.

Corrective Action: If the internal standard counts in the field samples are outside of the control limits, the field samples must be diluted and reanalyzed;

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any unauthorized deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 Sample Preparation

Solid and aqueous samples must be digested prior to analysis by the appropriate method (see SOPs DV-IP-0010, DV-IP-0015, and DV-IP-0017).

10.4 Calibration

10.4.1 Instrument Start Up

Set up the instrument with the operating parameters recommended by the manufacturer. Complete any required preventative maintenance and record in the ICPAES Preventative Maintenance Log. Preventive maintenance recommendations a list in the TestAmerica Denver Quality Assurance Manual. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required)

10.4.2 Initial Calibration (ICAL)

The calibration curve is established on each day of operation using a blank and one standard. The preparation of the ICAL standards is described in Section 7. The final concentrations of the ICAL standards are presented in Attachment 6. The validity of the calibration curve is confirmed by analysis of the ICV, CCV, ICB, RL Check standard and Low Level ICV/CCV) which are run immediately after the ICAL. Some programs require a high-level verification check as well.

10.4.3 Initial Calibration Verification (ICV)

Calibration accuracy is verified using a second-source standard (ICV) that is at or below a concentration near the mid-point of the working range. The ICV is analyzed immediately after the ICAL. The preparation of this standard is described in Section 7. The concentrations of the ICV standard are presented in Attachment 6.

Acceptance Criteria: For Method 6010C, the ICV result must fall within 10% of the true value for that solution. The standard deviation must be < 5% (the laboratory is using at least two exposures for all ICP analyses).

Corrective Action: If the ICV fails to meet acceptance limits, the standard may be reanalyzed without modification to the instrument operating conditions. Two consecutive, acceptable analyses are required before the analytical run may continue. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.4.4 Mid Level Continuing Calibration Verification (CCV)

The preparation of the CCV solution is described in Section 7. The final concentrations of the CCVs are presented in Attachment 6. Note that the CCV is made at a different concentration than the ICV to meet NELAC requirements. CCVs are analyzed after the ICV, after every ten samples, and at the end of the analytical run.

Acceptance Criteria: The CCV must be within 10% of the expected value to meet Method 6010C requirements. The relative standard deviation must be <5%.

Corrective Action: If the CCV fails to meet any of these criteria, the standard may be reanalyzed without modification to the instrument operating conditions. *Two consecutive, acceptable analyses are required before the analytical run may continue.* Otherwise, the instrument must be recalibrated and the samples reanalyzed since the last successful CCV must be reanalyzed.

10.4.5 Low Level Initial Calibration (LLICV) and Continuing Calibration Verification (LLCCV)

The preparation of the LLCCV solution is described in Section 7. The low-level CCV needs to be analyzed at the beginning and end of every run sequence. If low level samples are expected then the low-level CCV should also be run every ten samples.

Acceptance Criteria: The LLCCV must be within +/-30% of the expected value to meet Method 6010C requirements.

Corrective Action: If the LLCCV fails to meet any of these criteria, the standard may be reanalyzed without modification to the instrument operating conditions. *Two consecutive, acceptable analyses are required before the analytical run may continue.* If the calibration cannot be verified within theses specified limits, the analysis of samples containing the affected analytes at similar concentrations cannot continue until the cause is determined and the LLCCV standard successfully analyzed. Otherwise, the instrument must be recalibrated and the samples reanalyzed since the last successful CCV must be reanalyzed. TestAmerica will not hold samples with concentrations greater than 10x the reporting limit to the 30% acceptance criteria.

10.4.6 Initial Calibration Blank (ICB)

System cleanliness is verified by analyzing an ICB after the first CCV. The preparation of the ICB is described in Section 7.

Acceptance Criteria: Absolute values for the calibration blanks must be less than ½ the standard RL. Common lab contaminants such as sodium must be less than the RL. Client specific requirements take precedence. For example, DoD requires control of blanks to a concentration less than or equal to the LOD.

Corrective Action: If the ICB fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.4.7 RL Calibration Check Standard (ICP CRI)

Calibration accuracy at the RL is verified by analyzing a standard prepared at a concentration at or below the laboratory's standard reporting limit. The preparation of this standard is described in Section 7. Alternate RLSTD concentrations may be used as necessary to meet client requirements as long as an accurate description of the standard used is entered into the Reagents Module in TALS.

Acceptance Criteria: For routine work and for programs that allow the RL to be as low as 2 x MDL (e.g., AFCEE), the acceptance limits are ± 50% of the expected value.

For some programs (e.g., DoD QSM), the acceptance limit is ± 20%.

Corrective Action: If the RL Check standard fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.4.8 Lower Limit of Quantitation Check (LLQC)

The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits and on an as needed basis to demonstrate the desired detection capability. The difference between the LLQC and the LLICV/CCV is that this standard is carried through the entire preparation and analytical procedure.

Acceptance Criteria: LLQC is verified when all analytes are detected within ± 30% of their true value.

Corrective Action: If the LLQC fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified.

10.4.9 High-Level Calibration Check Standard

The method 6010 defines the linear working range used for daily analysis based on the LDR studies performed every six months, in which case this standard is not required. However, some programs require verification of the high end of the linear range at different frequencies. For example, the AFCEE QAPP, version 4.0, requires evaluation of a high check standard every three months.

Acceptance Criteria: The result for this standard must be within 10% of the expected value.

Corrective Action: If the High-Level Calibration Check standard fails to meet acceptance limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, the analysis should be terminated, the problem corrected, the instrument recalibrated, and the calibration re-verified. Alternately, results that do not exceed the level of the highest calibration standard may be accepted and reported.

10.4.10 Continuing Calibration Blank (CCB)

CCBs, prepared as in Section 7.3, are analyzed after each CCV.

Acceptance Criteria: Absolute values for the calibration blanks must be less than ½ the standard RL. Common lab contaminants such as sodium must be less than the RL. Client specific requirements take precedence. For example, DoD requires control of blanks to a concentration less than or equal to the LOD.

Corrective Action: If the CCB is greater than these limits, a single reanalysis may be attempted without modification to the instrument operating conditions. Otherwise, instrument maintenance should be considered, the calibration re-verified, and all samples analyzed since the last successful CCB must be reanalyzed.

10.5 Sample Analysis

10.5.1 Replicate Readings

The laboratory averages the results from two exposures for Axial and Dual View ICP for each standard, field sample, and QC sample due to sample volume limitations of the autosampler tube.

10.5.2 Rinse Time Between Samples

Prior to calibration and between each sample/standard, the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless following the protocol outlined in 12.7 it can be demonstrated that a shorter rinse time may be used.

10.5.3 The following analytical sequence is used:

Instrument Calibration
High Standard Verification
ICV
LLICV
CCV
ICB
RL Verification Standard
LLQC (as needed)
ICSA
ICSAB
LRA
CCV
CCB
LLCCV
10 samples

CCV
CCB
LLCCV
10 samples
CCV
CCB
LLCCV
Repeat sequence with 10 samples between CCV/CCB pairs
CCV
CCB
LLCCV

10.5.4 Full method-required QC must be available for each wavelength used in determining reported analyte results. Guidelines are provided in the appendices for minimizing contamination of samples and standards (Attachment 10) and troubleshooting (Attachment 9).

10.5.5 Dilutions for High Levels of Elements of Interest

For 6010, results must fall within the linear range. Dilute and reanalyze all samples for required analytes that exceed the linear range or use an alternate wavelength for which QC data are established. Dilutions must be prepared using the reagent blank solution to maintain the correct acid strength.

10.5.6 Dilutions for High Levels of Interfering Elements

Dilutions are also required for an element that is included in an IEC calculation if it exceeds the linear range. If a dilution is not performed, the IEC may be inaccurately applied. Therefore, even if an over-range analyte may not be required to be reported for a sample, if that analyte is an interferent for any requested analyte in that sample, the sample must be diluted to a level at or below the working range. An NCM will be written in these instances.

10.6 Instrument Maintenance

See Section 20 in the QAM.

10.7 Troubleshooting

See Attachment 9.

11.0 Calculations / Data Reduction

11.1 Detailed calibration equations can be found in the corporate Policy CA-Q-P-003 *Calibration Curves & Selection of Calibration Points* and under the public folder, *Arizona Calibration Training*.

11.2 ICV percent recoveries are calculated according to the following equation:

$$\%R = \left(\frac{\text{ICV Found Value}}{\text{ICV True Value}} \right) \times 100\%$$

11.3 CCV percent recoveries are calculated according to the following equation:

$$\%R = \left(\frac{\text{CCV Found Value}}{\text{CCV True Value}} \right) \times 100\%$$

11.4 Matrix Spike Recoveries are calculated according to the following equation:

$$\%R = \left(\frac{SSR - SR}{SA} \right) \times 100\%$$

Where:

SSR	=	Spike Sample Result
SR	=	Sample Result
SA	=	Spike Added

The relative percent difference (RPD) of matrix spike/matrix spike duplicates are calculated according to the following equation:

$$RPD = \left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2} \right)} \right] \times 100$$

Where:

MS	=	determined spiked sample concentration
MSD	=	determined matrix spike duplicate concentration

11.5 The final concentration for a digested aqueous sample is calculated as follows:

$$\text{Final Concentration (mg/L)} = \frac{C \times V1 \times D}{V2}$$

Where:

C	=	Concentration (mg/L) from instrument readout
D	=	Instrument dilution factor
V1	=	Final volume in liters after sample preparation
V2	=	Initial volume of sample digested in liters

11.6 The final concentration determined in digested solid samples when reported on a dry weight basis is calculated as follows:

$$\text{Final Concentration (mg/kg), dry weight} = \frac{C \times V \times D}{W \times S}$$

Where:

C	=	Concentration (mg/L) from instrument readout
D	=	Instrument dilution factor
V	=	Final volume in liters after sample preparation

W	=	Weight in Kg of wet sample digested
S	=	Percent solids/100

NOTE: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on wet weight basis the "S" factor should be omitted from the above equation.

11.7 The LCS percent recovery is calculated according to the following equation:

$$\%R = \left(\frac{\text{LCS Found Value}}{\text{LCS True Value}} \right) \times 100\%$$

11.8 The IEC's are calculated according to the following equation:

$$IEC = \left(\frac{\text{observed concentration}}{\text{observed concentration of the interfering element}} \right)$$

11.9 The dilution test percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} \times 100$$

Where:

I	=	Sample result (Instrument reading)
S	=	Dilution test result (Instrument reading $\times$ 5)

Appropriate factors must be applied to sample values if dilutions are performed.

11.10 Documentation and Record Management

11.10.1 All sample data is uploaded to TALS. All sample preparation and analytical batch information, including the batch number(s), list of samples, preparation analyst and date, instrument analyst and date, identification of reagents and standards used, and identification of all measuring equipment used (e.g., balances, thermometers, pipettes) is recorded in TALS.

11.10.2 Raw data is scanned or saved directly as a PDF and is attached to the analytical batch in TALS.

11.10.3 The initial data review is performed by the analyst and a second-level review is performed by the area supervisor or designee. Both reviews are documented on a Data Review Checklist. See SOP DV-QA-0020 for more detail on the review process.

11.10.4 If dilutions are required due to insufficient sample, interferences, or other problems, the reporting limit and MDL are multiplied by the dilution factor and the data may require flagging.

NOTE: Unless special instructions indicate otherwise, sample results less than the reporting limit are reported as ND.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. An initial method detection limit study is performed in accordance with Policy DV-QA-005P. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency. For DoD, AFCEE, and DOE projects, an MDL verification is performed quarterly. DOD QSM 5.0 requires the MDLV spike level to be 2-4 times the calculated MDL.

12.2 Instrument Detection Limit Study

12.2.1 Instrument detection limit (IDL) studies are conducted quarterly for each instrument and each wavelength used for analysis.

12.2.2 Run seven blanks on three non-consecutive days.

12.2.3 Calculate the standard deviation for each day. The final IDL concentration is the average of the three daily standard deviation values.

12.2.4 See Policy DV-QA-014P for a discussion of IDL studies and evaluation of IDL results.

12.3 Linear Dynamic Range (LDR)

12.3.1 The LDR must be determined initially (i.e., at initial setup) and then every three months for each analyte wavelength used on each instrument. The linear range is the concentration above which results cannot be reported without dilution of the sample.

12.3.2 The LDR must be determined from a linear calibration prepared in the normal manner using the normal operating procedures described in Sections 10 and 11.

12.3.3 The LDR is determined by analyzing successively higher standard concentrations of the analyte. A minimum of three standards is required for the initial and on-going studies, and one of the levels must be close to the upper end of the range. The highest concentration must be within 10% of the stated concentration.

12.3.4 The highest standard that meets this criterion defines the maximum concentration that can be reported for sample analysis without dilutions.

12.3.5 If the instrument is adjusted in any way that may affect the LDRs, new dynamic ranges must be determined. The LDR data must be documented and kept on file.

12.4 Background Correction Points

12.4.1 To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side adjacent to the wavelength of interest and record the apparent emission intensity from all other method analytes. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations.

12.4.2 Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Background correction points must be set prior to determining IECs. Refer to the ICP instrument manual for specific procedures to be used in setting background correction points.

12.5 Interelement Corrections (IECs)

12.5.1 ICP interelement correction (IEC) factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IECs, the IECs must be re-determined.

12.5.2 When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC, then the possibility of contamination should be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., GFAA or ICP-MS). Published wavelength tables (e.g., MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to evaluate the validity of the IECs.

12.5.3 Refer to the facility-specific instrument operation SOP and instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any interelement interference which produces a false analytical result with an absolute value greater than the RLs shown in Attachment 1. Note that the USACE program requires a control limit of 2x |MDL|, which is feasible when verified MDLs are used.

12.5.4 To determine IECs, run a single element standard at the established linear range. To calculate an IEC, divide the observed concentration of the analyte by the observed concentration of the "interfering element."

12.5.5 Dual-View ICP IECs are more sensitive to small changes in the plasma and instrument setup conditions. Adjustments in the IECs will be required on a more frequent basis for the CID detector instruments as reflected by the ICSA response.

12.6 Rinse Time Determination

12.6.1 Rinse times must be determined annually.

12.6.2 To determine the appropriate rinse time for a particular ICP system, a standard containing the highest concentration level that would be reported for samples is aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < RL will define the rinse time for a particular ICP system.

12.6.3 For some analytes it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level).

12.6.4 Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file if a concentration other than the linear range level is used to set the rinse time. The concentration levels used to establish the rinse time must be taken into consideration when reviewing the data.

12.6.5 The ICP instruments use an intelligent rinse program. The intelligent rinse lengthens the rinse time whenever a sample result for a known problem analyte is above a set concentration.

12.7 Demonstration of Capabilities

12.7.1 All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows:

12.7.2 Four LCS's are run using the same instrumental conditions and procedures used to analyze samples. Using these four LCS's demonstrates the analyst's ability to optimize and calibrate the instrument and to prepare analytical solutions. Calculate the mean recovery and standard deviation of the mean recovery for each analyte of interest.

12.7.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.7.4 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

12.7.5 The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. Further details concerning the training program are described in SOP DV-QA-0024.

12.8 Training Requirements

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. Further details concerning the training program are described in SOP DV-QA-0024.

13.0 Pollution Control

13.1 It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, order chemicals based on quantity needed, and prepare reagents based on anticipated usage and reagent stability).

13.2 Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in Section 13, *Waste Management and Pollution Prevention*, of the Corporate Safety Manual, and DV-HS-001P, *Waste Management Plan*.

14.2 The following waste streams are produced when this method is carried out:

14.2.1 Acid solutions from ICP drain - Waste Stream J

14.2.2 Metals waste potentially contaminated with Cat 1 radioactive materials – Waste Stream RJ

Note: Radioactive, mixed waste and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), Third Edition and all promulgated updates, EPA Office of Solid Waste, through January 2008.

15.1.1 Method 6010C, Revision 3, Update IV, February 2007.

15.1.2 Method 3005A, Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy, Revision 1,July 1992

15.1.3 Method 3010A, Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy, Revision 1, July 1992.

15.1.4 Method 3050B, Acid Digestion of Sediments, Sludges and Soils, Revision 2, December 1996.

15.2 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 4.2, 10/25/2010.

15.3 Department of Defense Quality Systems Manual for Environmental Laboratories Version 5.0, July 2013.

16.0 Method Modifications:

Item	Method	Modification
1	EPA 6010C	This procedure uses mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in house as recommended by the subject methods.
2	EPA 6010C	The alternate run sequence presented in Section 10.5.3 is consistent with method requirements. Additional QC (i.e., ICSA) analyses were added to accommodate the CLP protocol requirements.
3	EPA 6010C	Method 6010 states that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific "concentration range around the calibration blank." Because of the lack of definition for "concentration range around the calibration blank," the laboratory has adopted the procedure in EPA CLP ILMO4.0 for determining IECs,
4	EPA 6010C	Section 9.9 of Method 6010C states: "If less than acceptable accuracy and precision data are generated, additional quality control tests are recommended prior to reporting concentration data for the elements in this method." The dilution test helps determine if a chemical or physical interference exists. Because the laboratory sometimes does not have prior knowledge if the MS/MSD will be within criteria, the analyst may select to perform a dilution test on one sample in each preparation batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. In this procedure, matrix interference is determined by evaluating data for the LCS, MS/MSD, and serial dilutions. The laboratory must request documented, clear guidance when a unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample.

17.0 Attachments

Attachment 1 Metals Analyzed by ICP and Reporting Limits
Attachment 2 Matrix Spike and Aqueous Laboratory Control Sample Levels
Attachment 3 Low Level ICV and CCV Spiking Levels

Attachment 4 Interference Check Sample Concentrations
Attachment 5 TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels
Attachment 6 6500 Initial Calibration &Continuing Calibration Verification Standards
Attachment 7 Summary of Quality Control Requirements
Attachment 8 MSA Guidance
Attachment 9 Troubleshooting Guide
Attachment 10 Contamination Controls
Attachment 11 DoD QSM 5.0 QC Acceptance Criteria

18.0 Revision History

Revision 3, dated 31 July 2015
- Annual review
- Updated Section 7.4 for how to make the 5% HNO_3/5% HCl solution
- Updated Section 12.2 for MDLV spike level to 2-4x MDL
- Updated Section 12.8.2 to use LCSs instead of ICVs for the DOC
- Reformatting throughout
- Removed reference to silica holding time
- Added Maintenance and troubleshooting sections
- Replaced Section 11.10 to match current practice
- Removed Section 12.2
- Removed Sections 1.3.1 and 1.3.2
- Added new Section 1.6
- Removed reference to glass beads in Section 6.2
- Corrected Reagent and Standard formulae throughout to agree with current practice

Revision 2, dated 31 July 31 2014
- Annual review
- Updated Section 6.1.3 to specify purity of argon gas
- Added statement to section 9.1.2 to reference DoD QSM 5.0 criteria in Attachment 11
- Removed references to preparation of oil/oily samples throughout the document as the lab no longer supports this digestion method
- Added references for prep methods to section 15
- Added DOD QSM 5.0 QC acceptance criteria as Attachment 11

Revision 1, dated 15 July 2013
- Annual review
- Removed section 1.7
- Added section 3.8
- Corrected formatting
- Added section 11.12
- Removed Attachment 8, renumbered attachments and fixed references to attachments throughout the document

Revision 0.3, dated 13 July 2012
- Annual Review
- Clarified soil preservation for ICP only analysis, Section 8
- Updated section 9.1, 10.1, 10.2, and 12.1 to reflect current practice
- Updated sections 10.4.6 and 10.4.10 to control calibration blanks to ½ the RL

Revision 0.2, dated 30 June 2011
- Added reference to DV-IP-0017 “Microwave Digestion” throughout document

- Added section 6.3 “Computer Software and Hardware”
- Removed Uranium from the ICSA/ICSAB tables in sections 7.4, 7.5, and 7.6
- Updated sections 7.14 and 7.15 to reflect current practices
- Updated the Acceptance Criteria in sections 9.4, 9.6, and 9.10
- Referenced the TestAmerica Denver Quality Assurance Manual in section 10.4.1
- Updated section 11 to reference corporate SOP CA-Q-S-005, “Calibration Curves” and Arizona Calibration Training spreadsheet
- Added IEC calculation to section 11

Revision 0.1, dated 18 June 2010

- Basic Annual Review

Revision 0, dated 19 June 2009

Attachment 1

Metals Analyzed by ICP and Reporting Limits

ELEMENT	Symbol	CAS #	6010 Analyte	Reporting Limit (µg/L) Water	Reporting Limit (mg/kg) Soil
Aluminum	Al	7429-90-5	X	100	10
Antimony[trace]	Sb	7440-36-0	X	10	1
Arsenic[trace]	As	7440-38-2	X	15	1
Barium	Ba	7440-39-3	X	10	1
Beryllium	Be	7440-41-7	X	1	0.1
Bismuth	Bi	7440-69-9		100	10
Boron	B	7440-42-8	X	100	10
Cadmium[trace]	Cd	7440-43-9	X	5	0.5
Calcium	Ca	7440-70-2	X	200	20
Chromium	Cr	7440-47-3	X	10	1
Cobalt	Co	7440-48-4	X	10	1
Copper	Cu	7440-50-8	X	15	2
Iron	Fe	7439-89-6	X	100	10
Lead[trace]	Pb	7439-92-1	X	9	0.8
Lithium	Li	7439-93-2	X	10	5
Magnesium	Mg	7439-95-4	X	200	20
Manganese	Mn	7439-96-5	X	10	1
Molybdenum	Mo	7439-98-7	X	20	2
Nickel	Ni	7440-02-0	X	40	4
Phosphorus	P	7723-14-0	X	3,000	300
Potassium	K	7440-09-7	X	3,000	300
Selenium[trace]	Se	7782-49-2	X	15	1.3
Silicon	Si	7631-86-9		500	50
Silver[trace]	Ag	7440-22-4	X	10	1
Sodium	Na	7440-23-5	X	1	100
Strontium	Sr	7440-24-6	X	10	1
Sulfur	S	7704-34-9	X	200	2
Thallium[trace]	Tl	7440-28-0	X	15	1.2
Thorium	Th	7440-29-1		15	15
Tin	Sn	7440-31-5	X	100	10
Titanium	Ti	7440-32-6	X	10	1
Uranium	U	7440-61-1		60	20
Vanadium	V	7440-62-2	X	10	2
Zinc	Zn	7440-66-6	X	20	2
Zirconium	Zr	7440-67-7		15	1

Attachment 2

Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	LCS Level (µg/L)	Matrix Spike Level (µg/L)
Aluminum	2,000	2,000
Antimony	500	500
Arsenic	2,000	2,000
Barium	2,000	2,000
Beryllium	50	50
Bismuth	2,000	2,000
Boron	1,000	1,000
Cadmium	50	50
Calcium	50,000	50,000
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1,000	1,000
Lead	500	500
Lithium	1,000	1,000
Magnesium	50,000	50,000
Manganese	500	500
Molybdenum	1,000	1,000
Nickel	500	500
Phosphorous	10,000	10,000
Potassium	50,000	50,000
Selenium	2,000	2,000
Silicon	10,000	10,000
Si (as SiO_2)	21,400	21,400
Silver	50	50
Sodium	50,000	50,000
Strontium	1,000	1,000
Sulfur	2,000	2,000
Thallium	2,000	2,000
Thorium	2,000	2,000
Tin	2,000	2,000
Titanium	1,000	1,000
Uranium	2,000	2,000
Vanadium	500	500
Zinc	500	500
Zirconium	500	500

Attachment 3

Low Level ICV/CCV

ELEMENT	LCS Level (µg/L)
Aluminum	100
Antimony	10
Arsenic	15
Barium	10
Beryllium	1
Bismuth	100
Boron	100
Cadmium	5
Calcium	200
Chromium	10
Cobalt	10
Copper	15
Iron	100
Lead	9
Lithium	10
Magnesium	200
Manganese	10
Molybdenum	20
Nickel	40
Phosphorous	3,000
Potassium	3,000
Selenium	15
Silicon	500
Si (as SiO_2)	1070
Silver	10
Sodium	1,000
Strontium	10
Thallium	15
Thorium	15
Tin	10
Titanium	10
Uranium	60
Vanadium	10
Zinc	20
Zirconium	15

Attachment 4

Interference Check Sample Concentrations

Element	ICSA (µg/L)	ICSAB (µg/L)
Aluminum	500,000	500,000
Antimony	-	1,000
Arsenic	-	2,000
Barium	-	500
Beryllium	-	500
Bismuth	-	1,000
Boron	-	2,000
Cadmium	-	1,000
Calcium	500,000	500,000
Chromium	-	500
Cobalt	-	500
Copper	-	500
Iron	200,000	200,000
Lead	-	1,000
Lithium	-	1,000
Magnesium	500,000	500,000
Manganese	-	500
Molybdenum	-	1,000
Nickel	-	1,000
Phosphorous	-	2,000
Potassium	-	50,000
Selenium	-	5,000
Silicon	-	10,000
Silica	-	21,400
Silver	-	1,000
Sodium	-	50,000
Strontium	-	1,000
Sulfur	-	1,000
Thallium	-	10,000
Titanium	-	1,000
Vanadium	-	500

Attachment 4

Interference Check Sample Concentrations (cont'd)

Element	ICSA (µg/L)	ICSAB (µg/L)
Zinc	-	1,000
Tin	-	10,000
Thorium	-	10,000
Uranium	2,000	2,000
Zirconium	-	1,000

Attachment 5

TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	Reporting Level (µg/L)	Regulatory Limit (µg/L)	Spike Level (µg/L)
Arsenic	500	5000	4000
Barium	10000	100000	12000
Cadmium	100	1000	1100
Chromium	500	5000	5200
Lead	500	5000	5500
Selenium	250	1000	3000
Silver	500	5000	1050
Copper	100	N/A	2250
Zinc	200	N/A	2500

Attachment 6

6000 Dual View Calibration, ICV & CCV Standards

Element	Calibration Level	ICV (µg/L)	CCV (µg/L)
Aluminum Lo	1,000	250	500
Aluminum Hi	100,000	40,000	50,000
Antimony	2,000	250	1,000
Arsenic	2,000	250	1,000
Barium	1,000	250	500
Beryllium	1,000	250	500
Bismuth	2,000	500	1000
Cadmium	1,000	250	500
Calcium	10,000	2,000	5,000
Chromium	1,000	250	500
Cobalt	1,000	250	500
Copper	1,000	250	500
Iron Lo	5,000	250	2,500
Iron Hi	100,000	80,000	50,000
Lead	2,000	250	1000
Magnesium	40,000	10,000	20,000
Manganese	1,000	250	500
Molybdenum	1,000	250	500
Nickel	1,000	250	500
Phosphorous	2,000	2,000	1,000
Potassium	100,000	20,000	50,000
Selenium	2,000	500	1,000
Silver	1,000	250	500
Sodium Lo	10,000	2000	5,000
Sodium Hi	500,000	40,000	250,000
Strontium	1,000	250	500
Sulfur	10,000	4,000	5,000
Thallium	2,000	500	1,000
Thorium	10,000	3,000	5,000
Tin	2,000	500	1,000
Vanadium	1,000	250	500
Uranium	20,000	5,000	10,000
Zinc	1,000	250	500
Zirconium	1,000	250	500

Attachment 7
Summary Of Quality Control Requirements

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Two-point Initial Calibration	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criterion is not met	RSD between multiple exposures ≤5%	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
ICV	Beginning of every analytical run.	90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate.
CCV	After the ICV, after every 10 samples and at the end of the run.	90-110% recovery	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
RL Standard	At the beginning of the run	Results must within 50%	Terminate analysis; Correct the problem; Recalibrate.
LLICV/CCV	At the beginning of the run and after every 10 samples	Recovery must be within 30%	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable LLCCV.
ICB	Beginning of every analytical run, immediately following the initial CCV.	The result must be within +/- ½ RL from zero.	Terminate analysis; Correct the problem; Recalibrate.
CCB	Immediately following each CCV (except for the CCV following the ICV).	The result must be within +/- ½ RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB.
ICSA	Beginning of every run	See Section 9.10	See Section 9.10
ICSAB	Immediately following each ICSA.	Results must be within 80 - 120% recovery.	See Section 9.10
Dilution Test	One per prep batch.	For samples > 10x LOD (after dilution)' dilutions must agree within 10%.	Narrate the possibility of physical or chemical interference per client request.

See Section 10.5.3 for run sequence to be followed.

Attachment 7

Summary of Quality Control Requirements (Continued)

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Method Blank (MB)	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to ½ the RL. Sample results greater than 10x the blank concentration are acceptable. Samples for which the contaminant is < ½ RL may not require redigestion or reanalysis (see Section 9.3)	Re-run once in a clean tube. If > ½ RL, re-digest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	LCS must be within 80 - 120% recovery or in-house control limits. Samples for which the contaminant is < RL and the LCS results are > 120% may not require redigestion or reanalysis (see Section 9.4)	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS.
Matrix Spike (MS)	One per sample preparation batch of up to 20 samples.	75 – 125% recovery or tighter in-house control limits.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added.
Matrix Spike Duplicate (MSD)	One per sample preparation batch of up to 20 samples. 10% frequency for some programs (see 9.5)	75 – 125 % recovery; RPD ≤ 20% or tighter in-house control limits.	See Corrective Action for Matrix Spike.

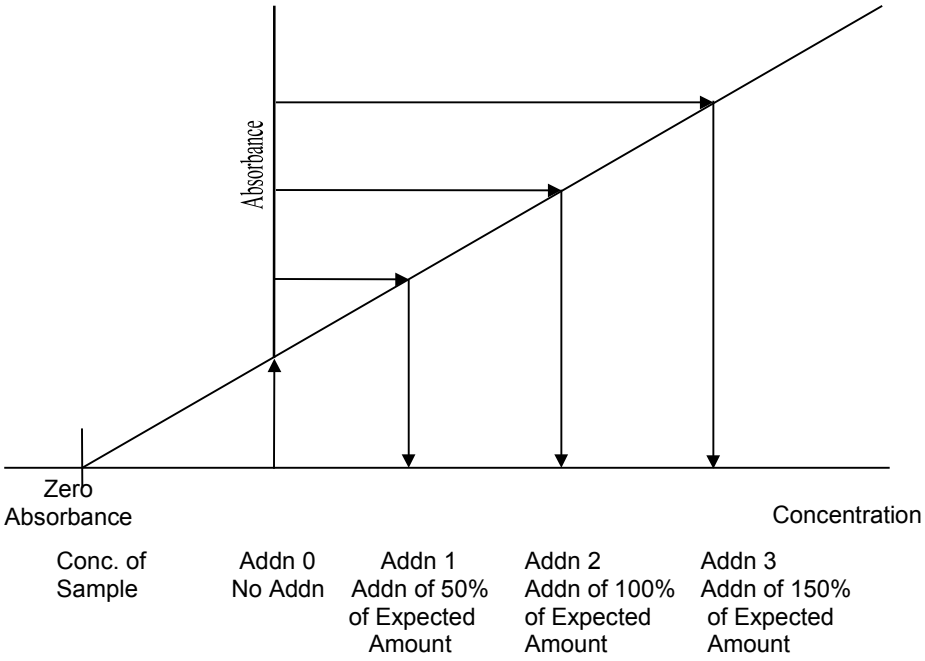
Attachment 8

MSA Guidance

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked standard should be the same.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the absolute value of the point of interception of the horizontal axis is the concentration of the unknown.



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration:

- The plot of the sample and standards must be linear (r=0.995 or greater) over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

Attachment 9

Troubleshooting Guide

Problem	Possible Cause/ Solution
High Blanks	Increase rinse time Clean or replace tip Clean or replace torch Clean or replace sample tubing Clean or replace nebulizer
Instrument Drift	RF not cooling properly Vacuum level is too low Replace torch (Crack) Clean or replace nebulizer (blockage) Check room temperature (changing) Replace pump tubing Room humidity too high Clean torch tip (salt buildup) Check for argon leaks Adjust sample carrier gas Replace RF generator
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks Adjust sample carrier gas Replace tubing (clogged) Check drainage(back pressure changing) Increase uptake time (too short) Increase flush time (too short) Clean nebulizer, torch or spray chamber Increase sample volume introduced Check that autosampler tubes are full Sample or dilution of sample not mixed Increase integration time (too short) Realign torch Reduce amount of tubing connectors
Standards reading twice normal absorbance or concentration	Incorrect standard used Incorrect dilution performed

Attachment 10

Contamination Control Guidelines

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered gloves should not be used in the metals laboratory because the powder contains silica and zinc as well as other metallic analytes.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

The following are helpful hints in the identification of the source of contaminants:

Yellow pipette tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The markings on glass beakers have been found to contain lead. If acid baths are in use for glassware cleaning, they should be periodically checked for contaminants since contaminant concentrations will increase over time.

New glassware especially beakers can be a source of silica and boron.

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

Attachment 11
DoD QSM 5.0 QC Criteria for Analysis by ICP

QSM 5.0 Table 8. Inorganic Analysis by ICP	
Requirement	**DoD QSM 5.0 and DOE QSAS 3.0**
Linear Dynamic Range (LDR) or high-level standard check	Run an LDR or high-level check standard at least once every 6 months. When calibrating with a single standard and a blank, the daily LDR standard must be analyzed at a concentration greater than any samples analyzed that day. Data cannot be reported above the high calibration range without an established/passing high-level check standard. Must be within ± 10% of expected value. Dilute samples within the calibration range or re-establish/verify the LDR.
Initial Calibration (ICAL)	Measure a minimum of one high standard and a calibration blank, daily. If more than one standard used, then $r^2 \geq 0.99$ ($r \geq 0.995$), otherwise no acceptance criteria. The ICAL must pass before running any samples. NOTE: The laboratory currently performs duplicate burns for the ICPAES method.
Initial Calibration Verification (ICV)	Run second-source standard once after each ICAL and prior to sample analysis. All reported analytes must be within ± 10% of expected value. Correct any problems, verify standard, and rerun ICV. If that fails, correct problem and rerun ICAL. Verification must pass before running any samples.
Continuing Calibration Verification (CCV)	Run CCV after every 10 field samples, and at the end of the analysis sequence. All reported values within ± 10% of expected value If the CCV is above the project acceptance limits and there are no detections in the samples, TestAmerica will report the non-detect results with a case narrative comment in addition to applying any data qualifier flags required by the project (3HR). Correct any problems then rerun CCV. If that fails, then repeat ICAL. Reanalyze all samples since last successful CCV. Results cannot be reported without a valid CCV. Or Immediately (within one hour) analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, take corrective action(s) and re-calibrate; then reanalyze all affected samples since the last acceptable CCV. If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analytes(s) in all samples since the last acceptable CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Low-Level Calibration Check Standard (Low-level ICV)	Run low-level standard at a concentration ≤ LOQ daily after one-point ICAL. All reported analytes must be within ± 20% of expected value. Correct any problems, then reanalyze or repeat ICAL. Results cannot be reported without a valid low-level calibration check standard.

Attachment 11
DoD QSM 5.0 QC Criteria for Analysis by ICP
(continued)

QSM 5.0 Table 8. Inorganic Analysis by ICP	
Requirement	**DoD QSM 5.0 and DOE QSAS 3.0**
Initial and Continuing Calibration Blank (ICB.CCB)	Analyze calibration blank before analyzing samples, after every 10 field samples, and at the end of the analysis sequence. No analytes detected > ½ LOQ (RL) or >1/10 the amount measured in any sample or 1/10 the regulatory limit, whichever is greater. (13ICP) If not accepted by client, ICB/CCB must be <LOD. If criteria not met, correct problem If reanalysis is not possible, apply B-flag to all results for the specific analyte(s) in all samples processed with the contaminated blank. Must be explained in the case narrative. Flagging is only appropriate when samples cannot be reanalyzed. Correct any problems and repeat ICAL. All samples following the last acceptable calibration blank must be reanalyzed. CCB failures due to carryover may not require an ICAL.
Interference Check Solution (ICS)	Run the ICS at the beginning of an analytical run (after ICAL and prior to sample analysis). ICS-A: Absolute value of concentration for all non-spiked analytes must be < LOD (unless they are a verified trace impurity from one of the spiked analytes). ICS-AB: Within ± 20% of expected value. (Note: ICS-AB not needed if instrument can read negative responses.) Correct any problems and reanalyze ICS. Do not analyze samples without a valid ICS. NOTE: TAL Denver has a letter from the ICSA standards manufacturer for many of the elements.
Method Blank	One per prep batch. No analytes detected > ½ LOQ (RL) or >1/10 the amount measured in any sample or 1/10 the regulatory limit, whichever is greater. Common lab contaminants not detected > LOQ. (2CLC) For ICP, common lab contaminants are: Al, Ca, Fe, K, Mg, Na, Si, Zn (Ba for TCLP) If criteria not met, correct problem. If required, reprep and reanalyze MB and all samples processed with the contaminated blank. If reanalysis is not possible, apply B-flag to all results for the specific analyte(s) in all samples processed with the contaminated blank. Must be explained in the case narrative. Flagging is only appropriate when samples cannot be reanalyzed.
LCS	One per prep batch. Recovery must meet DoD QSM limits. If the LCS recovery is above the project acceptance limits and there are no detections in the samples, TestAmerica will report the non-detect results with a case narrative comment in addition to applying any data qualifier flags required by the project (3HR). Correct any problems, then re-prep and reanalyze LCS and associated samples for failed analytes in all samples in the associated batch. If corrective action fails, apply Q-flag to specific analyte(s) in all samples in associated batch.

Attachment 11
DoD QSM 5.0 QC Criteria for Analysis by ICP
(continued)

QSM 5.0 Table 8. Inorganic Analysis by ICP	
Requirement	**DoD QSM 5.0 and DOE QSAS 3.0**
Matrix Spike (MS)	One MS per prep batch. Use DoD acceptance criteria for LCS. If MS fails, consult project-specific DQOs and contact client to see if additional measures need to be taken. For specific analyte(s) in parent sample, apply J-flag if acceptance criteria are not met. If MS falls outside LCS limits, evaluate data to determine the source of the difference and to determine if there is a matrix effect or analytical error.
MSD or Sample Duplicate	Analyze one MSD or sample duplicate per prep batch per matrix. RPD between duplicates must be ≤ 20%. For failures, consult project-specific DQOs and contact client for additional measures to be taken. If acceptance criteria are not met, apply J-flag. If MS falls outside LCS limits, evaluate data to determine the source of the difference and to determine if there is a matrix effect or analytical error.
Dilution Test	One per prep batch if MS or MSD fails. Only applicable for samples with concentrations >50x LOQ (prior to dilution). For samples with lower concentrations perform PDS. Five-fold dilution must agree within ± 10% of the original result. Apply J-flag if acceptance criteria not met and explain in the case narrative.
Post-Digestion Spike (PDS) Addition	Perform Recovery Test when dilution test fails or analyte concentration in all samples is <50 x LOQ. Recovery must be within 80-120 % of expected result. If test fails, then run samples by MSA or apply J-flag to all sample results (for same matrix) in which MSA was not run when recovery is outside of 80 - 120%.
Method of Standard Additions	When dilution or post digestion spike fails and if required by the project. Document use of MSA in case narrative.

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Electronic Copy Only -

Title: Mercury in Water by Cold Vapor Atomic Absorption (CVAA) [SW 7470A]

Approvals (Signature/Date):

Doug Gomer 8/10/15	Adam W Alban 11 Aug 15
Doug Gomer — Date	Adam Alban — Date
Technical Specialist	Health & Safety Manager / Coordinator
Margaret S. Sleevi 8/10/15	L.R.C. 8/10/15
Margaret S. Sleevi — Date	William S. Cicero — Date
Quality Assurance Manager	Laboratory Director

Facility Distribution No. _____ **Distributed To: _____**

1.0 Scope and Application

1.1 This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7470A.

1.2 Method 7470 is applicable to the preparation and analysis of mercury in ground water, aqueous samples, wastes, wipes, TCLP, EP and other leachates/extracts.

1.3 All matrices require sample preparation prior to analysis.

1.4 The final reporting limit is 0.0002 mg/L (0.2 μg/L), except for TCLP leachates that have a 0.002 mg/L (2 μg/L) reporting limit.

2.0 Summary of Method

This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration). All sample data are uploaded to the TestAmerica LIMS (TALS).

3.0 Definitions

3.1 Dissolved Metals: Those elements that pass through a 0.45-μm membrane. (Sample is acidified after filtration).

3.2 Total Metals: The concentration determined on an unfiltered sample following digestion.

3.3 Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and Policy DV-QA-003P, *Quality Assurance Program*, for definitions of general analytical and QA/QC terms.

4.0 Interferences

4.1 Chemical and physical interferences may be encountered when analyzing samples using this method.

4.2 Potassium permanganate, which is used to breakdown organic mercury compounds, also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.3 Copper also has been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.4 Chlorides can cause a positive interference. Seawaters, brines, and industrial effluents high in chlorides will require dilution. During the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

4.5 Interference from certain volatile organic materials that absorb at the wavelength used for the method may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.6 Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs, the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.7 The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3.2 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile or latex gloves must be worn while handling samples, standards, solvents,

and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.3.3 Potassium permanganate is a strong oxidizing agent. It is incompatible with and must be stored separately from hydroxylamine hydrochloride and stannous chloride, the reducing agents used in this procedure, and from acids.

5.4 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury (1,000 ppm in Reagent)	Oxidizer Corrosive Poison	0.1 mg/m^3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 mg/m^3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.

Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

6.1.1 Digestion Block, with adjustable heating, capable of maintaining a sample temperature of 90-95°C.

6.1.2 Mercury Auto-analyzers: The laboratory currently uses two CETAC QuickTrace™ Mercury Analyzer M-7500s with Autosamplers and Auto-Diluters.

6.2 Computer Software and Hardware

Please refer to the master list of documents, software and hardware located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

6.3 Supplies

6.3.1 Disposable 50 mL digestion tubes with caps. Accuracy at 30 mL verified to ±3% gravimetrically prior to use (by lot). See DV-QA-0008 for more information regarding volume verifications.

6.3.2 Disposable glass test tubes, 16 mm x 100 mm

6.3.3 Argon, 99.999% purity

6.3.4 Calibrated automatic pipettes or Class A glass volumetric pipettes (see SOP DV-QA-0008 for details on calibrating mechanical pipettes).

6.3.5 Class A volumetric flasks.

6.3.6 Thermometer, non-mercury column, accurate to ±1 °C at 95 °C (see SOP DV-QA-0001 for calibration details).

7.0 Reagents and Standards

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Suggested reagent and standard recipes are listed below. Alternate weights and volumes may be used as long as the final concentrations are maintained as

listed and the details are recorded in the Reagent module in TALS. All standard concentrations listed below refer to the on-instrument concentration except where otherwise noted.

7.1 **Reagent water:** Must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2 **Nitric acid (HNO_3):** concentrated, trace metal grade or better.

7.3 **Hydrochloric acid (HCl):** concentrated, trace metal grade or better.

7.4 **Sulfuric acid (H_2SO_4):** concentrated, trace metal grade or better.

7.5 **Reagent Blank:** This blank solution is used as the Calibration Blank (STD0), Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and as the starting solution for the Method Blanks (MBs). It is made as follows:

Add 0.5 L of concentrated HNO_3 to a 50-liter carboy partially filled with reagent water. Dilute to 50 L with reagent water. Mix carefully. Record the acid lot numbers and other required information in the Blank Reagent Logbook stored in the metals prep area.

7.6 **Stannous Chloride Solution, Hg grade, 10% (w/v) per manufacturer's (CETAC) instructions**

7.6.1 Place approximately 1000 g of deionized water in a tared 2-L HDPE jar on a top-loading balance.

7.6.2 Add 200 g of $SnCl_2$ to the flask.

7.6.3 Add deionized water until the total weight is 2000 g.

7.6.4 Place the jar in a fume hood and slowly add 200 mL of concentrated HCl to the flask and swirl to mix.

7.6.5 Close the jar and agitate until the reagent is dissolved.

7.7 **Sodium chloride-hydroxylamine hydrochloride solution (Hg grade):**

7.7.1 Place approximately 1000 g of deionized water in a tared 2-L HDPE jar on a top-loading balance.

7.7.2 Add 240 g of NaCl and 240 g of hydroxylamine hydrochloride (Hg grade) to the jar.

7.7.3 Add deionized water until the total weight is 2480 g.

7.7.4 Close the jar and agitate until the reagent is dissolved.

NOTE: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.8 Potassium permanganate ($KMnO_4$), 5% solution (w/v):

7.8.1 Place approximately 1000 g of deionized water in a tared 2-L HDPE jar on a top-loading balance.

7.8.2 Add 100 g of $KMnO_4$ (Hg grade) to the jar.

7.8.3 Add deionized water until the total weight is 2100 g.

7.8.4 Close the jar and agitate until the reagent is dissolved.

7.9 Potassium persulfate ($K_2S_2O_8$), 5% solution (w/v):

7.9.1 Place approximately 1000 g of deionized water in a tared 2-L HDPE jar on a top-loading balance.

7.9.2 Add 100 g of $K_2S_2O_8$ (Hg grade) to the jar.

7.9.3 Add deionized water until the total weight is 2100 g.

7.9.4 Close the jar and agitate until the reagent is dissolved.

7.10 Purchased Mercury Stock Solutions

7.10.1 Primary Mercury Calibration Standard Solution (Hg Ultra Prim), 1,000 mg/L

7.10.2 Second-source Mercury Standard (Hg ICV Stock), 100 mg/L. This standard is obtained from a different vendor than the Primary Mercury Calibration Standard.

7.11 Calibration Working Standard Solution (Hg Month Spike), 10 mg/L.

7.11.1 Add approximately 90 mL of 1% HNO_3 to a 100 mL Class A volumetric flask.

7.11.2 Pipet 1.00 mL of the 1000 mg/L primary mercury calibration standard solution (see Section 7.10.1) into the flask.

7.11.3 Dilute to the mark on the flask with Reagent Blank.

7.11.4 Stopper the flask and shake to mix.

7.11.5 Transfer the solution to a 125 mL Nalgene bottle.

7.11.6 Document the preparation of the solution in the Reagent Module in TALS.

7.11.7 Prepare this solution fresh monthly or more often if necessary.

7.12 Daily Calibration Working Solution (Hg Daily Spk), 100 µg/L

7.12.1 Add approximately 90 mL of 1% HNO_3 to a 100 mL Class A volumetric

flask.

7.12.2 Pipet 1.00 mL of the 10 mg/L Calibration Working Standard solution (see Section 7.11) into the flask.

7.12.3 Dilute to the mark on the flask with the Reagent Blank solution (final volume of 100.0 mL).

7.12.4 Stopper the flask and shake to mix.

7.12.5 Transfer the solution to a 125 mL Nalgene bottle.

7.12.6 Document the preparation of the solution in the Reagent Module in TALS.

7.13 Daily Initial Calibration (ICAL) Standards.

7.13.1 To each of seven 50 mL digestion tubes, add approximately 30 mL of the Reagent Blank solution.

7.13.2 For each calibration level, add the appropriate amount of Daily Calibration Working Solution to the tube as indicated in the following table. The final concentration for each calibration level is listed in the following table:

Daily ICAL Standards

Calibration Level	Volume of Daily Calibration Working Solution (100 µg/L) Added (mL)	Final Hg Concentration (µg/L)
1 (Hg STD1 0.1)	0.03	0.06
2 (Hg STD2 0.2)	0.06	0.12
3 (Hg STD3 0.5)	0.15	0.3
4 (Hg STD4 1.0)	0.3	0.6
5 (Hg STD5 2.0)	0.6	1.2
6 (Hg STD6 5.0)	1.5	3.0
7 (Hg STD7 10.0)	3.0	6.0

7.13.3 Close each tube and swirl to mix.

7.13.4 Prepare the calibration standards as samples.

7.13.5 Document the preparation of the solutions in the Reagent Module in TALS.

7.13.6 Prepare the calibration solutions each day prior to calibration.

7.13.7 The calibration blank is titled STD0 in TALS.

7.14 Continuing Calibration Verification Standard (Hg H20 CCV), 3.0 µg/L.

7.14.1 The CCV is prepared exactly as the 3.0 µg/L calibration standard, and from the same source. Refer to Section 7.13.

7.14.2 Prepare sufficient volume of the standard for analysis of a CCV after every 10 samples.

7.15 Second-Source Initial Calibration Verification Intermediate Standard (Hg Biwk ICV), 400 µg/L.

Add 0.4 mL of the 100 mg/L ICV stock standard (see Section 7.10.2) to a 100 mL volumetric flask partially filled with the Reagent Blank solution and dilute to the mark. Record this information in the Reagent Module in TALS.

7.16 Second-Source Initial Calibration Verification Daily Working Standard (Hg H20 ICV), 2.4 µg /L.

Add 0.3 mL of the 400 µg/L ICV intermediate standard (see Section 7.15) to a 50 mL digestion tube filled with 30 mL of Reagent Blank. Prepare as a sample. Record this information in the Reagent Module in TALS.

7.17 Laboratory Control Sample (LCS), 3 µg/L

The LCS is prepared by adding 1.5 mL of the 100 µg/L Daily Calibration Working Standard (Section 7.12) to 30 mL of Reagent Blank in a digestion tube. The LCS goes through the same digestion process as the samples.

7.18 Matrix Spike and Matrix Spike Duplicate (MS/MSD), 3 µg/L

7.18.1 The MS is prepared by adding 1.5 mL of the 100 µg/L Daily Calibration Working Solution (Section 7.12) to a digestion tube containing a second 30-mL aliquot of the selected sample.

7.18.2 The MSD is prepared in the same manner as the MS using a third aliquot of the selected sample.

7.18.3 The MS and MSD go through the same digestion process as the samples.

7.19 Reporting Limit (CRA) Check Standard (Hg H20 RL), 0.12 µg/L

The 0.12 µg/L calibration standard is analyzed as a sample to verify the reporting limit. Denoted as CRA in the run sequence.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Water	HDPE	50 mL	HNO_3, pH < 2	28 Days	40 CFR Part 136.3

[1] Inclusive of digestion and analysis.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the TALS Method Comments to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver Policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver Policy DV-QA-024P, *QA/QC Requirements for Federal Programs*. See Table 1 for a summary of these requirements. This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated. Any deviations or exceptions from QSM 5.0 requirements must have prior approval in the project requirements.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in TALS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Sample QC

9.2.1 Preparation Batch

A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank (MB), a laboratory control sample (LCS), and a matrix spike/matrix spike duplicate (MS/MSD) pair. As discussed in the

following sections, special program or project requirements can include additional requirements. Always refer to special project instructions for details before proceeding with the analysis.

9.2.2 Method Blank (MB)

The method blank consists of Reagent Blank containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. At least one method blank must be processed with each preparation batch.

Acceptance Criteria: The result for the method blank must be less than the project-specific data quality objectives. In the absence of project-specific data quality objectives, the blank must be less than ½ the reporting limit or less than 10% of the mercury concentration found in the associated samples, whichever is higher.

For DoD V5 the method blank is controlled to < ½ LOQ or 10% of the amount measured in any sample or 10% of the regulatory limit, whichever is greater.

Corrective Action: All samples associated with an unacceptable method blank must be re-prepared and reanalyzed. If mercury was not detected in the samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative.

9.2.3 Laboratory Control Sample (LCS)

The LCS is a blank to which a known concentration of the target analyte has been added. At least one aqueous LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure.

Acceptance Criteria: Maximum control limits for LCS recoveries for Method 7470A are 80-120%. In-house control limits based on three standard deviations of the mean of past results are used as long as they are at least as tight as the limits in the methods (see TestAmerica Denver Policy DV-QA-003P for further details on establishing control limits).

For DoD V5 the QSM Appendix C limits are required.

Corrective Action: If LCS recoveries are outside established control limits, the system is out of control and corrective action must occur. If recoveries are above the

upper control limit and mercury is not detected in samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative. In other circumstances, the entire batch must be re-prepared and reanalyzed.

9.2.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike (MS) is a second aliquot of a selected field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a third aliquot of the same sample (spiked exactly as the MS) prepared and analyzed along with the sample and matrix spike. One MS/MSD pair must be processed for each preparation batch. Some programs may require the use of sample duplicates in place of or in addition to MS/MSDs. In addition, some programs will allow spikes to be reported for project-related samples only. Spiking levels are provided in Attachment 1. When the MS/MSD concentration is above the linear range; the MS/MSD and parent sample **MUST** be re-analyzed at a dilution.

Acceptance Criteria: Control limits are statistically determined based on three standard deviations of the mean of the laboratory's historical data. The recoveries for the MS and MSD must fall within 75-125%. The relative percent difference between the MS and MSD cannot exceed 20%.

For DoD V5 the QSM appendix C limits are required

Corrective Action: MS and MSD data are sample/matrix specific and are not normally used to determine the validity of the entire batch. If analyte recoveries or the RPD between duplicates fall outside the acceptance range, the LCS recovery must be in control for the data to be reported. If there is no evidence of analytical problems and all other QC criteria are met, then qualified results may be reported and the situation must be described in the final report case narrative. If laboratory error is suspected, the batch must be re-prepared and reanalyzed. The following corrective actions are required for MS/MSD recovery failures to rule out lab error:

- Check calculation and instrument performance;
- Verify, if possible, that the MS and MSD were spiked correctly;

- Consider objective evidence of matrix interference (e.g., heterogeneous sample or interference demonstrated by prior analyses);
- Flag the data for any results outside of acceptance limits and note it on the final report.
- For any single RPD failure, check calculations; verify, if possible, that the MS and MSD were spiked correctly; check instrument performance; consider objective evidence of matrix interference or sample inhomogeneity; and flag the data.
- When the MS/MSD concentration is above the linear range; the MS/MSD and parent sample **MUST** be re-analyzed at a dilution.

NOTE: Some client programs require reanalysis to confirm matrix interferences. Check special project requirements for this corrective action.

If the native analyte concentration in the MS/MSD sample exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated).

For DoD V5 if the MS, MSD or RPD are outside of the control limits the parent sample is flagged "J". For all DoD projects a serial dilution and post digestion spike (PDS) are required if the MS or MSD fail.

9.2.5 Serial Dilution

Some programs require that a fivefold (1+4) dilution must be included in each analytical batch for each sample matrix.

Acceptance Criteria: The results must be within 10% of the expected value, assuming that the initial sample concentration is at least 25x the MDL concentration (or 50x the LOQ for DoD).

Corrective Action: If the control limit is not met, all associated sample results must be qualified and the failure addressed in the narrative.

9.2.6 Post-Digestion Spike

Some programs require the inclusion of a post-digestion spike in each analytical batch. The post-digestion spike is prepared by adding 0.3 mL of the 100 μg/L Daily Calibration Working Solution to 10 mL of sample digestate. Post-digestion spikes are performed as an additional check for matrix interference.

Acceptance Criteria: The percent recovery limits for the post-digestion spike are 80 to 120%.

Corrective Action: If the acceptance criteria are not met, all associated sample results must be qualified.

9.2.7 Method of Standard Addition (MSA)

The method of standard additions is an option for the analysis of samples shown to have significant matrix effects, e.g., unacceptably low MS/MSD recoveries or under certain conditions for TCLP analysis (see Attachment 3)

9.3 Instrument QC

9.3.1 Initial Calibration (ICAL)

9.3.1.1 Detailed information regarding calibration models and calculations can be found in Corporate Policy CA-Q-P-003, *Calibration Curves & Selection of Calibration Points*.

9.3.1.2 Calibration must be performed daily (every 24 hours) and each time the instrument is set up. All calibration standards and calibration QC samples will be recorded in prep batches and prepared as samples. The instrument calibration date and time must be included in the raw data.

9.3.1.3 Calibrate using seven standards and a blank. The concentration levels are listed in Attachment 1.

NOTE: It is generally not acceptable to reject calibration points for this method.

9.3.1.4 The calibration curve must have a correlation coefficient of $\geq$ 0.995 for an unweighted linear regression or the instrument shall be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient.

9.3.1.5 Record the microabsorbance for the 10 ppb standard in the instrument maintenance logbook.

9.3.2 Initial and Continuing Calibration Blank (ICB/CCB)

9.3.2.1 An initial calibration blank is tested immediately after the daily ICAL standards.

Acceptance Criteria: Absolute values for the calibration blanks must be less than ½ the standard RL. Client specific requirements take precedence. For example, DoD QSM 5 requires control of blanks to a concentration less than or equal to the LOD.

Corrective Action: If the blank acceptance limit is exceeded, the analysis should be terminated, the source of contamination identified, and the instrument recalibrated.

9.3.2.2 Continuing calibration blanks are run after every 10 samples and at the end of the run.

Acceptance Criteria: The absolute value of the blank result must be less than ½ the reporting limit. Some programs require that blanks be less than 2x the MDL or less than the LOD (refer to special project requirements).

Corrective Action: If the blank acceptance limit is exceeded, the analysis should be terminated, the source of contamination identified, and the instrument recalibrated.

9.3.3 Initial Calibration Verification (ICV), 2.4 µg/L

The accuracy of the calibration standards is verified by testing a second source standard (ICV).

Acceptance Criteria: The ICV result must be within 10% of the true value.

Corrective Action: If the ICV acceptance limit is exceeded, the analysis should be terminated, the accuracy of the calibration standards checked, and the instrument recalibrated.

9.3.4 Reporting Limit Check Standard (CRA), 0.12 µg/L

The accuracy of results at the reporting limit is verified by testing a standard in every analytical run that is prepared at the reporting limit concentration.

Acceptance Criteria: The results for this standard must be within 50% of the expected value

Corrective Action: If the RL check acceptance limit is exceeded, the analysis should be terminated, the instrument operation checked, and the instrument recalibrated.

9.3.5 Continuing Calibration Verification (CCV), 3.0 µg/L

Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples and at the end of the run. The CCV must be a mid-range standard at a concentration other than that of the ICV.

Acceptance Criteria: The CCV result must fall within 20% of the true value.

For DoD V5 the CCV result must be within 10%.

Correction Action: Sample results may be reported only when bracketed by valid CCV pairs. If a mid-run CCV fails, the CCV may be re-analyzed once without modification to the instrument's operating conditions. If the re-analyzed CCV is found to be in control, the CCV analysis must be repeated with successful results or the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV failure was not directly instrument related, the associated samples must be re-prepared and reanalyzed.

9.3.6 Linear Range

TAL Denver does not report values greater than the highest standard (10 µg/L) used for calibration. Any sample concentration greater than 90% of the highest standard will be diluted. The calibration curve is validated by running 3 check standards, 0.12 µg/L (CRA) , 3 ug/L (CCV), and 2.4 µg/L (ICV), during the analytical run. No further linear range study is warranted.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 Sample Preparation

10.3.1 All calibration and calibration verification standards (ICV, ICB, CCV, CCB), as well as the field samples, are processed through the digestion procedure.

10.3.2 Transfer 30.0 mL of well mixed sample to a clean sample digestion tube. The calibration standards may be prepared in duplicate to ensure sufficient volume to complete the analytical sequence. Additional aliquots of CCV and CCB solution may have to be prepared for larger sample runs to ensure that CCV and CCB samples bracket every 10 samples in the analytical sequence.

10.3.3 Prepare an MB, LCS, MS, and MSD for each batch.

10.3.3.1 The MB consists of 30.0 mL of Reagent Blank.

10.3.3.2 The LCS is prepared by adding 1.5 mL of the 100 μg/L Daily Calibration Working Solution to 30 mL of Reagent Blank in a digestion tube.

10.3.3.3 The MS is prepared by adding 1.5 mL of the 100 μg/L Daily Calibration Working Solution to a digestion tube containing a second 30-mL aliquot of the selected sample.

10.3.3.4 The MSD is prepared in the same manner as the MS using a third aliquot of the selected sample.

10.3.4 Add 1.5 mL of concentrated H_2SO_4 and 0.75 mL of concentrated HNO_3 to the samples in the digestion tubes, mixing after each addition.

10.3.5 Add 4.5 mL of 5% potassium permanganate solution to each sample. For samples high in organic materials or chlorides, dilute the sample until the purple color persists for at least 15 minutes.

10.3.6 Add 2.4 mL of potassium persulfate solution, cap the vial, and heat for two hours at 90 - 95°C. Record the start and stop times and the initial and final temperatures on the bench sheet. Verify that a purple color persists or a black precipitate is present after the two hours of heating. If this is not true, repeat the digestion using a smaller aliquot of sample.

10.3.7 Allow the samples and standards to cool at room temperature.

10.4 Calibration

10.4.1 All calibration standards are digested together with samples, as described in Section 10.3, prior to analysis.

10.4.2 Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration by starting the gas, lamp, heater, and sample pump (approximately 30 minutes of warm-up is required).

10.4.3 The mercury analyzer method uses external standard calibration. Use of an internal standard for this method is not appropriate.

10.5 Sample Analysis

NOTE: Because of differences between various makes and models of CVAA instrumentation, detailed push-button operating instructions are not provided here. Refer to the specific instrument-operating manual for detailed autosampler setup and operation protocols.

NOTE: The injection of samples and the addition of stannous chloride are done automatically by the instrument. Refer to the specific instrument manual for details.

10.5.1 When ready to begin analysis, add 1.8 mL of sodium chloride-hydroxylamine hydrochloride solution to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains).

10.5.2 Add additional Reagent Blank to the samples, QC samples and calibration standards to bring the final volume of each sample to 50 mL.

10.5.3 Aliquot each sample and calibration standard into a disposable test tube for analysis.

10.5.4 All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples that are within 10% of the highest calibration standard.

NOTE: The instrument can auto-dilute samples. Any sample that requires greater than a 10x dilution MUST be diluted manually.

10.5.5 If the sample results are negative and the absolute value is greater than the reporting limit, the sample must be diluted and reanalyzed.

10.5.6 The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

10.5.7 Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB.

10.5.8 The following analytical sequence must be used for Method 7470A. Refer to Quality Control Section 9.0 and Attachment 2 for quality control criteria to apply to Method 7470A.

Instrument Calibration

ICV
ICB
CRA
Maximum of 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete the run.
CCV
CCB

NOTE: Samples included in the count between CCVs include the method blank, LCS, MS, MSD, and field samples.

10.5.9 For TCLP samples, full four-point MSA will be required if all of the following conditions are met:

- Recovery of the analyte in the matrix spike is <50%;
- The concentration of the analyte does not exceed the regulatory level; and
- The concentration of the analyte is within 20% of the regulatory level.
- The reporting and matrix spike levels for TCLP analyses are detailed in Attachment 1. Attachment 3 provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

10.5.10 To facilitate the early identification of QC failures and samples requiring rerun, it is strongly recommended that sample data be reviewed periodically throughout the run.

10.5.11 See Attachment 5 for guidelines for minimizing contamination of samples and standards. See Attachments 4 and 6 for guidance on troubleshooting and preventive maintenance.

11.0 Calculations / Data Reduction

11.1 Detailed calibration equations can be found in the corporate Policy CA-Q-P-003, *Calibration Curves & Selection of Calibration Points* and under the public folder, *Arizona Calibration Training*.

11.2 Accuracy

$$\textbf{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\textbf{MS \% Recovery} = \frac{\text{(spiked sample) - (unspiked sample)}}{\text{spike concentration}} \times 100$$

11.3 Precision (RPD)

Matrix Duplicate (MD) = $\frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$

11.4 Concentration = Hg concentration (μg/L) = $\frac{C \times V_1 \times D}{V_2}$

Where:

C = Concentration (μg/L) from instrument readout
D = Instrument dilution factor
V_1 = Final volume in liters after sample preparation
V_2 = Initial volume of sample digested in liters

11.5 Appropriate factors must be applied to sample values if dilutions are performed.

11.6 Sample results should be reported with up to three significant figures in accordance with the TestAmerica significant figure policy (DV-QA-004P).

11.7 Documentation and Record Management

11.7.1 All sample data is uploaded to TALS. All sample preparation and analytical batch information, including the batch number(s), list of samples, preparation analyst and date, instrument analyst and date, identification of reagents and standards used, and identification of all measuring equipment used (e.g., balances, thermometers, pipettes) is recorded in TALS.

11.7.2 Raw data is scanned or saved directly as a PDF and is attached to the analytical batch in TALS.

11.7.3 The initial data review is performed by the analyst and a second-level review is performed by the area supervisor or designee. Both reviews are documented on a Data Review Checklist. See SOP DV-QA-0020 for more detail on the review process.

11.7.4 If dilutions are required due to insufficient sample, interferences, or other problems, the reporting limit and MDL are multiplied by the dilution factor and the data may require flagging.

NOTE: Unless special instructions indicate otherwise, sample results less than the reporting limit are reported as ND.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. An initial method detection limit study is performed in accordance with Policy DV-QA-005P. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency. For Texas TRRP, DoD, AFCEE, and DOE projects, an MDL verification is performed quarterly. DoD V5 requires the MDLV to be spiked at 2 - 4x the MDL.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

12.2.1 Four LCSs are analyzed using the same procedures used to analyze samples, including sample preparation.

12.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.2.4 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

12.3 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, order chemicals based on quantity needed, and prepare reagents based on anticipated usage and reagent stability).

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in Section 13, *Waste Management and*

Pollution Prevention, of the Corporate Environmental Health and Safety Manual, and DV-HS-001P, *Waste Management Program*.

14.2 The following waste streams are produced when this method is carried out:

14.2.1 Aqueous Acidic (Metals) - Corrosive - Waste Stream J

14.2.2 Expired reagents and standards – Contact the Waste Coordinator.

NOTE: Radioactive waste, mixed waste, and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Waste Coordinator for proper management of these materials.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury).

15.2 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 4.2, 10/25/2010.

15.3 U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0.

15.4 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 5.0, 7/2013

16.0 Method Modifications:

Item	Method	Modification
1	EPA 7470A	Chapter 1 of SW846 specifies the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.
2	EPA 7470A	This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, “Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology.”
3	EPA 7470A	Methods 7470A and 7471A state that working mercury standards “should be prepared fresh daily.” The laboratory frequently prepares up to three batches of mercury samples, including digested calibration standards, each day. The third batch is typically prepared and digested late in the day, and then is analyzed the morning of the next day. The laboratory has developed the following information demonstrating that analysis within 24 hours, but on the second calendar day from preparation produces reliable results and is acceptable to the EPA: • Successful proficiency testing PT results for samples that were

Item	Method	Modification
		prepared and analyzed within 24 hours, but on successive days (e.g., ERA WP-66); • Successful analysis of true NIST mercury standards within every analytical batch; and • A written comment from the EPA MICE Hotline stating that, with the supporting lab data, their opinion was that the laboratory's practice is "within the letter of the method as written."
4	EPA 7470A	Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above ½ the reporting limit.

17.0 Attachments

Attachment 1: Mercury Reporting Limits, Calibration Levels, QC Standard and Spiking Levels
Attachment 2: Summary of Quality Control Requirements
Attachment 3: MSA Guidance
Attachment 4: Troubleshooting Guide
Attachment 5: Contamination Control Guidelines
Attachment 6: Preventative Maintenance
Table 1: DOD QSM 5.0 QC Criteria for CVAA/Mercury

18.0 Revision History

- Revision 4 dated July 31, 2015
  - Annual review
  - Added 0.1 standard to Section 7.13.2
  - Updated MB control limit to ½ LOQ for DoD
  - Removed 20% DoD control for CRI from Section 9.3.4
  - Added DoD V5 spiking requirement for MDLV to Section 12.1
  - Updated Section 12.2 DOC to use LCS's
  - Added 0.1 standard to Attachment 1
  - Added TALS reference to Section 2.0
  - Added instructions to Section 7.5 regarding making reagent blank
  - Added TALS reagent IDs
  - Change LIMS to TALS throughout
  - Added Linear range section 9.3.6
  - Corrected Section 11.7 to match current practice
  - Removed figures one and two
  - Revised reagent Sections 7.6-7.9 to match current practice
  - Changed Sections 7.13-7.19 to reflect new procedure
  - Updated procedures in Section 10 to better meet traceability requirements

- Revision 3 dated July 31, 2014
  - Annual review
  - Added DoD V5 requirements to Sections 9.2.2, 9.2,3, 9.2.4, 9.3.2.1 and 9.3.5.
  - Added table 1 - DOD QSM 5.0 QC Criteria for CVAA/Mercury

- Revision 2 dated July 15, 2013
  - Annual review
  - Changes section 7.6 and 12 to reflect current practices
  - Remove reference to Standards Log to Reagent Module in the LIMS in section 7.11.6, 7.12.6, 7.13.4, 7.15 & 7.16.
  - Changed "RL" to "CRA" in sections 7.19, 9.3.4, 10.5.8
  - Added CRA (RL Standard) to Attachment 2
  - Removed Attachment 3 and re-number subsequent attachments
  - Clarified first bullet point under 10.5.9
  - Corrected references date for section 15.2
  - Added Texas TRRP to section 12.1

- Revision 1.2 dated July 13, 2012
  - Updated Sections 7.6 and 7.7 to state Hg reagents are used
  - Updated Sections 9.3.2.1 and 9.3.2.2 to control calibration blanks to ½ RL
  - Added Section 9.3.1.5 to record the counts for the 10 ppb high standard
  - Updated Sections 10.5.2 to bring samples to a final volume of 45 mL with 1% HNO_3
  - Formatting and grammatical changes

- Revision 1.1 dated February 03, 2012
  - Annual technical review
  - Added introductory statement to section 7.0 regarding reagent purity
  - Updated Section 9.1.2 and Attachment 2 for Method Blank acceptance criteria
  - Added dilution note to Section 10.3.4
  - Updated section 12.0 to reflect current laboratory practice
  - Removed Leeman instrument and replaced Nitrogen with Argon for Attachment 7

- Revision 1.0 dated 23 August 2011
  - Updated Section 7.15 ICV Intermediate Standard to 400ug/l
  - Updated Section 7.16 ICV Working Standard level to 4ug/l
  - Updated Section 9.2.3 ICV true value to 4ug/l
  - Updated Section 10.3.8 ICV and ICB run order

- Revision 0.5 dated 25 April 2011
  - Removed all references to the FIMS Analyzer
  - Sections 6.1 and 6.3 were updated to reflect the use of digestion blocks from water baths.
  - The reagent amounts were updated to reflect using a 30ml aliquot from 10ml.
  - Section 10.3.2 was updated to show a final volume of 40ml.

- Revision 0.4 dated 07 February 2011
  - Revised section 10 to reflect use of calibrated digestion tubes and calibration standard volumes
  - Revised supplies list
  - Revised section 6.2 to include reference to Master List of Documents, Software and Hardware
  - Added section 11.1 to reference corporate SOP CA-Q-S-005 "Calibration Curves"

- Revision 0.3 dated 01 September 2010
  - Section 7.0: Removed note about standards log with the change in LIMS systems

- Section 12.2 added section about MDLV verifications
- Updated Section 11.6 for new LIMS
- Removed Attachments 3a and 3b
- Annual Technical Review

- Revision 0.2 dated 07 August 2009
  - Sections 7.17 and 7.18 were updated to use 1% HNO3 from reagent blank.
  - Sections 10.1.3.1 and 10.1.3.2 were updated to use 1% HNO3 from reagent blank.
  - Changed SOP name DV-QA-003P from QC Policy to Quality Assurance Program.

- Revision 0.1, dated 16 February 2008
  - Section 9.1.2: Changed control limit to 10% to match soil SOP
  - Section 9.2.2: Changed the stated control limits for special projects from ½ the RL to 2x the MDL
  - Deleted section 12.2 for IDL requirements
  - Section 12.3: Noted that LCSs will be used for verification

Attachment 1

Mercury Reporting Limits, Calibration Levels, QC Standard and Spiking Levels (µg/L)

	Value at Instrument	Final Value
Standard Aqueous RL	0.12	0.2
Std 0	0	0
Std 1	0.06	0.1
Std 2	0.12	0.2
Std 3	0.3	0.5
Std 4	0.6	1.0
Std 5	1.5	2.0
Std 6	3.0	5.0
Std 7	6.0	10.0
ICV	2.4	4.0
CCV	3.0	5.0
LCS	3.0	5.0
Aqueous MS	3.0	5.0

Attachment 2

Summary of Quality Control Requirements

QC Parameter	Frequency *	Acceptance Criteria	Corrective Action
ICV	Beginning of every analytical run.	90 - 110% recovery	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.3.3).
RL Check Standard (CRA)	Following the ICV	50-150% recovery	Terminate analysis; correct the problem; recalibrate or re-prepare and reanalyze batch.
ICB	Beginning of every analytical run, immediately following the ICAL.	Absolute value must be < ½ RL, 2x the MDL for DoD	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.3.2).
CCV	Every 10 samples and at the end of the run.	80 - 120% recovery	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.3.5).
CCB	Immediately following each CCV.	Absolute value must be < ½ RL, 2x the MDL for DoD	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.3.2).
Method Blank	One per sample preparation batch of up to 20 samples.	Project specific or ½ RL Sample results greater than 10x the blank concentration are acceptable.	Re-digest and reanalyze samples. Note exceptions under criteria section. See Section 9.2.2 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	In-house 3 standard deviation control limits, not to exceed 80-120% recovery.	Terminate analysis; Correct the problem; Re-digest and reanalyze all samples associated with the LCS (see Section 9.2.3).
Matrix Spike	One per 10 samples preparation batch of up to 20 samples.	In-house 3 standard deviation control limits, not to exceed 75-125% recovery	In the absence of client-specific requirements, flag the data (see Section 9.2.4).
Matrix Spike Duplicate	See Matrix Spike	In-house 3 standard deviation control limits, not to exceed 20% RPD	See Corrective Action for Matrix Spike.

Attachment 3

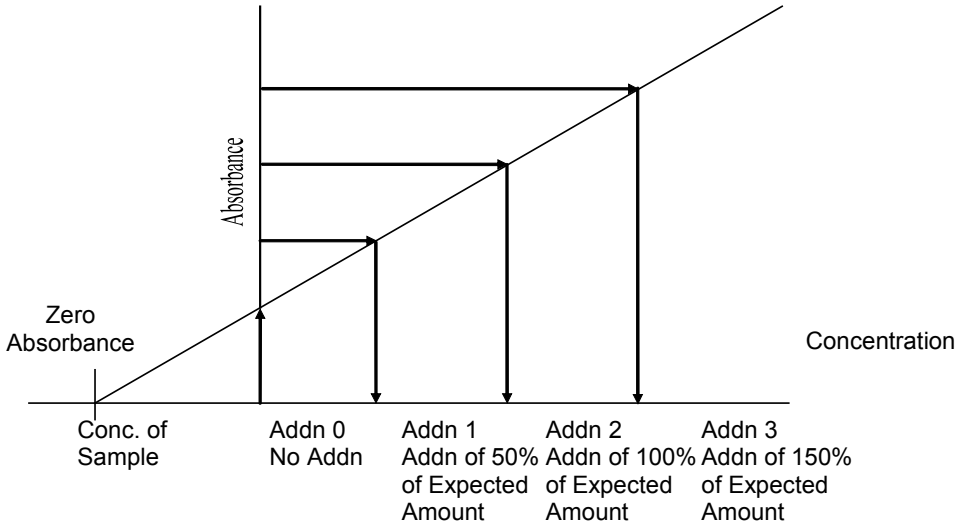
MSA Guidance

Method of Standard Addition (MSA)

Four equal volume aliquots of sample are measured and known amounts of standards are added to three of the aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration, and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of an analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. The absorbance (or response) is plotted on the vertical axis versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. The correlation coefficient (r) and the x-intercept (where y=0) of the curve are calculated. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.

- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

Attachment 4

Troubleshooting Guide

Problem	Possible Cause
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak
Erratic Readings	Source lamp not aligned properly Lamp not pre-warmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell
Background Correction Light Blinking	Background screen or attenuator faulty

Attachment 5

Contamination Control Guidelines

The following procedures are strongly recommended to prevent contamination:

- All work areas used to prepare standards and spikes should be cleaned before and after each use.
- All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.
- Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.
- Powdered gloves should not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes.
- Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.
- Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

- Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.
- Improper cleaning of glassware can cause contamination.
- If an unusually high sample is analyzed, segregate the glassware and soak with sulfuric acid prior to routine cleaning.

Attachment 6

Preventative Maintenance

A maintenance logbook is used to record when maintenance is performed on instruments. When an instrument problem occurs, record the date, time, and instrument number; describe the problem; and explain the corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational:

Cold Vapor Atomic Absorption (CETAC Analyzers)

Daily	Monthly	Annually
Change rinse solution.	Check Hg lamp intensity.	Change Hg lamp.
Optimize light path.		Check liquid/gas separator.
Check argon flow.		
Check tubing. Replace as needed.		
Check drain.		
Check condition of dryer		

Table 1
DOD QSM 5.0 QC Criteria for CVAA/Mercury

QSM 5.0 Table 7. Inorganic Analysis by CVAA/Mercury	
Requirement	**DoD QSM 5.0 and DOE QSAS 3.0**
Initial Calibration (ICAL)	Measure a minimum of 5 standards and a calibration blank daily and $r^2 \geq 0.99$ No samples shall be analyzed until ICAL has passed.
Initial Calibration Verification (ICV)	Run second-source standard once after each ICAL and prior to sample analysis. Must be within ± 10% of expected value. Correct any problems, verify standard, and rerun ICV. If that fails, correct problem and rerun ICAL. Verification must pass before running any samples.
Continuing Calibration Verification (CCV)	Run CCV after every 10 samples, and at the end of the analysis sequence: Reported analyte within ± 10% of expected value If the CCV is above the project acceptance limits and there are no detections in the samples, TestAmerica will report the non-detect results with a case narrative comment in addition to applying any data qualifier flags required by the project (3HR). Correct any problems, then rerun CCV. If that fails, then repeat ICAL. Reanalyze all samples since last successful CCV. Results cannot be reported without a valid CCV. Or Immediately (within one hour) analyze two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, take corrective action(s) and re-calibrate; then reanalyze all affected samples since the last acceptable CCV. If reanalysis cannot be performed, data must be qualified and explained in the case narrative. Apply Q-flag to all results for the specific analytes(s) in all samples since the last acceptable CCV. Flagging is only appropriate in cases where the samples cannot be reanalyzed.
Initial and Continuing Calibration Blank	Analyze calibration blank before analyzing samples, after every 10 field samples, and at the end of the analysis sequence. No analytes detected > LOD. Correct any problems, then re-prep and reanalyze the calibration blank and analyze all samples since the last acceptable calibration blank. Failures due to carryover may not require an ICAL.
Method Blank	One per prep batch. No analytes detected > ½ LOQ (RL) or >1/10 the amount measured in any sample or 1/10 the regulatory limit, whichever is greater If criteria not met, correct problem. If required, reprep and reanalyze MB and all samples processed with the contaminated blank. If reanalysis is not possible, apply B-flag to all results for the specific analyte(s) in all samples processed with the contaminated blank. Must be explained in the case narrative. Flagging is only appropriate when samples cannot be reanalyzed.

Table 1
DOD QSM 5.0 QC Criteria for CVAA/Mercury
(Continued)

QSM 5.0 Table 7. Inorganic Analysis by CVAA/Mercury	
DoD QSM 5.0 and DOE QSAS 3.0	
LCS	One per prep batch. Recovery must meet DoD QSM limits. If the LCS recovery is above the project acceptance limits and there are no detections in the samples, TestAmerica will report the non-detect results with a case narrative comment in addition to applying any data qualifier flags required by the project (3HR). Correct any problems, then re-prep and reanalyze LCS and associated samples for failed analytes in all samples in the associated batch. If corrective action fails, apply Q-flag to specific analyte(s) in all samples in associated batch.
Matrix Spike (MS)	One MS per prep batch. Use DoD acceptance criteria for LCS. If MS fails, consult project-specific DQOs and contact client to see if additional measures need to be taken. For specific analyte(s) in parent sample, apply J-flag if acceptance criteria are not met. If MS falls outside LCS limits, evaluate data to determine the source of the difference and to determine if there is a matrix effect or analytical error.
MSD or Sample Duplicate	Analyze one MSD or sample duplicate per prep batch per matrix. RPD between duplicates must be ≤ 20%. For failures, consult project-specific DQOs and contact client for additional measures to be taken. If acceptance criteria are not met, apply J-flag. If MS falls outside LCS limits, evaluate data to determine the source of the difference and to determine if there is a matrix effect or analytical error.

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Electronic Copy Only -

Title: Mercury in Solids by Cold Vapor Atomic Absorption

[Methods 7471A and 7471B]

Approvals (Signature/Date):

Doug Gomer — 2/26/15
Doug Gomer — Date
Technical Specialist

Alan Frey — 2/27/15
~~Adam Alban~~ Alan Frey for AA — Date
Health & Safety Manager / Coordinator

Margaret S. Sleevi — 2/27/15
Margaret S. Sleevi — Date
Quality Assurance Manager

W. S. C. — 2/27/15
William S. Cicero — Date
Laboratory Director

Facility Distribution No. _____ **Distributed To: _____**

1.0 Scope and Application

1.1 This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7471A.

1.2 Method 7471A and 7471B are applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits, and sludge-type materials. All matrices require sample preparation prior to analysis. This is not an appropriate procedure for the digestion of tissues or other organic matrices, which require the use of EPA 245.6 instead.

1.3 If sample preparation utilizing the Incremental Sampling Method is required, see SOP DV-OP-0013 for the procedure required prior to acid digestion for metals incorporating this procedure.

1.4 The routine reporting limit for mercury in solid matrices is 17 µg/kg.

2.0 Summary of Method

A representative portion of the sample is digested in aqua regia in the first digestion cycle and potassium permanganate in the second cycle. Mercury is reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorption of light at 253.7 nm is calibrated as a function of mercury concentration.

3.0 Definitions

3.1 Total Mercury: Inorganic forms of mercury are effectively dissolved by the acids used in the digestion. The potassium permanganate reagent breaks down organo-mercury compounds to inorganic forms that are detected by this procedure.

3.2 Aqua Regia: A 3:1 mixture of hydrochloric and nitric acids. This mixture is effective at dissolving metals in the solid form.

3.3 General Analytical Terms: Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and policy DV-QA-003P, *Quality Control Program*, for definitions of general analytical and QA/QC terms.

4.0 Interferences

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1 Potassium permanganate “suitable for mercury determination” is specified because of the potential for mercury contamination in the reagent. In addition, potassium permanganate crystals will absorb mercury vapors from the air. Reagent bottles must be kept tightly closed to avoid contamination.

4.2 Potassium permanganate, in addition to breaking down organic compounds, also

eliminates possible interferences from sulfide. Concentrations as high as 20 ppm of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.3 Copper has also been reported to interfere; however, copper concentrations as high as 10 ppm had no effect on the recovery of mercury from spiked samples.

4.4 Chlorides can cause a positive interference. Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

NOTE: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.5 Interference from certain volatile organic materials that absorb at the wavelength used for the method may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.6 Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs, the recovery of mercury will be low. The problem can be lessened by reducing the volume of original sample used.

4.7 The most common interference is laboratory contamination which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe,

nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile or latex gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately. A disposable face shield should be used when making up aqua regia.

5.3.2 Potassium permanganate is a strong oxidizing agent. It is incompatible and must be stored separately from hydroxylamine hydrochloride and stannous chloride, the reducing agents used in this procedure, and from acids.

5.4 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury Nitrate Solutions	Corrosive Poison	0.1 mg/m^3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydroxylamine Hydrochloride	Corrosive Poison	No OSHA PEL listed for this compound	Direct contact with skin or eyes causes irritation. May cause skin sensitization, an allergic reaction. Inhalation or ingestion may cause methemoglobinemia and resulting cyanosis (bluish discoloration of skin due to deficient oxygenation of the blood), and labored breathing.
Potassium Permanganate	Oxidizer	5 mg/m^3 for Mn compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

6.1.1 Digestion Block, with adjustable heating, capable of maintaining a sample temperature of 90-95°C.

6.1.2 Mercury Autoanalyzers:

CETAC Mercury Analyzer with Autosampler and Auto-Diluter

6.2 Computer Software and Hardware

Please refer to the master list of documents, software and hardware located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

6.3 Supplies

6.3.1 Disposable digestion tubes with caps, volume accuracy verified to +-3% gravimetrically prior to use.

6.3.2 Disposable glass autosampler tubes, 16 mm x 100 mm

6.3.3 Argon, 99.999% purity

6.3.4 Calibrated automatic pipettes or Class A glass volumetric pipettes (see SOP DV-QA-0008 for details on calibrating mechanical pipettes).

6.3.5 Class A volumetric flasks.

6.3.6 Thermometer, non-mercury column, accurate to ±1°C at 95 °C (see SOP DV-QA-0001 for calibration details).

6.3.7 Glass beads, <1 mm diameter, acid washed.

7.0 Reagents and Standards

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Primary and secondary standards used for data production are recorded in the Reagent Module of the TestAmerica LIMS (TALS).

7.1 **Reagent water:** Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2 **Nitric acid (HNO_3):** concentrated, trace metal grade or better.

7.3 **Hydrochloric acid (HCl):** concentrated, trace metal grade or better.

7.4 **Aqua Regia:** Add 600ml concentrated HCL and 200ml concentrated HNO3 to a 1L container. Aqua Regia will be prepared immediately before use.

7.5 **Calibration Blank, Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and Method Blank (MB), 1% HNO_3:**

7.5.1 Add 0.5 L of concentrated HNO_3 to a 50-L carboy partially filled with reagent water.

7.5.2 Dilute to 50 L with reagent water.

7.5.3 Record the acid lot number and other required information in the Blank Reagent Logbook stored in the metals prep area.

7.6 **Stannous chloride solution ($SnCl_2$), Hg grade, 10% (w/v) per manufacturer's instructions:**

7.6.1 Place approximately 100 mL of reagent water into a 2-L volumetric flask.

7.6.2 Slowly add 200 mL of concentrated HCl to the flask and swirl to mix.

7.6.3 Add 200 grams of $SnCl_2$ to the flask.

7.6.4 Mix the contents of the flask until the reagent is completely dissolved.

7.6.5 Bring solution to a final volume of 2 L with reagent water.

7.7 **Sodium chloride-hydroxylamine hydrochloride solution (Hg grade):**

Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride (Hg grade) to every 100 mL of reagent water.

NOTE: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.8 Potassium permanganate, 5% solution (w/v):

Dissolve 5 g of potassium permanganate (reagent grade, "suitable for mercury determination") for every 100 mL of reagent water.

7.9 Purchased Mercury Stock Solutions

7.9.1 Second source initial calibration verification (ICV) stock solution 100 mg/L (Hg ICV Stock).

7.9.2 Primary Mercury Calibration Standard Solution, 1,000 mg/L (Hg Ultra Prim).

7.10 Monthly Calibration Working Standard Solution, 10 mg/L (Hg Mnth Spike)

7.10.1 Add approximately 90 mL of 1% HNO_3 to a 100 mL Class A volumetric flask.

7.10.2 Pipet 1.00 mL of the 1,000 mg/L primary mercury calibration standard solution into the flask.

7.10.3 Dilute to the mark on the flask with 1% HNO_3.

7.10.4 Stopper the flask and shake to mix.

7.10.5 Transfer the solution to a 125-mL Nalgene bottle.

7.10.6 Document the preparation of the solution in the Reagent Module in TALS.

7.10.7 Prepare this solution fresh monthly or more often if necessary.

7.11 Daily Calibration Working Spike, 100 µg/L (Hg Daily Spk)

7.11.1 Add approximately 90 mL of 1% HNO_3 to a 100-mL volumetric flask.

7.11.2 Add 1.00 mL of the 10 mg/L Calibration Working Standard (see section 7.10).

7.11.3 Bring the solution to a final volume of 100.0 mL.

7.11.4 Stopper and mix thoroughly.

7.11.5 Document the preparation in the reagent module of the LIMS.

7.11.6 Prepare this solution each day prior to calibration.

7.12 Initial Calibration (ICAL) Standards

The initial calibration standards are prepared directly in the digestion tubes as follow:

ICAL	Daily Calibration Working Spike (mL)	1% HNO_3 (mL)	Final Conc. (µg/L)
Blank	0.0	5.0	0.0
Std 1	0.1	4.9	0.20
Std 2	0.25	4.75	0.50
Std 3	0.5	4.5	1.0
Std 4	1.0	4.0	2.0
Std 5	2.5	2.5	5.0
Std 6	5.0	0.0	10.

7.13 Second-Source Initial Calibration Verification Intermediate Standard, 400 µg/L (Hg Biwk ICV)

Add 400 uL of the 100 mg/L ICV Standard to a 100-mL volumetric flask partially filled with 1% HNO_3 and dilute to the mark. Record this information in the Reagent Module in TALS.

7.14 Second-Source Initial Calibration Verification (ICV) Daily Working Standard, 4.00 µg/L (Hg Soil ICV)

Add 0.5 mL of the 400 µg/L ICV Intermediate Standard (see section 7.13) to a soil digestion tube and add 4.5 mL of 1% HNO_3. Record this information in the Reagent Module in TALS.

7.15 Continuing Calibration Verification (CCV) Standards, 5 µg/L (Hg Soil CCV)

7.15.1 The CCVs are prepared exactly as the 5.0 µg/L ICAL standard shown above (see section 7.12).

7.15.2 Prepare sufficient volume of the standard for analysis of a CCV after every 10 samples.

7.16 Laboratory Control Sample (LCS), 417 µg/kg

7.16.1 The LCS is prepared in an empty digestion tube or 0.6 g of glass beads (<1mm) are used if required.

7.16.2 Add 2.5 mL of the 100 µg/L Daily Calibration Working Spike (see Section 7.11) to a digestion tube. See Section 9.4 for additional detail.

7.16.3 This is equivalent to a 5.0 µg/L ICAL standard, which is the concentration that appears on the raw data printout from the instruments.

7.17 Matrix Spike and Matrix Spike Duplicate (MS/MSD), 417 µg/kg

MS/MSD pairs are spiked in the same manner as the LCS (see section 7.16) and prepared in the same manner as the samples, using 0.6 g of sample.

7.18 Reporting Limit (CRA) Check Standard, 0.2 µg/L (Hg Soil RL)

7.18.1 Add 0.1 mL of 100 µg/L Daily Calibration Working Spike (see section 7.11) and 4.9 mL of reagent water to a digestion tube.

7.18.2 This is equivalent to a 0.2 µg/L ICAL standard, which is the concentration that appears on the raw data printout from the instruments.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time	Reference
Soil	Glass	10 grams	Cool, $\leq 6^{o}C$	28 Days	N/A

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the TALS Method Comments to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver Policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver Policy DV-QA-024P, *QA/QC Requirements for Federal Programs*. This procedure meets all criteria for DOD QSM 5 unless otherwise stated.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in TALS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Preparation Batch

A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, an LCS, and a matrix spike/matrix spike duplicate pair (MS/MSD). As discussed in the following sections, special program or project requirements can include additional requirements. Always refer to special project instructions for details before proceeding with the analysis.

9.3 Method Blank (MB)

The MB consists of an empty vessel or <1-mm glass beads (for DoD and AFCEE projects) containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. At least one method blank (MB) must be processed with each preparation batch.

Acceptance Criteria: The result for the method blank must be less than the project-specific data quality objectives. In the absence of project-specific data quality objectives, the blank must be less than ½ RL or less than 10% of the mercury concentration found in the associated samples, whichever is higher.

Corrective Action: All samples associated with an unacceptable method blank must be re-prepared and reanalyzed. If mercury was not detected in the samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative.

NOTE: DOD QSM 5 does not allow this exception. Results may not be reported without a valid method blank unless sample cannot be re-prepared or re-analyzed.

9.4 Laboratory Control Sample (LCS), 417 µg/kg

The preparation of the LCS is described in Section 7.16. At least one LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure.

Acceptance Criteria: Maximum control limits for LCS recoveries are 80-120%. In-house control limits based on three standard deviations of the mean of historical results are used as long as they are at least as tight as 80-120% (see Policy DV-QA-003P for further details on establishing control limits).

NOTE: DOD QSM 5 Solid matrix LCS Limits are 80-124%**.**

Corrective Action: If LCS recoveries are outside established control limits, the system is out of control and corrective action must occur. If recoveries are above control limits and mercury is not detected in samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative. In other circumstances, the entire batch must be re-prepared and reanalyzed.

NOTE: Reporting sample results with failing LCS recoveries is not acceptable for DOD QSM 5 unless samples cannot be re-prepared or reanalyzed.

9.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD), 417µg/kg

One MS/MSD pair must be processed for each preparation batch. Some programs may require the use of sample duplicates in place of or in addition to MS/MSDs. In addition, some programs will allow spikes to be reported only for project-related samples. Samples identified as field blanks cannot be used for MS/MSD analysis.

Acceptance Criteria: Control limits are statistically determined based on three standard deviations of the mean of the laboratory's historical data. The MS/MSD recovery must fall within 75-125%; the relative percent difference (RPD) between the MS and MSD cannot exceed 20%.

NOTE: DOD QSM 5 Solid matrix MS/MSD Limits are 80-124%**.**

Corrective Action: If analyte recovery or RPD fails acceptance criteria, the LCS recovery must be in control for the data to be reported. If there is no evidence of analytical problems and all other QC criteria are met, then qualified results may be reported and the situation must be described in the final report case narrative. In other circumstances, the

batch must be re-prepared and reanalyzed.

If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC, then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

NOTE: DOD QSM 5 results outside control limits need to be evaluated to assess matrix effect or analytical error.

9.6 Method of Standard Addition (MSA)

The method of standard additions is an option for the analysis of samples shown to have significant matrix effects, e.g., unacceptably low MS/MSD recoveries or under certain conditions for TCLP analysis (see Attachment 2 for details).

NOTE: DOD QSM 5: Performed only when required by the project and the SD or PDS fails. Must be documented with an NCM and included in the case narrative.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 Sample Preparation

10.3.1 All calibration and calibration verification standards (ICV, ICB, CCV, CCB), as well as the field samples, are processed through the digestion procedure. Prepare digestion tubes containing volumes of standards required for each tube as listed in Section 7.

10.3.2 Weigh 0.5 – 0.6 g of each well-homogenized sample into a sample digestion tube. See SOP DV-QA-0023 for additional information on subsampling.

10.3.3 If preparing Incremental Samples a 3 g sample aliquot is required. This aliquot will be prepared by utilizing the procedure described in *Incremental Sampling Methodology for Soils and Sediments* (DV-OP-0013). Divide the 3 g aliquot into five 0.6 g samples. Digest the five individual aliquots and combine them back into one after adding the sodium chloride-hydroxylamine hydrochloride reagent. All batch QC samples must also be processed in this fashion.

10.3.4 Prepare a MB, LCS, MS, and MSD for each batch. The MB is either an empty digestion tube or is prepared by placing 0.6 g of glass beads in a digestion tube, depending on client requirements. The LCS is prepared by adding 2.5 mL of the 100 µg/L Daily Calibration Working Spike to a digestion tube. The MS is prepared by adding 2.5 mL of the 100 µg/L Daily Calibration Working Spike to a digestion tube containing a second aliquot of the chosen matrix sample. The MSD is prepared in the same manner as the MS using a third aliquot of the chosen sample.

NOTE: The spike must be added after the sample aliquot but before the addition of reagents.

10.3.5 Add 5.0 mL of reagent water to all un-spiked field samples and the method blanks. Add 2.5 mL of reagent water to the LCS, MS and MSD.

10.3.6 Add 5.0 ml of Aqua regia to each tube.

10.3.7 Heat for 2 minutes at 95 ± 3 °C. Record the start and stop times and the temperature on the bench sheet in TALS.

10.3.8 Allow the samples and standards to cool at room temperature.

10.3.9 Add 19 mL of reagent water.

10.3.10 Add 15 mL of 5% potassium permanganate solution. A purple color must persist for at least 15 minutes. If the color does not persist, the sample must be re-prepared using a smaller sample aliquot.

NOTE: It is important that equal volumes of the potassium permanganate solution are added to all solutions in the batch. Unequal volumes used with the automated method will result in dilution errors.

10.3.11 Cap the samples and standards and heat for 30 minutes at 95 ± 3 °C. Record the start and stop times and the temperature on the bench sheet in TALS. The analyst will verify that a purple color persists or a black precipitate is present after the thirty minutes of heating. If this is not true, the digestion must be repeated using a smaller sample aliquot.

10.3.12 Allow the samples and standards to cool at room temperature.

10.3.13 Add 6 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce the excess permanganate. Verify that the volume is at 50 mL.

10.3.14 For samples aliquoted using the Incremental Sampling Method combine the 5 individual sample cups for each sample and QC into one marked 250 mL container.

10.4 Calibration

10.4.1 All calibration standards are digested together with samples, as described in Section 10.3, prior to analysis. Preparation of calibration standards is described in Section 7.12.

10.4.2 Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.4.3 Detailed information regarding calibration models and calculations can be found in Corporate Policy CA-Q-P-003, *Calibration Curves and the Selection of Calibration Points*, and under the public folder, *Arizona Calibration Training*.

10.4.4 Initial Calibration (ICAL)

10.4.4.1 Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4.4.2 Calibrate using six standards and a blank (see section 7.12).

NOTE: It is not acceptable to reject calibration points for this method.

10.4.4.3 The calibration curve must have a correlation coefficient (r^2) ≥ 0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient. The calibration curve is processed with an unweighted linear regression.

10.4.4.4 Record the microAbsorbance (µAbs.) for the 10 ppb standard in the instrument maintenance log.

10.4.5 Initial and Continuing Calibration Blanks

10.4.5.1 An initial calibration blank (ICB) is tested immediately after the daily ICAL standards.

Acceptance Criteria: Absolute values for the calibration blanks must be less than ½ the standard RL. Client specific requirements take precedence. For example, DOD QSM 5 requires control of blanks to a concentration

less than or equal to the LOD.

Corrective Action: If the blank acceptance limit is exceeded, the analysis should be terminated, the source of contamination identified, and the instrument recalibrated.

10.4.5.2 Continuing calibration blanks (CCBs) are run after every 10 samples and at the end of the run.

Acceptance Criteria: The absolute value of the blank result must be less than ½ the reporting limit. As just noted, DOD QSM 5 requires that results for blanks must be less than the LOD (refer to special project requirements).

Corrective Action: If the blank acceptance limit is exceeded, the analysis should be terminated, the source of contamination identified, and the instrument recalibrated.

10.4.6 Initial Calibration Verification (ICV), 4.0 µg/L (Hg Soil ICV)

The accuracy of the calibration standards is verified by testing a second source standard (ICV).

Acceptance Criteria: The ICV recovery must be within 90-110%.

Corrective Action: If the ICV acceptance limit is exceeded, the analysis should be terminated, the accuracy of the calibration standards checked, and the instrument recalibrated.

10.4.7 Reporting Limit Check Standard (CRA), 0.2 µg/L (Hg Soil RL)

The accuracy of results at the reporting limit is verified by testing a standard in every analytical run that is prepared at the reporting limit concentration.

Acceptance Criteria: The results for this standard must be within 50% of the expected value (20% for some programs).

Corrective Action: If the RL check acceptance limit is exceeded, the analysis should be terminated, the instrument operation checked, the instrument recalibrated, and associated samples reanalyzed.

10.4.8 Continuing Calibration Verification (CCV), 5.0 µg/L (Hg Soil CCV)

Calibration accuracy is monitored during the analytical run through the analysis of a known standard after every 10 samples and at the end of the run.

Acceptance Criteria: The CCV recovery must be within 80-120% except for QSM 5.0 where the CCV recovery limits are 90-110%.

Correction Action: Sample results may be reported only when bracketed by valid CCV pairs. If a mid-run CCV fails, the CCV may be reanalyzed once without modification to the instrument's operating conditions. If the reanalyzed CCV is found to be in control, the CCV analysis must be repeated with successful results or the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV failure was not directly instrument related, the associated samples must be re-prepared and reanalyzed.

10.4.9 CCV Acceptance Criteria for sample run under a DOD QSM program

CCVs must have a percent recovery of 90-110%. If the CCV fails the following options are available: Recalibrate and reanalyze all affected samples since the last acceptable CCV or immediately (within an hour) analyzed two additional consecutive CCVs. If both pass, samples may be reported without reanalysis. If either fails, take corrective action(s) and re-calibrate then reanalyze all affected samples since the last acceptable CCV.

10.5 Sample Analysis

10.5.1 Set up the instrument and autosampler according to the manufacturer's instructions.

10.5.2 Allow the samples to cool to room temperature prior to analysis or a decrease in the response signal can occur.

10.5.3 Pipet 10 mL of each sample and calibration standard into a disposable test tube for analysis

10.5.4 Analyze the standards and samples according to the manufacturer's instructions.

10.5.5 All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples with mercury concentrations that exceed the highest calibration standard.

NOTE: The instrument auto-dilutes samples. Any samples that require greater

than a 10x dilution MUST be diluted manually.

10.5.6 If the sample results are negative and the absolute value is greater than the reporting limit, the sample must be reanalyzed.

10.5.7 Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB.

10.5.8 The analytical sequence listed below must be followed. Refer to Quality Control Section 9.0 and for quality control limits.

Instrument Calibration
ICV
ICB
CRA
CCV
CCB
Maximum of 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

NOTE: Samples included in the count between CCVs include the method blank, LCS, MS, MSD, and field samples.

10.5.9 Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.0 Calculations / Data Reduction

Detailed calibration equations can be found in the corporate Policy CA-Q-P-003, *Calibration Curves and Selection of Calibration Points* and under the public folder, *Arizona Calibration Training*.

11.1 Accuracy

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{spike concentration}} \times 100$$

$$\text{MS \% Recovery} = \frac{\text{(spiked sample) - (unspiked sample)}}{\text{spike concentration}} \times 100$$

11.2 Precision (RPD)

Matrix Duplicate (MD) = $\frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$

11.3 Concentration = mg/kg or L = $\frac{C \times V \times D}{W}$

Where:

C = sample concentration in extract (ppm)
V = Volume of extract (mL)
D = Dilution Factor
W = Weight/Volume of sample aliquot extracted (grams or mLs)

NOTE: All dry weight corrections are made in TALS at the time the final report is prepared.

11.4 Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

11.4.1 Sample data entered into the preparation batch in TALS, which includes the batch number, list of samples, preparation analyst and date, identification of reagents and standards used, and identification of all measuring equipment used (e.g., balances, thermometers, pipettes).

11.4.2 Raw data (direct instrument printout as a PDF) with the analyst name and all required calibration information.

11.4.3 Data review checklist - See SOP DV-QA-0020.

11.5 Reporting

11.5.1 Standard units for reporting solid sample results are mg/kg.

11.5.2 If dilutions are required due to insufficient sample, interferences, or other problems, the reporting limit and MDL are multiplied by the dilution factor, and the data may require flagging.

11.5.3 Solid samples are reported on a dry-weight basis unless otherwise requested by the client. Reporting limits are adjusted for both sample size and percent solids.

11.5.4 All associated data are entered or uploaded into TALS as required.

11.5.5 Unless special instructions indicate otherwise, samples less than the reporting limit are reported as ND.

11.5.6 The initial data review is performed by the analyst while the second-level data review is performed by the area supervisor or designee. Both reviews are documented on a Data Review Checklist. See SOP DV-QA-0020 for a copy of the checklist and for more detail on the review process.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. An initial method detection limit study is performed in accordance with Policy DV-QA-005P. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency. For Texas TRRP, DoD, AFCEE, and DOE projects, an MDL verification (MDLV) is performed quarterly.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

12.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.

12.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.2.4 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

12.3 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, order chemicals based on quantity needed, and prepare reagents based on anticipated usage and reagent stability).

14.0 Waste Management

All waste will be disposed of in accordance with Federal, State, and local regulations.

Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in Section 13, *Waste Management and Pollution Prevention*, of the Corporate Environmental Health and Safety Manual, and Policy DV-HS-001P, *Waste Management Program*.

14.1 The following waste streams are produced when this method is carried out:

14.1.1 Aqueous Acidic (Metals) - Corrosive - (J)

14.1.2 Expired reagents and standards – Contact the Waste Coordinator.

NOTE: Radioactive waste, mixed waste, and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of these materials.

15.0 References / Cross-References

15.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A (Mercury).

15.2 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, Update IV, February 2007, Method 7471B (Mercury).

15.3 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 4.2, 10/25/2010.

15.4 Department of Defense Department of Energy Consolidated Quality Systems Manual for Environmental Laboratories, Version 5.0, July 2013.

15.5 U.S.EPA Statement of Work for Inorganic Analysis, ILMO3.0

16.0 Method Modifications:

Item	Method	Modification
1	7471A	An additional QC analysis, RL verification, is added
2	7471A	Methods 7470A and 7471A state that working standards "should be prepared fresh daily." The laboratory frequently prepares up to three batches of mercury samples, including digested calibration standards, each day. The third batch is typically prepared and digested late in the day, and then is analyzed the morning of the next day. The laboratory had developed the following information demonstrating that analysis within 24 hours, but on the second calendar day from preparation produces reliable results and is acceptable to the EPA: • Successful proficiency testing (PT) results for samples that were prepared and analyzed within 24 hours, but on successive days • Successful analysis of true NIST mercury

Item	Method	Modification
		standards within every analytical batch; and • A written comment from the EPA MICE Hotline stating that, with the supporting lab data, their opinion was that the laboratory's practice is "within the letter of the method as written."
3	7471A	Chapter 1 of SW-846 specifies the use of reagent water with a purity equivalent of ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.
4	7471A	Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above ½ the reporting limit.
5	7471B	Method 7471B uses reagent water for the method blank. TestAmerica Denver is currently using glass beads when required.
6	7471B	Section 11.1 requires 50 mL of reagent water to be added to the sample with 15 mL of Potassium permanganate. TestAmerica Denver utilizes digestion tubes which do not allow for 50 mL of reagent water. 19 mL of reagent water is currently being added.
7	7471A	Section 7.1 specifies triplicate 0.2-g portions of sample for solids analysis. TestAmerica Denver instead utilizes a 0.5-0.6 g weight range in order to avoid targeting of specific weights and to comply with the requirements of the most recent method revision.

17.0 Attachments

Attachment 1: Summary of Quality Control Requirements
Attachment 2: MSA Guidance
Attachment 3: Instrument Maintenance
Attachment 4: Troubleshooting Guide

18.0 Revision History

- Revision 7 dated 28 Feb 2015
  - Annual Technical Review
  - Removed reference to purging sample headspace from Section 4.4, outdated.
  - Section 4.6 – Removed reference to method 245.6
  - Changed MSDS to SDS
  - Removed references to "Cetac Only"
  - Added Section 7.5.3 regarding recording of data in TALS
  - Added TALS reagent IDs to standard names
  - Corrected concentrations of Cal Stds
  - Corrected Section references
  - Changed units of RL std to water units
  - Changed minimum sample volume to 10 g to accord with corporate policy

  - Added DoD V5 references
  - Changed sample aliquot to 0.5 – 0.6 g
  - Deleted references to adjust volume with 1% HNO3
  - Updated temperature of digestion to 95 ± 3 ^{o}C
  - Deleted Section 10.4.4.3 (Redundant)
  - Changed “counts” in Section 10.4.4.4 to microAbsorbance
  - Removed “Approximately” from ICV true values
  - Removed GC references from Section 10.4.9
  - Removed references to “resloping”
  - Added initial CCV/CCB pair to sequence
- Revision 6 dated 28 Feb 2014
  - Annual Technical Review
  - Removed references to Serial Dilutions and Post Digestion Spikes
  - Section 10.4 for incremental sampling was merged into Section 10.3
  - Updated Section 10.4.4.1 and 10.4.4.2 to note DOD QSM 5 criteria
  - Updated Section 10.4.7 to note DOD QSM 5 CCV criteria is 90-110.
  - Updated Attachment 2 for ICB,CCB and CCV criteria to DOD QSM 5
  - Added Attachment 5 for Troubleshooting
- Changed Revision 5 dated 15 July 2013
  - Annual Technical Review
  - Correction to formatting
  - Changed reference to Standards Log to Reagent Module in the LIMS
  - Added General Analytical Terms information to definition section
  - Edited section 7.6, 10.4.8, 12.1 & 12.2 to reflect current practices.
  - Changed RL reference in sections 7.18, 10.5.6, 10.6.8 and Attachment 2 to CRA
  - Removed bullet point 5 under 11.5
  - Removed Attachment 3 and renumbered the subsequent attachments
  - Corrected references date for section 15.2
  - Added Texas TRRP to section 12.1
- Revision 4 dated 30 September 2012
  - Clarified the language in Section 9.4 to be one LCS per batch.
  - Modified Section 7.16.2 to refer to Section 10.4.4 for additional detail.

- Revision 3.2 dated 13 July 2012
  - Updated Sections 7.6 and 7.7 to state Hg grade reagents are used
  - Updated Sections 10.4.11 to include a note about bringing samples to a final volume before the sample is mixed
  - Updated Section 10.5.4 and Attachment 2 to control calibrations blanks to ½ the RL.
  - Added Sections 10.5.3.5 to record the number of counts for the 10 ppb standard
  - Formatting and grammatical changes throughout

- Revision 3.1 dated 03 February 2012
  - Changed references of Multi-Incremental Sampling to Incremental Sampling throughout document
  - Annual Technical Review
  - Section 1.3 Added Incremental Sampling Method statement to SOP
  - Added introductory statement to section 7.0 regarding reagent purity
  - Updated section 9.5 and Attachment 2 for method blank control criteria
  - Section 10.2 Added Incremental Sampling Method preparation amount
  - Section 10.2.12 Added Incremental Sampling Method combination procedure

  - Section 10.2.13 Added Incremental Sampling Method final volume
  - Added dilution note to Section 10.3.5
  - Updated section 12.0 to reflect current laboratory practices

- Revision 3 dated 23 August 2011
  - Updated Section 5.1.1 to include using a face shield when making up aqua regia
  - Added Section 7.4 for how to make aqua regia
  - Removed previous Section 7.6 (FIMS information)
  - Updated Section 7.14 ICV daily intermediate standard level to 400ug/l
  - Updated Section 7.15 ICV daily working standard level to 4ug/l
  - Updated Section 10.2.3 ICV level to 4ug/l
  - Changed run order for ICV and ICB in section 10.3.8
  - Added a note to section 10.1.3 for the addition of the LCS/MS spike before the reagents.

- Revision 2.5, dated 25 April 2011
  - Removed all references to the FIMS Hg Analyzer
  - Sections 6.1 and 6.3 were updated to reflect the use of digestion blocks from water baths

- Revision 2.4, dated 07 February 2011
  - Updated supplies list for implementation of calibrated tube
  - Updated Section 10 for implementation of calibrated tube
  - Updated section 6 to include reference to the Master List of Documents, Software and Hardware
  - Added section 11.1 to reference corporate SOP CA-Q-S-005 “Calibration Curves”

- Revision 2.3, dated 01 September 2010
  - Annual Technical Review
  - Removed comment about Standards Log program in Section 7
  - Updated Section 11.4 for new LIMS
  - Removed Example prep sheet (Attachment 3)

- Revision 2.2, dated 07 August 2009
  - Removed Reagent Blank from Section 7.4
  - Changed table header name in section 7.12 to say 1%HNO_3 from Reagent Water
  - Changed sections 7.13 and 7.14 to use 1% HNO_3 from reagent blank

- Revision 2.1, dated 16 February 2009
  - Section 10.2.5: Update the corrective action to match the other Hg SOPs
  - Deleted Section 12.3 for IDL requirement

- Revision 2, dated 28 December 2007
  - Integration for TestAmerica and STL operations.
  - Changed aliquot size from 0.3g to 0.6g.
  - Made changes to concentration to reflect the aliquot change throughout the SOP.
  - Reformatted the SOP.

- Revision 1, dated 11 October 2005
  - The method summary has been updated to reflect the actual procedure performed.
  - The definition of aqua regia was corrected to indicate three parts HCl to one part

HNO_3.

- In section 10.4.6, changed the true value for the ICV to “approximately 2.0 µg/L,” since the value can change slightly each time the standard is prepared.
- Corrected section 10.3.11 to add verification that the permanganate color persists during the thirty minute digestion.
- Corrected 10.3.13 to reflect the laboratory’s preference for using hydroxylamine hydrochloride to reduce the excess permanganate.
- Added recipe for 1.3 % $SnCl_2$ for the PE FIMS analyzer.
- Corrected sections 7.10 and 7.11 to reflect a volumetric preparation rather than gravimetric.
- Added instructions to prepare reagent blank in section 7.5.
- Added detailed preparation information for the ICV.
- Added instructions for preparing the MB, LCS, MS, and MSD to section 10.3.3.
- Added instructions add 2.5 ml of reagent water to the MB and field samples to compensate for the volume of the spikes added to the samples and the LCS in section 0.

Attachment 1

Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICB	Immediately following ICAL	Absolute value < ½ RL (<LOD for QSM 5.0)	Terminate analysis; correct the problem; recalibrate or re-prepare and reanalyze batch.
ICV	Following ICB	90- 110% recovery	Terminate analysis; correct the problem; recalibrate or re-prepare and reanalyze batch.
RL Check Standard (CRA)	Following the ICV	50-150% recovery	Terminate analysis; correct the problem; recalibrate or re-prepare and reanalyze batch.
CCV	Every 10 samples and at the end of the run	80 - 120 % recovery. 90-110% for QSM 5.0	Terminate analysis; correct the problem; recalibrate and rerun all samples not bracketed by acceptable CCVs or re-prepare and reanalyze batch.
CCB	Immediately following each CCV	Absolute value < ½ RL (<LOD for QSM 5.0)	Terminate analysis; correct the problem; recalibrate and rerun all samples not bracketed by acceptable CCVs or re-prepare and reanalyze batch.
Method Blank	One per sample preparation batch of up to 20 samples.	Project specific or ≤ ½ RL Sample results greater than 10% the blank concentration are acceptable.	Redigest and reanalyze samples. Note exceptions under criteria section.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Recovery must be within statistical control limits, not to exceed 80 - 120%	Terminate analysis; correct the problem; redigest and reanalyze all samples associated with the failed LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples.	Recovery must be within statistical control limits, not to exceed 75-125%	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added.
Matrix Spike Duplicate	See Matrix Spike	Recovery within statistical control limits, not to exceed 75-125 % recovery or in-house control limits; RPD ≤ 20%	See Corrective Action for Matrix Spike.

Attachment 2

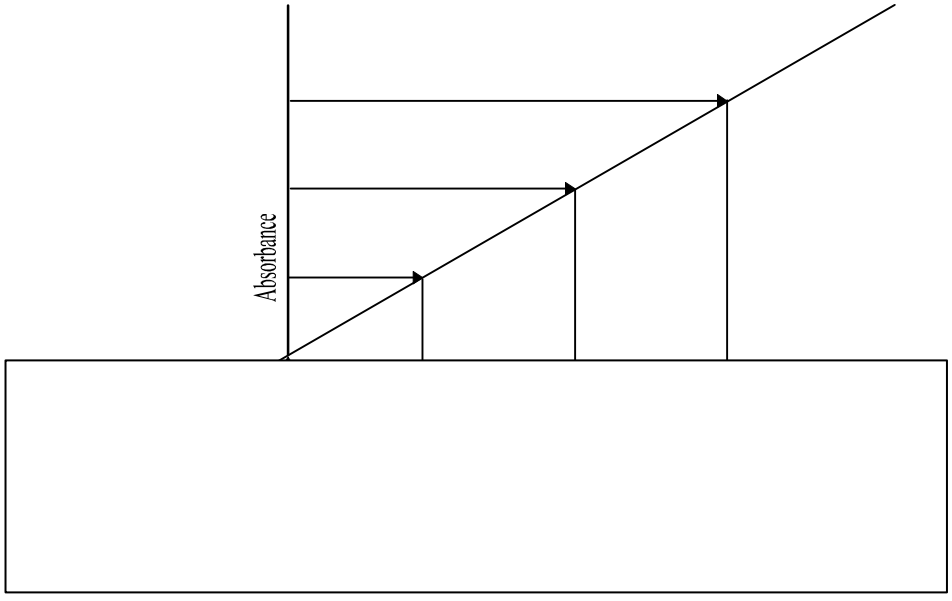
MSA Guidance

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

Attachment 3

Instrument Maintenance

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs, record the date, time and instrument number, then identify the problem and corrective action in the maintenance log. When the instrument is returned to service, record the return to service, the date, and any tests performed to verify proper operation.

The following preventative maintenance procedures are <u>required</u> to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption

Daily	Monthly	Annually
Change rinse solution.	Check Hg lamp intensity.	Change Hg lamp.
Optimize light path.		Check liquid/gas separator.
Check argon flow.		
Check tubing. Replace as needed.		
Check drain.		
Check condition of dryer		

Attachment 4

Troubleshooting Guide

Problem	Possible Cause
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak
Erratic Readings	Source lamp not aligned properly Lamp not pre-warmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell

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Electronic Copy Only -

Title: Mercury in Water by Cold Vapor Atomic Absorption (CVAA) [EPA 245.1]

Approvals (Signature/Date):

Doug Gomer 8/10/15
Doug Gomer Date
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Margaret S. Sleevi 8/10/15
Margaret S. Sleevi Date
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William S. Cicero Date
Laboratory Director

Facility Distribution No. _____ **Distributed To: _____**

1.0 Scope and Application

1.1 This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using MCAWW Method 245.1.

1.2 Method 245.1 is applicable to the determination of mercury in drinking, surface and saline waters, and domestic and industrial wastes.

1.3 All matrices require sample preparation prior to analysis.

1.4 The final reporting limit is 0.0002 mg/L (0.2 μg/L)

2.0 Summary of Method

This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration). All sample data are uploaded to the TestAmerica LIMS (TALS).

3.0 Definitions

3.1 Dissolved Metals: Those elements that pass through a 0.45-μm membrane. (Sample is acidified after filtration).

3.2 Total Metals: The concentration determined on an unfiltered sample following digestion.

3.3 Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and Policy DV-QA-003P, *Quality Assurance Program*, for definitions of general analytical and QA/QC terms.

4.0 Interferences

4.1 Chemical and physical interferences may be encountered when analyzing samples using this method.

4.2 Potassium permanganate, which is used to breakdown organic mercury compounds, also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.3 Copper also has been reported to interfere; however, copper concentrations as

high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.4 Chlorides can cause a positive interference. Seawaters, brines, and industrial effluents high in chlorides will require dilution. During the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

4.5 Interference from certain volatile organic materials that absorb at the wavelength used for the method may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.6 Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs, the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.7 The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual, Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3.2 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile or latex gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be

removed and discarded; non-disposable gloves must be cleaned immediately.

5.3.3 Potassium permanganate is a strong oxidizing agent. It is incompatible and must be stored separately from hydroxylamine hydrochloride and stannous chloride, the reducing agents used in this procedure, and from acids.

5.4 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Mercury (1,000 ppm in Reagent)	Oxidizer Corrosive Poison	0.1 mg/m^3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 mg/m^3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.

Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Instrumentation

6.1.1 Digestion Block, with adjustable heating, capable of maintaining a sample temperature of 90-95°C.

6.1.2 Mercury Auto-analyzers: The laboratory currently uses two CETAC QuickTrace™ Mercury Analyzer M-7500s with Autosamplers and Auto-Diluters.

6.2 Computer Software and Hardware

Please refer to the master list of documents, software and hardware located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

6.3 Supplies

6.3.1 Disposable 50 mL digestion tubes with caps. Accuracy at 30 mL verified to ±3% gravimetrically prior to use (by lot). See DV-QA-0008 for more information regarding volume verifications.

6.3.2 Disposable glass test tubes, 16mm x 100mm

6.3.3 Argon, 99.999% purity

6.3.4 Calibrated automatic pipettes or Class A glass volumetric pipettes (see SOP DV-QA-0008 for details on calibrating mechanical pipettes).

6.3.5 Class A volumetric flasks.

6.3.6 Thermometer, non-mercury column, accurate to ±1°C at 95 °C (see SOP DV-QA-0001 for calibration details).

7.0 Reagents and Standards

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Suggested reagent and standard recipes are listed below. Alternate weights and volumes may be used as long as the final concentrations are maintained as listed and the details are recorded in the

Reagent module in TALS. All standard concentrations listed below refer to the on-instrument concentration except where otherwise noted.

7.1 Reagent water: Must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2 Nitric acid (HNO_3): concentrated, trace metal grade or better.

7.3 Hydrochloric acid (HCl): concentrated, trace metal grade or better.

7.4 Sulfuric acid (H_2SO_4): concentrated, trace metal grade or better.

7.5 Reagent Blank: This blank solution is used as the Calibration Blank (STD0), Initial Calibration Blank (ICB), Continuing Calibration Blank (CCB), and as the starting solution for the Method Blanks (MBs). It is made as follows:

Add 0.5 L of concentrated HNO_3 to a 50-liter carboy partially filled with reagent water. Dilute to 50 L with reagent water. Mix carefully. Record the acid lot numbers and other required information in the Blank Reagent Logbook stored in the metals prep area.

7.6 Stannous chloride solution, Hg grade, 10% (w/v) per manufacturer's (CETAC) instructions

7.6.1 Place approximately 1000 g of deionized water in a tared 2-L HDPE jar on a top-loading balance.

7.6.2 Add 200 g of $SnCl_2$ to the flask.

7.6.3 Add deionized water until the total weight is 2000 g.

7.6.4 Place the jar in a fume hood and slowly add 200 mL of concentrated HCl to the flask and swirl to mix.

7.6.5 Close the jar and agitate until the reagent is dissolved.

7.7 Sodium chloride-hydroxylamine hydrochloride solution (Hg grade):

7.7.1 Place approximately 1000 g of deionized water in a tared 2-L HDPE jar on a top-loading balance.

7.7.2 Add 240 g of NaCl and 240 g of hydroxylamine hydrochloride (Hg grade) to the jar.

7.7.3 Add deionized water until the total weight is 2480 g.

7.7.4 Close the jar and agitate until the reagent is dissolved.

NOTE: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.8 Potassium permanganate ($KMnO_4$), 5% solution (w/v):

7.8.1 Place approximately 1000 g of deionized water in a tared 2-L HDPE jar on a top-loading balance.

7.8.2 Add 100 g of $KMnO_4$ (Hg grade) to the jar.

7.8.3 Add deionized water until the total weight is 2100 g.

7.8.4 Close the jar and agitate until the reagent is dissolved.

7.9 Potassium persulfate ($K_2S_2O_8$), 5% solution (w/v):

7.9.1 Place approximately 1000 g of deionized water in a tared 2-L HDPE jar on a top-loading balance.

7.9.2 Add 100 g of $K_2S_2O_8$ (Hg grade) to the jar.

7.9.3 Add deionized water until the total weight is 2100 g.

7.9.4 Close the jar and agitate until the reagent is dissolved.

7.10 Purchased Mercury Stock Solutions

7.10.1 Primary Mercury Calibration Standard (Hg Ultra Prim), 1,000 mg/L.

7.10.2 Second-source Mercury Standard (Hg ICV Stock), 100 mg/L. This standard is obtained from a different vendor than the Primary Mercury Calibration Standard.

7.11 Calibration Working Standard Solution (Hg Month Spike), 10 mg/L.

7.11.1 Add approximately 90 mL of the Reagent Blank solution to a 100 mL Class A volumetric flask.

7.11.2 Pipet 1.00 mL of the 1000 mg/L primary mercury calibration standard (see Section 7.10.1) into the flask.

7.11.3 Dilute to the mark on the flask with Reagent Blank.

7.11.4 Stopper the flask and shake to mix.

7.11.5 Transfer the solution to a 125 mL Nalgene bottle.

7.11.6 Document the preparation of the solution in the Reagents module in TALS.

7.11.7 Prepare this solution fresh monthly or more often if necessary.

7.12 Daily Calibration Working Solution (Hg Daily Spk), 100 µg/L

7.12.1 Add approximately 90 mL of the Reagent Blank solution to a 100 mL

Class A volumetric flask.

7.12.2 Pipet 1.00 mL of the 10 mg/L Calibration Working Standard solution (see Section 7.11) into the flask.

7.12.3 Dilute to the mark on the flask with the Reagent Blank solution (final volume of 100.0 mL).

7.12.4 Stopper the flask and shake to mix.

7.12.5 Transfer the solution to a 125 mL Nalgene bottle.

7.12.6 Document the preparation of the solution in the Reagents module in TALS.

7.13 Daily Initial Calibration (ICAL) Standards**.**

7.13.1 To each of seven 50 mL digestion tubes, add approximately 30 mL of the Reagent Blank solution.

7.13.2 For each calibration level, add the appropriate amount of Daily Calibration Working Solution to the tube as indicated in the following table. The final concentration for each calibration level is listed in the following table:

Daily ICAL Standards

Calibration Level	Volume of Daily Calibration Working Solution (100 µg/L) Added (mL)	Final Hg Concentration (µg/L)
1 (Hg STD1 0.1)	0.03	0.06
2 (Hg STD2 0.2)	0.06	0.12
3 (Hg STD3 0.5)	0.15	0.3
4 (Hg STD4 1.0)	0.3	0.6
5 (Hg STD5 2.0)	0.6	1.2
6 (Hg STD6 5.0)	1.5	3.0
7 (Hg STD7 10.0)	3.0	6.0

7.13.3 Close each tube and swirl to mix.

7.13.4 Prepare the calibration standards as samples.

7.13.5 Document the preparation of the solutions in the Reagents Module in TALS.

7.13.6 Prepare the calibration solutions each day prior to calibration.

7.13.7 The calibration blank is titled STD0 in TALS.

7.14 Continuing Calibration Verification Standard (Hg H20 CCV), 3.0 µg/L.

7.14.1 The CCV is prepared exactly as the 3.0 µg/L calibration standard, and from the same source. Refer to Section 7.13.

7.14.2 Prepare sufficient volume of the standard for analysis of a CCV after every 10 samples.

7.15 Second-Source Initial Calibration Verification Intermediate Standard (Hg Biwk ICV), 400 µg/L.

Add 0.4 mL of the 100 mg/L ICV stock standard (see Section 7.10.2) to a 100 mL volumetric flask partially filled with the Reagent Blank solution and dilute to the mark. Record this information in the Reagents module in TALS.

7.16 Second-Source Initial Calibration Verification Daily Working Standard (Hg H20 ICV), 2.4 µg /L.

Add 0.3 mL of the 400 µg/L ICV intermediate standard (see Section 7.15) to a 50 mL digestion tube filled with 30 mL of Reagent Blank. Prepare as a sample. Record this information in the Reagent Module in TALS.

7.17 Laboratory Control Sample (LCS), 3 µg/L

The LCS is prepared by adding 1.5 mL of the 100 µg/L Daily Calibration Working Standard (Section 7.12) to 30 mL of Reagent Blank solution in a digestion tube. The LCS goes through the same digestion process as the samples.

7.18 Matrix Spike and Matrix Spike Duplicate (MS/MSD), 3 µg/L

7.18.1 The MS is prepared by adding 1.5 mL of the 100 µg/L Daily Calibration Working Solution (Section 7.12) to a digestion tube containing a second 30-mL aliquot of the selected matrix sample.

7.18.2 The MSD is prepared in the same manner as the MS using a third aliquot of the selected sample.

7.18.3 The MS and MSD go through the same digestion process as the samples.

7.19 Reporting Limit (RL) Check Standard (Hg H20 RL), 0.12 µg/L

The 0.12 µg/L calibration standard (see Section 7.13) is analyzed as a sample to verify the reporting limit. Denoted as CRA in the run sequence.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Water	HDPE	50 mL	HNO_3, pH < 2	28 Days	40 CFR Part 136.3

[1] Inclusive of digestion and analysis.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the TALS Method Comments to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver Policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, *QA/QC Requirements for Federal Programs*.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in TALS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Sample QC

9.2.1 Preparation Batch

A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank (MB) and a laboratory control sample (LCS). A matrix spike/matrix spike duplicate (MS/MSD) pair must be included with every 10 samples. As discussed in the following sections, special program or project requirements can include additional requirements. Always refer to special project instructions for details before proceeding with the analysis.

9.2.2 Method Blank (MB)

The method blank consists of Reagent Blank solution containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. At least one method blank must be processed with each preparation batch.

Acceptance Criteria: The result for the method blank must be less than the project-specific data quality objectives. In the absence of project-specific data quality objectives, the blank must be less than ½ the reporting limit or less than 10% of the mercury concentration found in the associated samples, whichever is higher.

Corrective Action: All samples associated with an unacceptable method blank must be re-prepared and reanalyzed. If mercury was not detected in the samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative.

9.2.3 Laboratory Control Sample (LCS)

The LCS is a blank to which a known concentration of the target analyte has been added. At least one aqueous LCS must be processed with each preparation batch. The LCS must be carried through the entire analytical procedure.

Acceptance Criteria: Maximum control limits for LCS recoveries for Method 245.1 are 85-115%. In-house control limits based on three standard deviations of the mean of past results are used as long as they are at least as tight as the limits in the methods (see TestAmerica Denver Policy DV-QA-003P for further details on establishing control limits).

Corrective Action: If LCS recoveries are outside established control limits, the system is out of control and corrective action must occur. If recoveries are above the upper control limit and mercury is not detected in samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative. In other circumstances, the entire batch must be re-prepared and reanalyzed.

9.2.4 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike (MS) is a second aliquot of a selected field sample to which

known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a third aliquot of the same sample (spiked exactly as the MS) prepared and analyzed along with the sample and matrix spike. One MS/MSD pair must be processed for every 10 samples. Some programs may require the use of sample duplicates in place of or in addition to MS/MSDs. In addition, some programs will allow spikes to be reported for project-related samples only. Spiking levels are provided in Attachment 1. When the MS/MSD concentration is above the linear range; the MS/MSD and parent sample **MUST** be re-analyzed at a dilution.

Acceptance Criteria: Control limits are statistically determined based on three standard deviations of the mean of the laboratory's historical data. The recoveries for the MS and MSD must fall within 70-130%. The relative percent difference between the MS and MSD cannot exceed 20%.

Corrective Action: MS and MSD data are sample/matrix specific and are not normally used to determine the validity of the entire batch. If analyte recoveries or the RPD between duplicates fall outside the acceptance range, the LCS recovery must be in control for the data to be reported. If there is no evidence of analytical problems and all other QC criteria are met, then qualified results may be reported and the situation must be described in the final report case narrative. If laboratory error is suspected, the batch must be re-prepared and reanalyzed. The following corrective actions are required for MS/MSD recovery failures to rule out lab error:

- Check calculation and instrument performance;
- Verify, if possible, that the MS and MSD were spiked correctly;
- Consider objective evidence of matrix interference (e.g., heterogeneous sample or interference demonstrated by prior analyses);
- Flag the data for any results outside of acceptance limits and note it on the final report.
- For any single RPD failure, check calculations; verify, if possible, that the MS and MSD were spiked correctly; check instrument performance; consider objective

evidence of matrix interference or sample inhomogeneity; and flag the data.

- When the MS/MSD concentration is above the linear range; the MS/MSD and parent sample **MUST** be re-analyzed at a dilution.

NOTE: Some client programs require reanalysis to confirm matrix interferences. Check special project requirements for this corrective action.

If the native analyte concentration in the MS/MSD sample exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated).

9.2.5 Method of Standard Addition (MSA)

The method of standard additions is an option for the analysis of samples shown to have significant matrix effects, e.g., unacceptably low MS/MSD recoveries or under certain conditions for TCLP analysis (see Attachment 3).

9.3 Instrument QC

9.3.1 Initial Calibration (ICAL)

9.3.1.1 Detailed information regarding calibration models and calculations can be found in Corporate Policy CA-Q-P-003, *Calibration Curves & Selection of Calibration Points*.

9.3.1.2 Calibration must be performed daily (every 24 hours) and each time the instrument is set up. All calibration standards and calibration QC samples will be recorded in prep batches and prepared as samples. The instrument calibration date and time must be included in the raw data.

9.3.1.3 Calibrate using seven standards and a blank. The concentration levels are listed in Attachment 1.

NOTE: It is generally not acceptable to reject calibration points for this method.

9.3.1.4 The calibration curve must have a correlation coefficient of $\geq$ 0.995 for an unweighted linear regression or the instrument shall be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient.

9.3.1.5 Record the microabsorbance for the 10 ppb standard in the

instrument maintenance logbook.

9.3.2 Initial and Continuing Calibration Blanks

9.3.2.1 An initial calibration blank is tested immediately after the daily ICAL standards.

Acceptance Criteria: Absolute values for the calibration blanks must be less than ½ the standard RL. Client specific requirements take precedence.

Corrective Action: If the blank acceptance limit is exceeded, the analysis should be terminated, the source of contamination identified, and the instrument recalibrated.

9.3.2.2 Continuing calibration blanks are run after every 10 samples and at the end of the run.

Acceptance Criteria: Absolute values for the calibration blanks must be less than ½ the standard RL. Client specific requirements take precedence.

Corrective Action: If the blank acceptance limit is exceeded, the analysis should be terminated, the source of contamination identified, and the instrument recalibrated.

9.3.3 Initial Calibration Verification (ICV), 2.4 µg/L

The accuracy of the calibration standards is verified by testing a second source standard (ICV).

Acceptance Criteria: The ICV result must be within 5% of the true value.

Corrective Action: If the ICV acceptance limit is exceeded, the analysis should be terminated, the accuracy of the calibration standards checked, and the instrument recalibrated.

9.3.4 Reporting Limit Check Standard (RL), 0.12 µg/L

The accuracy of results at the reporting limit is verified by testing a standard in every analytical run that is prepared at the reporting limit concentration.

Acceptance Criteria: The results for this standard must be within 50% of the expected value.

Corrective Action: If the RL check acceptance limit is exceeded, the analysis should be terminated, the instrument operation checked, and the instrument recalibrated.

9.3.5 Continuing Calibration Verification (CCV), 3.0 µg/L

Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples and at the end of the run. The CCV must be a mid-range standard at a concentration other than that of the ICV.

Acceptance Criteria: The CCV result must fall within 10% of the true value.

Correction Action: Sample results may be reported only when bracketed by valid CCV pairs. If a mid-run CCV fails, the CCV may be re-analyzed once without modification to the instrument's operating conditions. If the re-analyzed CCV is found to be in control, the CCV analysis must be repeated with successful results or the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV failure was not directly instrument related, the associated samples must be re-prepared and reanalyzed.

NOTE: The first CCV following the initial calibration must fall within 5% of the true value or the analytical run must be stopped, the failure investigated, and the instrument recalibrated.

9.3.6 Linear Range

TAL Denver does not report values greater than the highest standard (10 µg/L) used for calibration. Any sample concentration greater than 90% of the highest standard will be diluted. The calibration curve is validated by running 3 check standards, 0.12 µg/L (CRA), 3 µg/L (CCV), and 2.4 µg/L (ICV), during the analytical run. No further linear range study is warranted.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client

can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.3 Sample Preparation

10.3.1 All calibration and calibration verification standards (ICV, ICB, CCV, CCB), as well as the field samples, are processed through the digestion procedure.

10.3.2 Transfer 30.0 mL of well mixed sample to a clean sample digestion tube. The calibration standards may be prepared in duplicate to ensure sufficient volume to complete the analytical sequence. Additional aliquots of CCV and CCB solution may have to be prepared for larger sample runs to ensure that CCV and CCB samples bracket every 10 samples in the analytical sequence.

10.3.3 Prepare an MB, LCS, MS, and MSD for each batch.

10.3.3.1 The MB consists of 30.0 mL of Reagent Blank solution.

10.3.3.2 The LCS is prepared by adding 1.5 mL of the 100 μg/L Daily Calibration Working Solution to 30 mL of 1% HNO_3 in a digestion tube.

10.3.3.3 The MS is prepared by adding 1.5 mL of the 100 μg/L Daily Calibration Working Solution to a digestion tube containing a second 30-mL aliquot of the selected sample.

10.3.3.4 The MSD is prepared in the same manner as the MS using a third aliquot of the selected sample.

10.3.4 Add 1.5 mL of concentrated H_2SO_4 and 0.75 mL of concentrated HNO_3 to the samples in the digestion tubes, mixing after each addition.

10.3.5 Add 4.5 mL of 5% potassium permanganate solution to each sample. For samples high in organic materials or chlorides, dilute the sample until the purple color persists for at least 15 minutes.

10.3.6 Add 2.4 mL of potassium persulfate solution, cap the vial, and heat for two hours at 90 - 95°C. Record the start and stop times and the initial and final temperatures on the bench sheet. Verify that a purple color persists or a black precipitate is present after the two hours of heating. If this is not true, repeat the digestion using a smaller aliquot of sample.

10.3.7 Allow the samples and standards to cool at room temperature.

10.4 Calibration

10.4.1 All calibration standards are digested together with samples, as described in Section 10.3, prior to analysis.

10.4.2 Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration by starting the gas, lamp, heater, and sample pump (approximately 30 minutes of warm-up is required).

10.4.3 The mercury analyzer method uses external standard calibration. Use of an internal standard for this method is not appropriate.

10.5 Sample Analysis

NOTE: Because of differences between various makes and models of CVAA instrumentation, detailed push-button operating instructions are not provided here. Refer to the specific instrument-operating manual for detailed autosampler setup and operation protocols.

NOTE: The injection of samples and the addition of stannous chloride are done automatically by the instrument. Refer to the specific instrument manual for details.

10.5.1 When ready to begin analysis, add 1.8 mL of sodium chloride-hydroxylamine hydrochloride solution to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains).

10.5.2 Add additional Reagent Blank to the samples, QC samples and calibration standards to bring the final volume of each sample to 50 mL.

10.5.3 Aliquot each sample and calibration standard into a disposable test tube for analysis.

10.5.4 All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples that are within 10% of the highest calibration standard.

NOTE: The instrument can auto-dilute samples. Any sample that requires greater than a 10x dilution MUST be diluted manually.

10.5.5 If the sample results are negative and the absolute value is greater than the reporting limit, the sample must be diluted and reanalyzed.

10.5.6 The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

10.5.7 Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB.

10.5.8 The following analytical sequence must be used for Method 245.1. Refer

to Quality Control Section 9.0 and Attachment 2 for quality control criteria to apply to Method 245.1.

Instrument Calibration
ICV
ICB
CRA
Maximum of 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete the run.
CCV
CCB

NOTE: Samples included in the count between CCVs include the method blank, LCS, MS, MSD, and field samples.

10.5.9 To facilitate the early identification of QC failures and samples requiring rerun, it is strongly recommended that sample data be reviewed periodically throughout the run.

10.5.10 See Attachment 5 for guidelines for minimizing contamination of samples and standards. See Attachments 4 and 6 for guidance on troubleshooting and preventive maintenance.

11.0 Calculations / Data Reduction

11.1 Detailed calibration equations can be found in the corporate Policy CA-Q-P-003, *Calibration Curves & Selection of Calibration Points* and under the public folder, *Arizona Calibration Training*.

11.2 Accuracy

$$\text{ICV / CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{known concentration}} \times 100$$

$$\text{MS \% Recovery} = \frac{\text{(spiked sample) - (unspiked sample)}}{\text{spiked concentration}} \times 100$$

11.3 Precision (RPD)

$$\text{Matrix Duplicate (MD)} = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

11.4 Concentration = Hg concentration (μg/L) = $\frac{C \times V_1 \times D}{V_2}$

Where:

C = Concentration (μg/L) from instrument readout
D = Instrument dilution factor
V_1 = Final volume in liters after sample preparation
V_2 = Initial volume of sample digested in liters

11.5 Appropriate factors must be applied to sample values if dilutions are performed.

11.6 Sample results should be reported with up to three significant figures in accordance with the TestAmerica significant figure policy (DV-QA-004P).

11.7 Documentation and Record Management

11.7.1 All sample data is uploaded to TALS. All sample preparation and analytical batch information, including the batch number(s), list of samples, preparation analyst and date, instrument analyst and date, identification of reagents and standards used, and identification of all measuring equipment used (e.g., balances, thermometers, pipettes) is recorded in TALS.

11.7.2 Raw data is scanned or saved directly as a PDF and is attached to the analytical batch in TALS.

11.7.3 The initial data review is performed by the analyst and a second-level review is performed by the area supervisor or designee. Both reviews are documented on a Data Review Checklist. See SOP DV-QA-0020 for more detail on the review process.

11.7.4 If dilutions are required due to insufficient sample, interferences, or other problems, the reporting limit and MDL are multiplied by the dilution factor and the data may require flagging.

NOTE: Unless special instructions indicate otherwise, sample results less than the reporting limit are reported as ND.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. An initial method detection limit study is performed in accordance with Policy DV-QA-005P. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency. For DoD, AFCEE, and DOE projects, an MDL verification is performed quarterly.

12.2 Demonstration of Capabilities

12.2.1 All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually.

12.2.2 IDOCs and on-going proficiency demonstrations are conducted as follows. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample is typically the LCS spike level. The results of the IDOC study are summarized in the NELAC format, as described in SOP DV-QA-0024. IDOCs are approved by the Quality Assurance Manager and the Technical Director. IDOC records are maintained by the QA staff in the central training files.

12.3 Training Requirements

12.3.1 The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

13.0 Pollution Control

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, order chemicals based on quantity needed, and prepare reagents based on anticipated usage and reagent stability).

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in Section 13, *Waste Management and Pollution Prevention*, of the Corporate Environmental Health and Safety Manual, and Policy DV-HS-001P, *Waste Management Plan*.

14.2 The following waste streams are produced when this method is carried out:

14.2.1 Aqueous Acidic (Metals) - Corrosive - Waste Stream J

14.2.2 Expired reagents and standards – Contact the Waste Coordinator.

NOTE: Radioactive waste, mixed waste, and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Waste Coordinator for proper management of these materials.

15.0 References / Cross-References

15.1 "Methods for the Determination of Metals in Environmental Samples", EPA-600/R-94/111, U.S.EPA, 1994, Method 245.1, Revision 3.0, "Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry."

15.2 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 3, March 2005.

15.3 U.S.EPA Statement of Work for Inorganics Analysis, ILMO3.0.

16.0 Method Modifications:

Item	Method	Modification
1	EPA 245.1	This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, "Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology."
2	EPA 245.1	Method 245.1 Section 12.8 states that concentrations between 1 and 10 μg/L should be reported to one significant figure, and results above 10 μg/L to the nearest μg/L unit value (e.g. two figures in 10-99 μg/L range, three figures in 100-999 μg/L range, etc.). TestAmerica reports all Hg results under this SOP to two significant figures.
3	EPA 245.1	Method 245.1, Section 11.2.2, states that the calibration standards are not heated. TestAmerica Denver does not heat the calibration standards associated with drinking water compliance samples, but does heat the calibration standards for all other samples.
4	EPA 245.1	Method 245.1 Section 9.3.4 states that the calibration blanks should be controlled to less than the MDL. TestAmerica Denver controls all calibration blanks to ½ the reporting limit.
5	EPA 245.1	Method 245.1 Section 9.3.1 states that the method blanks should be controlled to less than 2.2 times the MDL. TestAmerica Denver controls all method blanks to ½ the reporting limit as per corporate policy.

17.0 Attachments

Attachment 1: Mercury Reporting Limits, Calibration Levels, QC Standard and Spiking Levels
Attachment 2: Summary of Quality Control Requirements
Attachment 3: MSA Guidance
Attachment 4: Troubleshooting Guide
Attachment 5: Contamination Control Guidelines
Attachment 6: Preventative Maintenance

18.0 Revision History

- Revision 7 dated 31 August 2015
  - Added Section 3.3 reference to QAM
  - Rewrote reagents Sections 7.5-7.19 to reflect new procedure
  - Rewrote corrective action in Section 9.2.4
  - Updated procedures in Section 10 to better meet traceability requirements

- Revision 6 dated 31 January 2015
  - Annual Technical Review
  - Added reference to TALS
  - Removed references to drinking water
  - Changed MSDS to SDS
  - Defined mercury analyzer models
  - Rewrote reagents Sections 7.5-7.19 to reflect current practice
  - Deleted Section 7.15, reagent no longer used
  - Grammar and formatting corrections throughout
  - Changed MB limit from 2.2 x MDL to ½ RL
  - Rewrote corrective action in Section 9.2.4
  - Removed Sections 9.2.5 and 9.2.6 as they only apply to DoD work
  - Removed Sections 9.3.1.1-9.3.1.3 as they were duplicated in Section 10.4
  - Removed reference to resloping in Section 10.5.7
  - Converted bullets in Section 11.8 to numbers, rewrote entries to comply with current practice
  - Removed Figures 1 and 2
  - Removed Attachment 3, Example Raw Data Checklist
  - Renumbered Attachments
  - Removed Figures 1 and 2
  - Added method modification number 5

- Revision 5 dated 31 January 2014
  - Annual Technical Review
  - Removed Section on 2012 MUR QC requirements
  - Formatting and editorial changes throughout document

- Revision 4.02 dated 04 January 2013
  - Added section 9.3 for 2012 MUR QC requirements

- Revision 3.2 dated 13 July 2012
  - Updated Sections 7.6 and 7.7 to say Hg grade standards are used
  - Updated Sections 9.3.2 to control calibration blanks to ½ the RL
  - Added 10.4.4-10.4.7 about calibration criteria and recording counts for 10 ppb standard
  - Updated 10.5.2 to bring the samples to a final volume of 45 mL with 1% HNO_3

- Revision 3.1 dated 03 February 2012
  - Annual technical review
  - Added introductory statement to section 7.0 regarding reagent purity
  - Section 9.1.4 Updated MS/MSD control limit minimums to method limits
  - Added dilution note to Section 10.3.4
  - Added to section 10.3.4 to dilute samples within 10% of high standard
  - Updated section 12.0 reflect current laboratory practice
  - Updated control limit minimums for the LCS and MS/MSD for Attachment 2
  - Replaced Nitrogen reference with Argon and removed Leeman instrument

- Revision 3.0 dated 23 August 2011
  - Section 7.16 Changed ICV Intermediate Standard to 400ug/l
  - Section 7.17 Changed ICV level to 4ug/l
  - Section 9.2.3 Changed ICV level to 4ug/l

- Section 10.3.8 Changed ICV and ICB order

- Revision 2.5 dated 25 April 2011
  - Removed all references to the FIMS Analyzer
  - Sections 6.1 and 6.3 were updated to reflect the use of digestion blocks from water baths.
  - The reagent amounts were updated to reflect using a 30 mL aliquot from 10ml.
  - Section 10.3.2 was updated to show a final volume of 40 mL.

- Revision 2.4 dated 14 February 2011
  - Revised Section 10 to reflect use of calibrated digestion tubes and calibration standard volumes
  - Revised section 6 to include reference to the Master List of Documents, Software and Hardware

- Revision 2.3 dated 01 September 2010
  - Annual Technical Review
  - Removed comment in Section 7 about Standards Log program
  - Updated Section 11.7 for new LIMS
  - Removed attachments 3a and 3b.

- Revision 2.2 dated 07 August 2009
  - Updated sections 7.18 and 7.19 to use 1% HNO_3 from reagent water
  - Updated sections 10.1.3.1 and 10.1.3.2 to use 1% HNO_3 from reagent water

- Revision 2.1, dated 16 February 2009
  - Section 9.2.6: Added requirement to dilute all samples with concentrations greater than 90% of the highest standard
  - Deleted section 12.2 for IDL requirements
  - Sections 12.3: Noted that IDOCs will use LCSs for verification
  - Section 16: Added item 4 that all calibration blanks are controlled to the reporting limit

- Revision 2, dated 21 March 2008
  - Integration for TestAmerica and STL operations.
  - Split the Mercury Water SOP into 2 SOPs – 245.1 Mercury and 7470A Mercury.
  - Deleted all references of Method 7470A from this SOP.
  - Updated formatting.
  - Updated References.
  - Referenced an MS/MSD for every 10 samples per method 245.1.

- Revision 1.1, dated 19 June 2006
  - Revised Section 9.1 to reference policy QA-024, which summarizes QA/QC requirements for Federal programs.
  - Revised Section 10.3.5 to state definitively that the method blank and LCS must be filtered if any samples in the batch require filtering.
  - Made minor cosmetic changes to formatting and corrected typographical errors.
  - Revised Sections to summarize requirements and reference the appropriate SOPs.

- Revision 1, dated 09 November 2005
  - Section 7.5: Added instructions to prepare reagent blank.
  - Added instructions to prepare Stannous Chloride Solution, reagent grade, 1.3%

(w/v).

- Corrected Sections 7.11 and 7.12 to reflect a volumetric preparation rather than gravimetric.
- Sections **Error! Reference source not found.**, 7.15, and 7.16: Added detailed preparation information for the ICV.
- Section 9.2.2: Added method blank acceptance criteria for EPA 245.1 drinking water samples.
- Section 10.3.3: Added instructions for preparing the MB, LCS, MS, and MSD.
- Sections 4.4 and 10.3.5: Removed the provision allowing additional potassium permanganate to be added to samples with high chloride concentrations and added the requirement to dilute and re-prepare the sample when matrix interferences are suspected.
- Section 7.19: Added information regarding the analysis of the lowest calibration point to verify the reporting limit.
- Added section to describe the preparation of the 3% HCl carrier solution.
- Section 9.3.5: Modified the corrective action for a CCV failure to allow for a re-analysis of the CCV.
- Section 10.3.6: Added the requirement to cap the vials prior to digestion.
- Corrected Attachment 1 to reflect the actual concentrations of Std 4, Std 5, and Std 6 used during analysis.
- Section 10.1: Added the clarification for EPA 245.1 drinking water compliance samples, namely that undigested calibration standards will be used.
- Section 10.3.6: Added a note to explain that unheated calibration standards are to be used for drinking water samples.
- Added Section 0 to explain that heated calibration standards are used for all but drinking water samples.

Attachment 1

Mercury Reporting Limits, Calibration Levels, QC Standard and Spiking Levels (µg/L)

	Value at Instrument	Final Value
Standard Aqueous RL	0.12	0.2
Std 0	0	0
Std 1	0.06	0.1
Std 2	0.12	0.2
Std 3	0.3	0.5
Std 4	0.6	1.0
Std 5	1.5	2.0
Std 6	3.0	5.0
Std 7	6.0	10.0
ICV	2.4	4.0
CCV	3.0	5.0
LCS	3.0	5.0
Aqueous MS	3.0	5.0

Attachment 2

Summary of Quality Control Requirements

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
ICV	Beginning of every analytical run.	95 - 105% recovery	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.3.3).
ICB	Beginning of every analytical run, immediately following the ICAL.	Absolute value must be < ½ RL	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.3.1.1.1).
CCV	Every 10 samples and at the end of the run.	90 - 110% recovery (The first CCV after the ICAL must meet 95 - 105% recovery)	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.3.5).
CCB	Immediately following each CCV.	Absolute value must be < ½ RL	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.3.1.1.2).
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than 1/2 the RL. Sample results greater than 10x the blank concentration are acceptable.	Re-digest and reanalyze samples. Note exceptions under criteria section (see Section 9.2.2).
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	In-house 3 standard deviation control limits, not to exceed 85-115% recovery.	Terminate analysis; Correct the problem; Re-digest and reanalyze all samples associated with the LCS (see Section 9.2.3).
Matrix Spike	One per 10 samples preparation batch of up to 20 samples.	In-house 3 standard deviation control limits, not to exceed 70-130% recovery	In the absence of client-specific requirements, flag the data (see Section 9.2.4).
Matrix Spike Duplicate	See Matrix Spike	In-house 3 standard deviation control limits, not to exceed 20% RPD	See Corrective Action for Matrix Spike (see Section 9.2.4).

Attachment 3

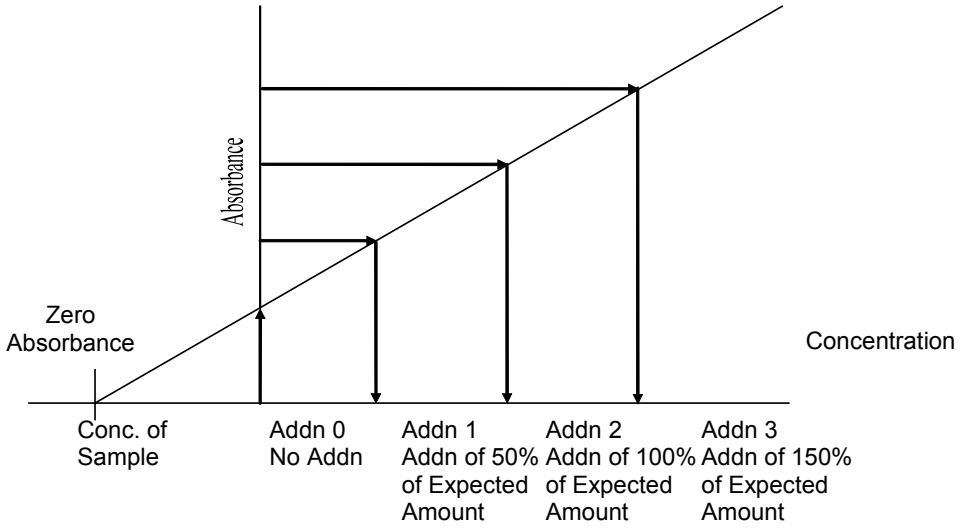
MSA Guidance

Method of Standard Addition (MSA)

Four equal volume aliquots of sample are measured and known amounts of standards are added to three of the aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration, and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of an analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. The absorbance (or response) is plotted on the vertical axis versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. The correlation coefficient (r) and the x-intercept (where y=0) of the curve are calculated. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.

- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.

- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

Attachment 4

Troubleshooting Guide

Problem	Possible Cause
Poor or No Absorbance or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak
Erratic Readings	Source lamp not aligned properly Lamp not pre-warmed GLS capillary partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Autosampler probe hitting outside of tube Autosampler probe coated or not set properly Autosampler probe partially clogged Leak in sample tubing Power fluctuations Air bubbles in tubing
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell

Attachment 5.

Contamination Control Guidelines

The following procedures are strongly recommended to prevent contamination:

- All work areas used to prepare standards and spikes should be cleaned before and after each use.
- All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.
- Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.
- Powdered gloves should not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes.
- Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.
- Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

- Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.
- Improper cleaning of glassware can cause contamination.
- If an unusually high sample is analyzed, segregate the glassware and soak with sulfuric acid prior to routine cleaning.

Attachment 6.

Preventative Maintenance

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs, record the date, time, and instrument number; describe the problem; and explain the corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational:

Cold Vapor Atomic Absorption (CETAC Analyzers)

Daily	Monthly	As Needed
Change rinse solution.	Check Hg lamp intensity.	Change Hg lamp.
Check lamp current.		Check liquid/gas separator.
Check argon flow.		Change Nafion dryer.
Check tubing. Replace as needed.		
Check drain.		
Check condition of Nafion dryer.		

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Title: ACID DIGESTION OF SOLIDS [Method EPA 3050B]

Approvals (Signature/Date):

Doug Gomer 3/27/15
Doug Gomer Date
Technical Specialist

Adam W Alban 30 March 15
Adam Alban Date
Health & Safety Manager / Coordinator

Margaret S. Sleevi 3/30/15
Margaret S. Sleevi Date
Quality Assurance Manager

L. S. L. 3/31/15
William S. Cicero Date
Laboratory Director

Facility Distribution No. _____ **Distributed To: _____**

1.0 Scope and Application

1.1 This is a strong acid digestion procedure for the preparation of sediments, sludge, soils, and other types of solid materials by EPA Method 3050B for analysis by inductively coupled plasma atomic emission spectroscopy (ICP) or inductively coupled plasma-mass spectrometry (ICP/MS).

1.2 Method 3050B is designed to determine the concentration of "environmentally available" metals, and is not a true "total metals" digestion (see discussion below). The procedure is used primarily for hazardous waste characterization and other Resource Conservation and Recovery Act (RCRA) compliance testing.

1.3 The elements approved for Method 3050B are shown in Table I. The source method also mentions that other elements may be prepared by the method if the quality control requirements are met. The complete list of elements routinely included in this procedure by TestAmerica Denver is shown in Table II.

1.4 If sample preparation utilizing the Incremental Sampling Method is required, see SOP DV-OP-0013 for the procedure required prior to acid digestion for metals incorporating this procedure.

2.0 Summary of Method

A representative 1 to 2 gram portion of sample is digested with two cycles of nitric acid additions, followed by hydrogen peroxide digestion. For ICP analysis, the sample is also refluxed with hydrochloric acid. The resulting solution is filtered and diluted to 100 mL with reagent water. For the Incremental Sampling Method, 10g of sample is used and brought to a final volume of 500ml.

3.0 Definitions

3.1 Total Metals: Although Method 3050B is often referred to as a "total metals" digestion, it is important to understand that there are many compounds formed from these elements that are not efficiently dissolved using this digestion procedure. It is more accurately termed a strong acid digestion procedure. The limitations are discussed further in Section 4 (Interferences) below. The method itself states, "This method is not a total digestion technique for most samples." There are a variety of total digestion procedures used for metal assay, geochemical analysis, etc., that involve more vigorous digestions than 3050B.

3.2 Preparation Batch: A group of up to 20 samples that are of the same matrix and are processed together using the same lots of reagents and standards. The minimum QC elements in a batch are outlined in Section 9.

3.3 Other quality control terminology used in this procedure is based on SW-846, and is defined in the glossary section of the TestAmerica Denver Quality Assurance Manual (QAM).

4.0 Interferences

4.1 There are common compounds formed by the elements of interest (e.g., barium sulfate, beryllium oxide, silicon dioxide, crystalline silicates, titanium dioxide, etc.) that are not efficiently dissolved using this EPA approved procedure.

4.2 Silicon or silica are occasionally requested as part of the Method 3050B digestion. However, this digestion will include only acid-soluble silicon, and will not dissolve crystalline silica. The analysis is for silicon, but the final result is sometimes expressed as silica rather than silicon.

4.3 Antimony and silver have poor solubility in dilute nitric acid solution. Therefore it is strongly recommended that these elements are determined by the ICP procedure that includes HCl as the final digestion acid. See Section 11.7.8 of this SOP.

4.4 Potential sources of trace metals contamination include metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.5 The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Attachment 1 for additional contamination control guidelines.

4.6 Boron and silica from the glassware will dissolve into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.7 Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents, and other matrix materials may not be digested using these methods if they are not soluble in acids. If physical interferences are present, they should be documented.

4.8 Allowing samples to boil or go dry during digestion may result in the loss of volatile metals or conversion of metals to insoluble forms. For example, antimony is easily lost by volatilization from hydrochloric media. If this occurs the sample must be re-prepared.

4.9 Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.10 Samples Requiring Additional Digestion Reagents

A few examples of types of samples that might require additional digestion reagents follow. It is very important to note situations where samples are not behaving normally. However, do not assume that adding additional reagents will be acceptable for the project, even if it is obvious that the digestion will be

incomplete without it. The situation must be discussed with the project manager and documented in a Nonconformance Memo (NCM), whether or not the variations suggested in the following examples are approved.

4.10.1 Samples with high organic content may require additional nitric acid and/or hydrogen peroxide for a thorough digestion, but these oxidizing reagents should be added very carefully to avoid violent reactions.

4.10.2 Samples with high concentrations of metal in the elemental form or refractory oxides may require additional hydrochloric acid for a thorough digestion. As an example, blasting sand used to remove paint from the hull of ships typically consists of 30% cupric oxide. Following 3050B exactly will produce results as low as 0.1% without additional hydrochloric acid, and increasing the volume of hydrochloric acid can produce results approaching the true copper concentration.

4.10.3 Highly alkaline materials may require larger volumes of acid than specified in this procedure.

4.10.4 If the use of extra digestion reagents is approved, the same volume of reagents must be added to all field samples and QC samples in the batch. Usually the method blank results will not be elevated. To ensure that the QC sample results accurately reflect sample results, the QC samples must be treated exactly like the samples.

5.0 Safety

5.1 Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

5.2 This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.3 Specific Safety Concerns or Requirements

5.3.1 Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.3.2 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.4 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Hydrogen Peroxide, H_2O_2	Oxidizer Corrosive Poison	1 ppm TWA 1.4 mg/m^3 TWA 75 ppm IDLH	Contact with other materials may cause fire. Eye contact may result in permanent eye damage. Causes eye and skin burns. Corrosive: May cause severe respiratory tract irritation. Harmful if swallowed, may cause digestive tract irritation or burns.
Nitric Acid, HNO_3	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid, HCl	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
(1) Always add acid to water to prevent violent reactions. (2) Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 Top-loading balance capable of accurately weighing to the nearest 0.01 grams.

NOTE: Balances are serviced annually and the accuracy checked daily using 3 standard masses. See SOP DV-QA-0014 for details.

6.2 Digestion "Hot Block" or equivalent heating device capable of maintaining a temperature of 90-95°C. The Hot Block temperature must be monitored separately for each unit. The temperature of each Hot Block is checked by placing a calibrated thermometer through a cap on a digestion tube that is filled approximately to the middle of the tube with water. The temperature is recorded on the preparation benchsheet.

6.3 Thermometers (non-mercury liquid filled or digital) that cover a temperature range including 80-110°C with 1°C increments clearly visible.

NOTE: Thermometers are calibrated before use and periodically as described in SOP DV-QA-0001.

6.4 Hot Block plastic digestion tubes, 50ml and 125 mL, disposable. The volumetric markings on the tubes are checked for each lot received to ensure accuracy of at least ± 3%. The documentation is kept on file in the Metals area.

6.5 Ribbed plastic cover, similar to a watch glass, for the digestion tubes; disposable.

6.6 Ahlstrom grade 55 filter paper, Fisher Q8 filter paper (acid washed), or equivalent.

6.7 Disposable plastic funnels.

6.8 Disposable wooden spatula for subsampling.

6.9 Centrifuge, capable of at least 2,000 rpm.

6.10 Graduated cylinder, 100 mL and 500 mL, capable of ± 3% accuracy.

6.11 Calibrated automatic pipettes with corresponding pipette tips or Class A glass volumetric pipettes.

NOTE: Mechanical pipettes are calibrated before use and monthly as described in SOP DV-QA-0008.

6.12 Class A volumetric flasks.

6.13 pH indicator strips (pH range 0 – 6).

7.0 Reagents and Standards

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is

of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1 Reagent water – Millipore DI system or equivalent, 10-18.2 megohm-cm. See SOP DV-QA-0026 for daily water monitoring procedure.

7.2 Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.3 Nitric acid (HNO_3), 5%

Add 5 mL of concentrated HNO_3 to approximately 900 mL of reagent water and dilute to 1 liter.

7.4 Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.5 30% Hydrogen peroxide (H_2O_2), reagent grade.

7.6 Glass beads, ≤ 1 mm diameter, washed with aqua regia (for AFCEE and DoD projects)

7.7 Standards

7.7.1 All standards must be NIST traceable. Unless purchased directly from NIST, the accuracy of each standard is verified before use, as described in SOP DV-QA-0015.

7.7.2 Storage and Shelf Life of Metal Standards

7.7.2.1 Standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. They are stored at room temperature.

7.7.2.2 Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.7.3 LCS and MS Spike Solution for ICP

7.7.3.1 ICP spike solutions are purchased as custom-made solutions from a commercial vendor at ready-to-use concentrations. No further dilutions are needed. Spikes are prepared as follows:

- Routine ICP: Add 1.0 mL of spike
- AFCEE/DoD ICP: Add 1.0 mL of spike to 1.0 g of glass beads

The resulting spike concentrations for each element are given in Table II.

7.7.3.2 ICP/MS spike solutions are also purchased as custom-made solutions from a commercial vendor at ready-to-use concentrations. No further dilutions are needed. 1.0 mL of spike solution is added to samples. The concentrations of the elements in the stock standard and the resulting concentrations

in samples are shown in Table III.

7.7.4 If a non-routine element is required that is not contained in the custom-made solution, single-element solutions from a commercial vendor may also be used.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2 Soil samples do not require chemical preservation, but are stored at 4 ± 2 °C until the time of analysis.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Soils	Glass	3 grams	Cool 4 ± 2°C	180 Days	N/A

[1] Inclusive of digestion and analysis.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. The process of establishing control limits, and the use of control charts are described more completely in DV-QA-003P, *QualityAssurance Program*. Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents.

9.3 Initial Demonstration of Capability

An initial demonstration of capability must be performed by analysts before digesting samples using this procedure. See Section 13 of this SOP for further details.

9.4 Minimum QC Elements in a Preparation Batch

Each preparation batch must contain a method blank (MB), a laboratory control sample (LCS), and a matrix spike/matrix spike duplicate (MS/MSD) pair. Note that some programs require an unspiked duplicate sample in place of or in addition to the duplicate matrix spike. Be sure to check special instructions in the laboratory LIMS. If clients specify specific samples for MS and MSD, the batch may contain multiple MS/MSD pairs.

9.5 Sample Count

Laboratory generated QC samples (method blanks, LCS, MS/MSD) are not counted towards the maximum 20 samples in a batch. Field QC samples are included in the batch count.

9.6 Method Blank (MB) One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. Soil method blanks are prepared by taking 5 mL or 5 g of reagent water through the procedure described in Section 11.

The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data.

Acceptance Criteria: Criteria for the acceptance of blanks are contained within the individual analytical method SOPs.

Corrective Action: If the method blank does not meet the criteria contained within the analytical method SOPs, the blank and all associated samples in the batch must be re-digested and reanalyzed.

9.7 Laboratory Control Sample (LCS)

9.7.1 One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure.

9.7.2 The spike solution described in Section 7.7.3 is used to prepare LCSs as follows:

- Routine ICP: Add 1.0 mL of spike
- AFCEE/DoD ICP: Add 1.0 mL of spike to 1.0 g of glass beads
- ICP/MS: Add 1.0 mL of spike

The resulting spike concentrations for each element are given in Table 2 and Table 3.
Incremental Sampling Method LCS's are spiked with 5ml of spike.

9.7.3 The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

Acceptance Criteria: Criteria for the acceptance of LCS results are contained within the individual analytical method SOPs.

Corrective Action: When LCS results fail to meet control limits, the LCS and all associated samples in the batch must be re-prepared and reanalyzed.

9.8 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

9.8.1 One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a second aliquot of a field sample to which known concentrations of target analytes have been added. A matrix spike

duplicate (MSD) is a third aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Samples identified as field blanks cannot be used for MS/MSD analysis.

9.8.2 The spike solution described in Section 7.7.3 is also used to prepare matrix spikes, as follows:

- ICP: Add 1.0 mL of spike
- ICP/MS: Add 1.0 mL of spike

The resulting spike concentrations for each element are given in Tables II through IV.

Incremental Sampling Method MS/MSD's are spiked with 5ml of spike.

9.8.3 The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process.

Note: The spike must be added after the sample aliquot but before any reagents.

Acceptance Criteria: Criteria for the acceptance of MS and MSD recoveries and the relative percent difference (RPD) between the MS and MSD results are contained within the individual analytical method SOPs.

Corrective Action: If any analyte recovery or RPD falls outside the established acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery for the LCS is also outside of established limits, corrective action must be taken. Corrective action will include re-preparation and reanalysis of the batch. Corrective action when MS results alone fail to meet control limits does not include repreparation of samples unless the results indicate that a spiking error may have occurred.

10.0 Calibration

Not applicable. This SOP addresses sample preparation only for subsequent ICP or ICP/MS analysis. Calibration of the measurement system is covered in the SOPs for the determinative methods.

11.0 Procedure

11.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is approved by the supervisor and then automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA

department also receives NCMs by e-mail for tracking and trending purposes. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

11.2 Sample Custody

11.2.1 Custody of samples is transferred from the Sample Control group to the Metals group, which is documented using the internal program, Sample Transfer Utility (see SOP DV-QA-0003 for details).

11.2.2 Proper sample identification is extremely important in any preparation procedure. Labeling of digestion tubes and bottles must be done in a manner to ensure connection with the proper sample.

11.3 Subsampling

11.3.1 It is not acceptable to simply collect 1.0 g off of the top of the sample. Samples must be mixed and incrementally subsampled to obtain a representative subsample. At a minimum, mix by stirring with a disposable wooden spatula. If there is insufficient room in the sample container to allow for proper mixing, refer to SOP DV-QA-0023, "Subsampling" for directions.

11.3.2 Select at least three incremental subsamples from different locations in the original sample to obtain a final subsample weight of 1.0 to 1.2 g in a digestion tube, and record the exact weight to the nearest 0.01 g. A 2.0-g sample size may also be used if needed to meet the reporting limits.

11.3.3 Measure additional aliquots for QC samples required in the batch and spike as required (see Section 9 for details).

11.4 Digestion of 10g sample aliquot obtained utilizing previously prepared Incremental Sampling Method soil aliquot

The Method 3050B digestion reagents are increased 5x to maintain the same chemistry as is used for a 1-2 gram subsample. 10g of sample is digested in 125ml tubes.

11.5 Initial Digestion Cycle with 1:1 Nitric Acid

11.5.1 Add approximately 5mL of reagent water to each digestion tube.

11.5.2 Add 5 mL of concentrated HNO_3, and mix the sample.

11.5.3 Place a ribbed cover on each tube.

11.5.4 Heat samples to 95°C, and reflux for 15 minutes without boiling.

NOTE: **DO NOT ALLOW SAMPLE TO BOIL OR GO DRY** during any part of the digestion. Doing so will result in the loss of analyte and the sample must be re-prepared.

11.5.5 Allow sample to cool before proceeding with the next step.

11.5.6 Record the start time, starting temperature, end time, and ending temperature in LIMS.

11.6 Second Digestion Cycle Using Concentrated Nitric Acid

11.6.1 Add 5 mL of concentrated HNO_3, and replace the ribbed cover.

11.6.2 Reflux at 95°C for 30 minutes. Add reagent water as needed to ensure that the volume of solution is not reduced to less than 5 mL.

11.6.3 If brown fumes are observed, this means that material in the sample is actively being oxidized. There may not be enough HNO_3 acid to complete the oxidation, and there could be violent reaction of the sample with peroxide in the third digestion step. For that reason, it is necessary to repeat the previous two steps until no more fumes are evolved.

11.6.4 Allow the sample to evaporate to 5 mL, while ensuring that no portion of the bottom of the beaker is allowed to go dry. Alternatively, heat at 95°C for 2 hours.

11.6.5 Allow the samples to thoroughly cool before proceeding.

11.7 Third Digestion Cycle Using Hydrogen Peroxide

11.7.1 Add 2 mL of reagent water to each tube.

11.7.2 Add 3 mL of 30 % H_2O_2 a few drops at a time. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence.

11.7.3 Replace the ribbed cover and heat sample until effervescence subsides.

11.7.4 Allow the sample to cool.

11.7.5 Continue adding 30% H_2O_2 in 1-mL increments with warming until effervescence is minimal or sample appearance is unchanged. If additional peroxide is added to a sample then it must also be added to the method blank and LCS

NOTE: Do not add more than a total of 10 mL of 30 % H_2O_2.

11.7.6 Continue heating at 95°C until the volume is reduced to approximately 5 mL. Alternatively the sample may be heated for 2 hours.

11.7.7 Allow the sample to cool

11.7.8 If samples will be analyzed by ICP, continue on with the fourth digestion step using HCl in step 11.7.8. If the samples will be analyzed by ICP/MS, skip the HCl digestion step and go to step 11.9.

11.8 Fourth Digestion Cycle for ICP Using Concentrated Hydrochloric Acid

11.8.1 If the sample is being prepared for ICP analysis, add 10 mL of concentrated HCl to the sample in the digestion tube, and cover with ribbed cover.

11.8.2 Reflux for an additional 15 minutes without boiling.

11.8.3 Allow the sample to cool.

11.9 Separating Undigested Solids from the Digestion Solution

11.9.1 Filter sample through filter paper into a measured 125ml bottle whose accuracy is documented to be better than ± 3%.

NOTE: In place of filtering, the samples, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.9.2 For samples digested by the incremental Sampling Method use a 500mL poly bottle that has been marked by pouring out 500mL of DI water from a graduated cylinder.

11.9.3 Wash the digestion tube and ribbed cover with reagent water to ensure quantitative transfer of all of the digestion solution.

11.9.4 Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.9.5 Re-volume sample to 100 mL with reagent water. This must be done volumetrically, rather than by weight. Record the final volume in TAL's. For Multi-Incremental samples the final volume is 500ml.

11.10 Documentation and Record Management

11.10.1 The following information must be recorded for each preparation batch. This information is entered into the LIMS system

- Batch number,
- List of samples,
- Initial sample weight and final digestion volume,
- Preparation analyst and date,
- Matrix,
- Preparation type,
- Identification of reagents and standards used, and
- Identification of all measuring and test equipment used (e.g., balances, thermometers, pipettes).

11.11 Antimony for Analysis by ICP-MS

11.11.1 Weigh 1.0 to 1.2g soil sample using sub sampling in digestion vessel.

11.11.2 Add 5-mL of reagent water to the blank, LCS/LCSD and samples.

11.11.3 Spike LCS/LCSD, MS, MSD with 1.0 mL 200.8 CAL-2.

11.11.4 Add 2.5-mL conc. HNO_3 and 2.5 mLs conc. HCI to each sample and QC.

11.11.5 Cover with a watch glass and reflux on hot block set at 95°C (c overed container of water) for 15 minutes.

11.11.6 Filter through Ahlstrom 55 into 100-mL vessel while still hot.

11.11.7 Rinse with hot 1.25mls (~95°C) conc. HCI.

11.11.8 Rinse 3X with hot (95°C) reagent water (5mL rinses .)

11.11.9 Place the filter paper and soil residue back into the original sample digestion vessel. Add 2.5 mLs conc. HCI, cover and reflux on hot block for 20 minutes or until paper dissolves.

11.11.10 Filter through Ahlstrom 55 adding to the original filtrate. Rinse 3X with

reagent water. (5mL rinses.)

11.11.11 Bring to final volume of 100 mL with reagent water.

12.0 Calculations / Data Reduction

Not applicable. Calculations of final results are described in the determinative analytical SOPs.

13.0 Method Performance

13.1 Method Detection Limit (MDL)

An MDL must be determined for each analyte/matrix prior to the analysis of any samples. See the SOPs for the determinative analysis methods for details.

13.2 Initial Demonstration Study

This requires the analysis of four QC check samples. The QC check sample is a well-characterized, laboratory-generated sample used to monitor method performance, which should contain all the analytes of interest. Typically this is the LCS. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

13.2.1 Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

13.2.2 Calculations and acceptance criteria for QC check samples are given in the determinative SOPs for ICP/MS and ICP (DV-MT-0002 and DV-MT-0012, respectively).

13.3 Training Qualification:

The group leader or supervisor has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

14.0 Pollution Control

Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

15.0 Waste Management

15.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, “Waste Management and Pollution Prevention”, of the Environmental Health and Safety Manual, and DV-HS-001P, “Waste Management Program.”

15.2 The following waste streams are produced when this method is carried out:

15.2.1 Aqueous Acidic (Metals) - Corrosive – Waste Stream J

15.2.2 Radioactive waste, mixed waste, and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of these materials.

16.0 References

16.1 Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, December 1996; Method 3050B.

16.2 Department of Defense Quality Systems Manual for Environmental Laboratories, Final Version 4.2, 10/25/2010.

16.3 Department of Defense Quality Systems Manual for Environmental Laboratories Version 5.0, July 2013.

17.0 Method Modifications:

Item	Method	Modification
1	3050B	Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.
2	3050B	Section 7.5 digestion for Sb was modified to add less HCL to limit the interference on the ICPMS instrument.

18.0 Figures, Tables, and Attachments

Figure 1: Soil Sample Preparation Flowchart
Figure 2: Soil Sample Preparation Flowchart for Antimony by ICP-MS
Table 1: Method 3050B Approved Analyte List for ICP/ICP-MS
Table 2: Soil LCS and MS/MSD Spikes for ICP
Table 3: Soil LCS and MS/MSD Spikes for ICP-MS

Attachment 1: Contamination Control Guidelines

19.0 Revision History

- Revision 6 dated 31 March 2014
  - Annual Review
  - Formatting changes throughout document
  - Added to Section 11.7.5 to add additional peroxide to QC if added to samples
  - Updated section number in text to 11.8 in section 11.7.8
  - Added references for DoD QSM
  - Removed Attachment 2

- Revision 5 dated 04 March 2013
  - Section 7.7.3.1 Added DoD to the glass beads requirement
  - Section 11.11.2 Added that 5ml of water is added to the samples
  - Section 11.11.3 Changed spike name to 200.8 Cal-2

- Updated spike level to 1.0ml in Table 3
- Updated work instructions to current revision.
- Formatting changes throughout document

- Revision 4 dated 3 February 2012
  - Changed references of Multi-Incremental Sampling to Incremental Sampling Method throughout document
  - Section 2.0 Added reference to Incremental Sampling Method
  - Section 6.4 Added 50 mL digestion tubes
  - Added introductory statement to section 7.0 regarding reagent purity
  - Section 7.1 Updated acceptable criteria for the reagent water
  - Section 9.7.2 Added LCS Incremental Sampling Method spike amounts
  - Section 9.8.2 Added MS/MSD Incremental Sampling Method spike amounts
  - Section 11.4 Updated sample amount for Incremental Sampling Method to 1 10g aliquot
  - Section 11.9 Added Incremental Sampling Method final volume

- Revision 3.5, dated 24 August 2011
  - A note has been added to section 9.8.3 for the addition of the LCS/MS spike before reagents.

- Revision 3.4, dated 01 September 2010
  - Annual Technical Review
  - Updated documentation in section 11.10 to reference new LIMS.
  - Updated Section 11.11 and Figure 2 to reference current HCL amount used. Added method modification to digestion in Section 17.
  - Added Bismuth to Table 2
  - Updated Figure 2
  - Removed Example prep sheets (Attachments 2 – 4)
  - Updated work instruction WI-DV-015 (Attachment 5 now Attachment 2)

- Revision 3.3, dated 17 August 2009
  - Sections 11.3.2 and 11.11.1: Updated amount of sample used to range from 1.0 to 1.2g.
- Revision 3.2, dated 28 April 2009
  - Sec 6.6: Updated filter paper from Whatman No. 541 to Ahlstrom grade 55.
  - Sec 7.6: Added glass beads to DoD projects.
  - Sec 7.7.3.1: Removed ICPMS spike from this section.
  - Sec 7.7.3.2: Updated spike volume to 1.0ml for ICPMS.
  - Table 3: Updated ICPMS spike level to 1.0ml.

- Revision 3.1, dated 28 May 2008
  - The spiking amount for LCS, MS and MSD was changed from 0.2 mL to 1.0 mL for ICP-MS.

- Revision 3, dated 12 October 2007
  - Integration for TestAmerica and STL operations.
  - Added reference to SOP DV-OP-0015 for Multi-Incremental Subsampling Preparation of Soil Aliquots
  - Removed references to Graphite Furnace Atomic Absorption Analysis

- Revision 2.3, dated 11 November 2005
    - Section 6.3: Replaced the specification to use a mercury thermometer with a non-mercury thermometer.
    - Section 6.4: The Hot Block digestion tube volume was changed from 60 mL to 125 mL.
    - Section 6.6: Whatman No. 41 filters were changed to Whatman 541, or Fisher Q8 (acid washed) filters.
    - Section 6.14: This section, which specified HDPE plastic bottles for storing digested samples, was removed. The digests are stored in the Hot Block tubes.

    - Section 7.7.3.2: The volume of spike solution used for ICP/MS samples was changed from 1.0 mL to 0.2 mL.
    - Section 9.7.2: Added the volume of spike used for ICP-MS, i.e., 0.2 mL.
    - Item 9.8.2: Added the volume of spike used for ICP-MS, i.e., 0.2 mL.
    - Section 11.7.8: Added information concerning the use of HCL for Sb analysis.
    - The Safety Section 5 and the Waste Management section 15 were updated to current STL Corporate requirements.
    - Added examples of preparation bench sheets as Attachments 2, 3, 4, and 5.

Figure 1.

Soil Sample Preparation Flowchart
(Page 1)

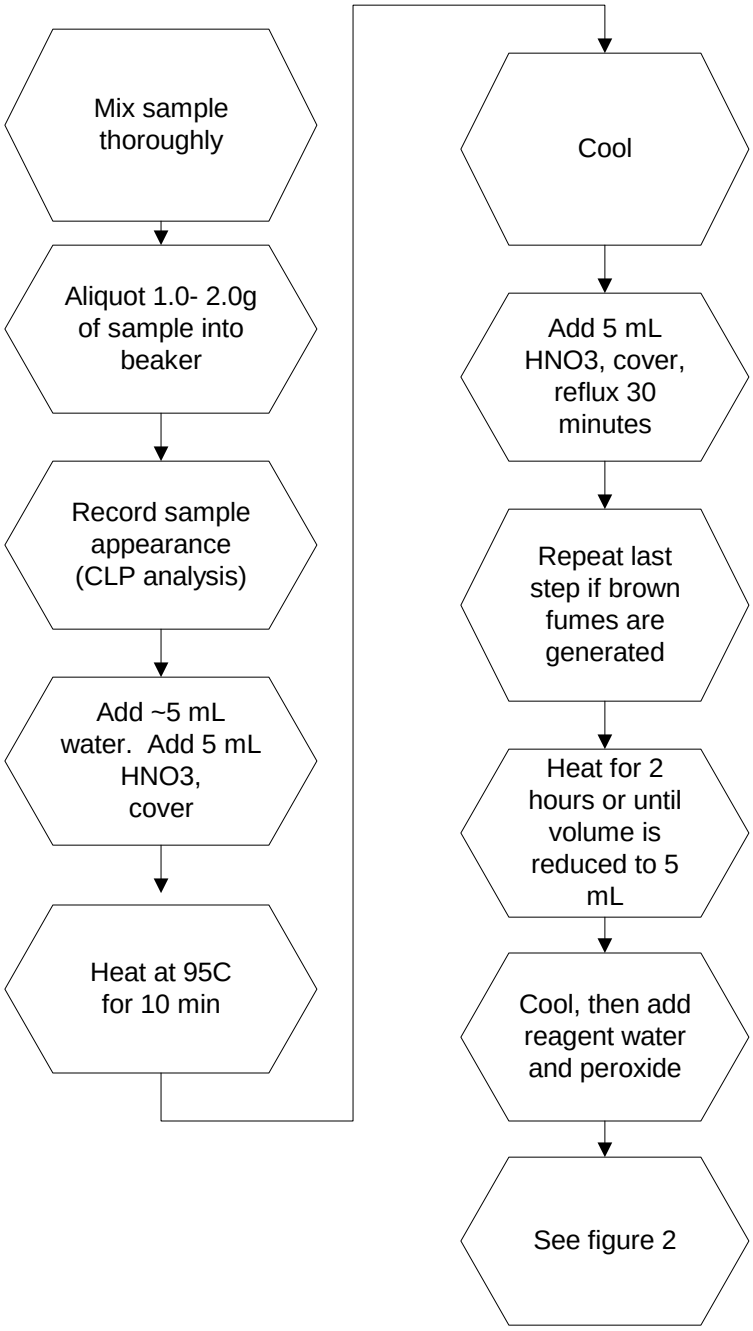

Figure 1. (continued)

Soil Sample Preparation Flowchart
(Page 2)

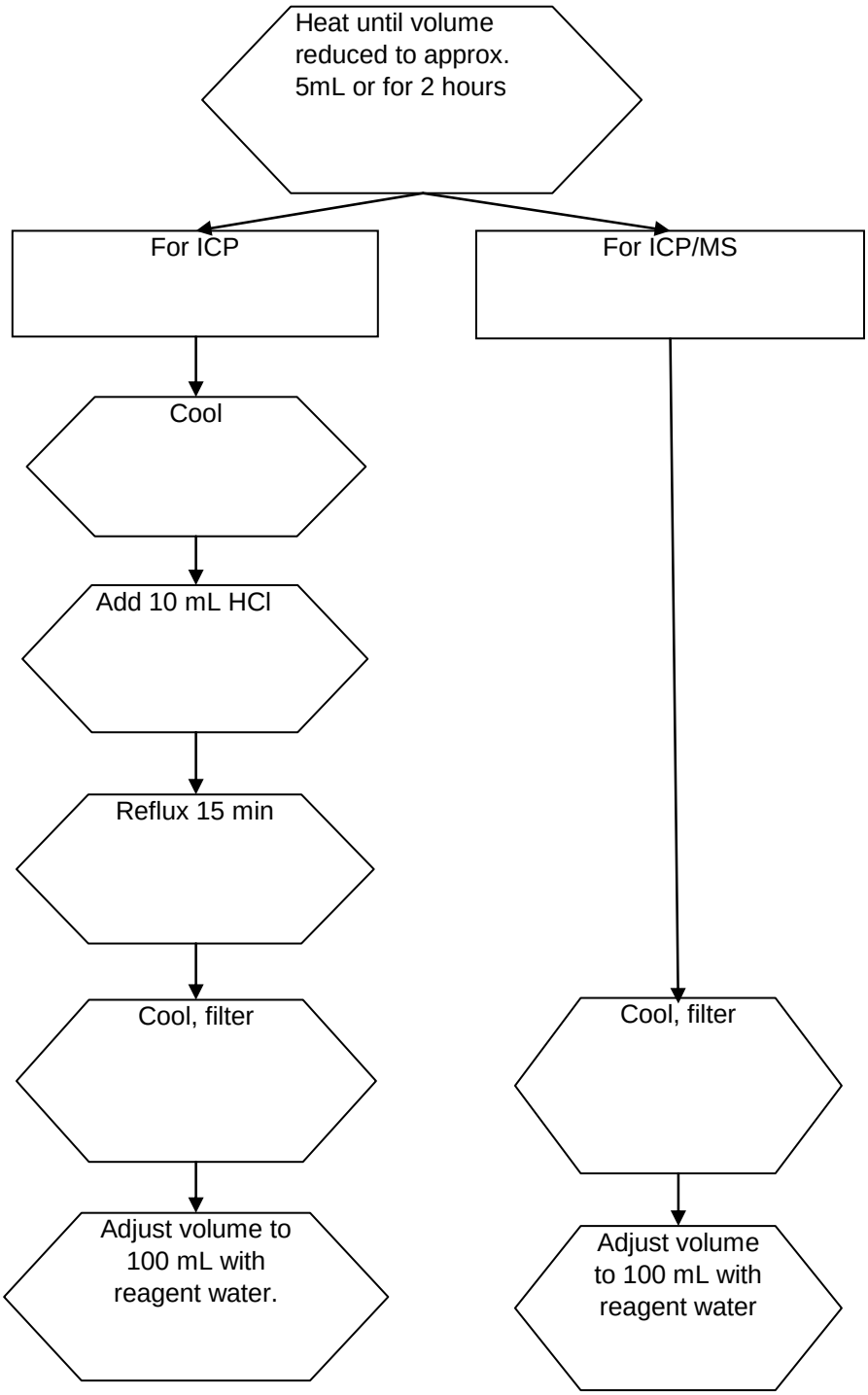

Figure 2

Soil Sample Preparation Flowchart for "Hot" Antimony by ICP-MS

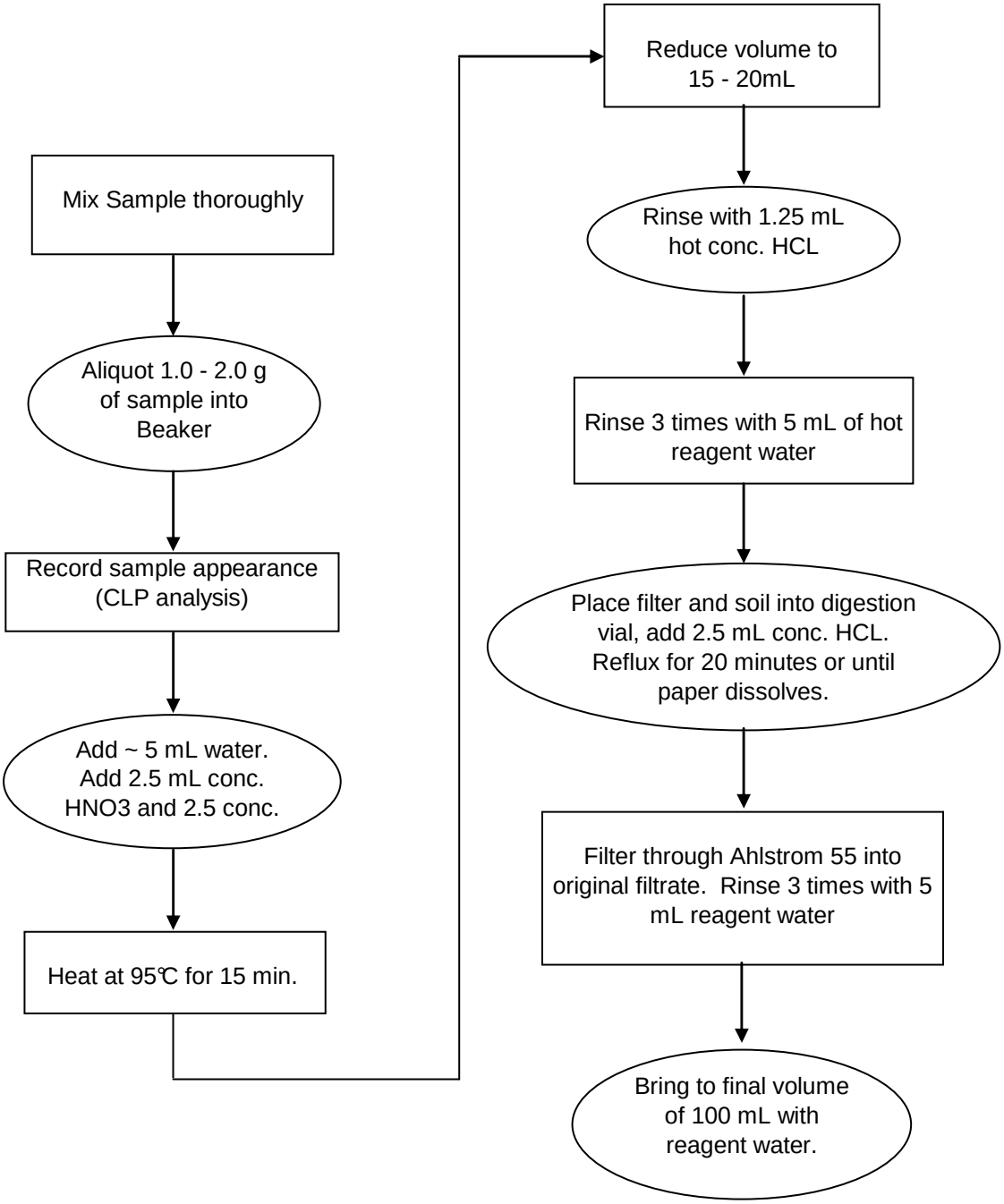

Table 1.

Method 3050B Approved Analyte List for ICP/ICP-MS

ELEMENT	Symbol	CAS Number
Aluminum	Al	7429-90-5
Antimony	Sb	7440-36-0
Arsenic	As	7440-38-2
Barium	Ba	7440-39-3
Beryllium	Be	7440-41-7
Cadmium	Cd	7440-43-9
Calcium	Ca	7440-70-2
Chromium	Cr	7440-47-3
Cobalt	Co	7440-48-4
Copper	Cu	7440-50-8
Iron	Fe	7439-89-6
Lead	Pb	7439-92-1
Magnesium	Mg	7439-95-4
Manganese	Mn	7439-96-5
Molybdenum	Mo	7439-98-7
Nickel	Ni	7440-02-0
Potassium	K	7440-09-7
Selenium	Se	7782-49-2
Silver	Ag	7440-22-4
Sodium	Na	7440-23-5
Thallium	Tl	7440-28-0
Vanadium	V	7440-62-2
Zinc	Zn	7440-66-6

Table 2.

Soil LCS and MS/MSD Spikes for ICP

ELEMENT	Stock Standard (mg/L)	Sample Spike (mg/kg)	Final Digested Solution (mg/L)
Aluminum	200	200	2.0
Antimony	50	50	0.5
Arsenic	100	100	1.0
Barium	200	200	2.0
Beryllium	5	5	0.050
Bismuth	200	200	2
Boron	100	100	1.0
Cadmium	10	10	0.1
Calcium	5000	5000	50.
Chromium	20	20	0.20
Cobalt	50	50	0.50
Copper	25	25	0.25
Iron	100	100	1.0
Lead	50	50	0.50
Lithium	100	100	1.0
Magnesium	5000	5000	50.
Manganese	50	50	0.50
Molybdenum	100	100	1.0
Nickel	50	50	0.50
Phosphorous	1000	1000	10.
Potassium	5000	5000	50.
Selenium	200	200	2.0
Silica	1000	1000	10.
Silver	5	5	0.050
Sodium	5000	5000	50.
Strontium	100	100	1.0
Thallium	200	200	2.0
Thorium	100	100	1.0
Tin	200	200	2.0
Titanium	100	100	1.0
Uranium	200	200	2.0
Vanadium	50	50	0.50
Zinc	50	50	0.50
Zirconium	50	50	0.5

NOTE: Final soil spike concentration based on the addition of 1.0 mL stock standard to 1.0 g of sample, which is then digested to produce a 100 mL final volume.

Table 3.

Soil LCS and MS/MSD Spikes for ICP-MS

ELEMENT	Stock Standard (mg/L)	Sample Spike (mg/kg)	Final Digested Solution (µg/L)
Aluminum	20	20	200
Antimony	20	20	200
Arsenic	20	20	200
Barium	20	20	200
Beryllium	20	20	200
Cadmium	20	20	200
Chromium	20	20	200
Cobalt	20	20	200
Copper	20	20	200
Lead	20	20	200
Manganese	20	20	200
Molybdenum	20	20	200
Nickel	20	20	200
Selenium	20	20	200
Silver	20	20	200
Thallium	20	20	200
Tin	20	20	200
Titanium	20	20	200
Uranium	20	20	200
Vanadium	20	20	200
Zinc	20	20	200

NOTE: Final soil spike concentration based on the addition of 1.0 mL stock standard to 1.0 g of sample, which is then digested to produce a 100 mL final volume.

Attachment 1

Contamination Control Guidelines

The following procedures are strongly recommended to prevent contamination:

- All work areas used to prepare standards and spikes should be cleaned before and after each use.
- All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.
- Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.
- Powdered or Latex Gloves should not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes.
- Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.
- Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

- Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.
- Improper cleaning of glassware can cause contamination.
- Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

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Title: Acid digestion of Aqueous Samples for Analysis by ICP- MS [SW-846 3005A, 3020A, 3050B and EPA Method 200.8.]

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1.0 Scope and Application

1.1 This procedure describes the preparation of aqueous samples for the analysis of metals by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) using EPA Method 200.8, and SW-846 Methods 3005A, 3020A, and 3050B.

1.2 Aqueous samples also include TCLP & SPLP Leachates, aqueous equipment rinse blanks for soil sampling. In some cases, where the associated soil samples require the SW-846 Method 3050B, Section 7.5, optional treatment to improve solubility and recovery of Sb, Ag, and Sn. The client may require that the aqueous equipment blank receive the same treatment. Refer to section 10.14 for this prep.

1.3 The applicability of each of these preparation protocols to specific analytes is detailed in the TestAmerica LIMS System (TALS). Additional elements may be analyzed following digestion by these protocols, provided that the method performance criteria specified in Section 12.0 of this SOP are met.

1.4 This SOP provides procedures applicable to the preparation of dissolved, total recoverable, potentially dissolved, and total metallic elements in ground water, aqueous samples, aqueous sludges, aqueous wastes, aqueous air sampling media, and leachates/extracts. This SOP is not applicable to samples that contain or consist of oil or other immiscible organic solvents.

NOTE: Samples that are known to be immiscible with water, e.g., contain or consist of oil or other immiscible organic solvents should be logged with a waste matrix and subbed out to a different TestAmerica laboratory for digestion and analysis.

1.5 SW-846 Method 3005A is used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by ICP-MS. Although digestion is not specifically required by the method (SW-846 3005A section 2.2) for dissolved samples, the standard operating procedure at TestAmerica Denver is for all matrices to be digested prior to analysis.

1.6 EPA Method 200.8 Section 11.2 is used to prepare surface water, and domestic and industrial waste samples for total recoverable and dissolved metals.

1.7 SW-846 Method 3020A is used to prepare aqueous samples, TCLP leachates, SPLP leachates and aqueous wastes that contain suspended solids for total metals analysis by ICP-MS.

1.8 The following table lists the sample preparation methods that are covered in this SOP and the specific section of this SOP for each preparation method. Prepared samples are analyzed by inductively coupled plasma-mass spectrometry (ICP-MS).

PREPARATION METHOD	SOP SECTION	DETERMINATIVE METHOD	ANALYTICAL SOPS #
Method – 3020A Total	10.10	ICP-MS	DV-MT-0018 DV-MT-0022
Method – 3005A Total Rec./Dissolved	10.11	ICP-MS	DV-MT-0018 DV-MT-0022
Method 200.8 – Total Rec.	10.12	ICP-MS	DV-MT-0002
Method 200.8 – Dissolved	10.12	ICP-MS	DV-MT-0002
Method - 3050B Special Sb Prep	10.13	ICP-MS	DV-MT-0018 DV-MT-0022

2.0 Summary of Method

2.1 Method 3005A, Acid Digestion of Waters for Total Recoverable or Dissolved Metals.

This preparation method is used for total recoverable and dissolved metals analysis by ICP-MS method 6020 and 6020A. A representative aliquot of sample is heated with nitric acid and substantially reduced in volume. The digestate is diluted to volume and then filtered (if necessary).

2.2 Method 3020A, Acid Digestion of Aqueous Samples and TCLP/SPLP Leachates for Total Metals.

This preparation method is used for total metals analysis by ICP-MS method 6020 and 6020A. A representative aliquot of sample is refluxed with nitric acid. This step is repeated until the digestate is light in color or until its color has stabilized. The digestate is diluted to volume and then filtered (if necessary).

2.3 Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry.

This preparation method is used for metals analysis by ICP-MS method 200.8. A representative aliquot of sample is refluxed with nitric and hydrochloric acids. The digestate is diluted to volume and then filtered (if necessary).

3.0 Definitions

Additional definitions of terms used in this SOP may be found in the glossary of the QAM.

- Dissolved Metals: The concentration of metals determined in a sample after the sample is filtered through a 0.45-μm membrane (Method 3005A). (The sample is acidified after filtration).

- Total Metals: The concentration of metals determined in an unfiltered sample following digestion (Method 3020A).

- Total Recoverable Metals: The concentration of metals determined in an unfiltered sample following treatment with hot, dilute mineral acid (Method 200.8 and Method 3005A).

- Potentially Dissolved Metals: An acidified sample is filtered between 8- 96 hours following acidification and the filtrate is digested using Method 3005A.

- Refer to the Glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and policy DV-QA-003P, *Quality Control Program*, for definitions of general analytical and QA/QC terms.

4.0 Interferences

4.1 There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include the following: metallic or metal-containing labware (e.g., latex gloves coated with talc, which contains high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2 The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix A for additional contamination control guidelines.

4.3 Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents, and other matrices may not be digested using these methods if they are not soluble in acids. If physical interferences are present, they should be documented.

4.4 Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.5 Allowing samples to boil or go dry during digestion may result in the loss of volatile metals. If this occurs, the sample must be re-prepared.

4.6 Specific analytical interferences are discussed in the ICP-MS determinative method SOPs, e.g., DV-MT-0002, DV-MT-0018, and DV-MT-0022.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual, and this document.

5.1 Specific Safety Concerns

5.1.1 Samples that contain high concentrations of carbonates or organic material, or samples that are at elevated pH can react violently when acids

are added.

5.1.2 The digestion solution must be cooled sufficiently before adding hydrogen peroxide (H_2O_2) to avoid a reaction and possible violent effervescence, or boiling over of the digestion solution.

5.1.3 Care must be taken when handling the digestion tubes. The tubes may become very hot during the digestion procedure. Allow the tubes to cool before attempting to touch the sample digestate.

5.1.4 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating.This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table.A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material [(1)]	Hazards	Exposure Limit [(2)]	Signs and Symptoms of Exposure
Hydrogen Peroxide	Oxidizer Corrosive	1 ppm (TWA)	Vapors are corrosive and irritating to the respiratory tract. Vapors are very corrosive and irritating to the eyes and skin.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm (TWA) 4 ppm (STEL)	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage

Material [1]	Hazards	Exposure Limit [2]	Signs and Symptoms of Exposure
Hydrochloric Acid	Corrosive Poison	5 ppm (Ceiling)	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

(1) Always add acid to water to prevent violent reactions.

(2) Exposure limit refers to the OSHA regulatory exposure limit.

6.0 Equipment and Supplies

6.1 Instrumentation

6.1.1 Digestion block, with adjustable heating, capable of maintaining a sample temperature of 85 - 95 °C.

6.1.2 Thermometer that covers a temperature range of at least 80 - 110 °C.

6.1.3 Centrifugation equipment (if desired method of removing particulate material is centrifugation).

6.2 Supplies

6.2.1 Disposable digestion tubes, with volume accuracy verified to ± 3% gravimetrically prior to use. See SOP DV-QA-0008.

6.2.2 Watch glasses, ribbed or equivalent, or disposable digestion tube covers.

6.2.3 Whatman GD/XP - PVDF membrane, 0.45-micron syringe filters, No. 6973-2504, for trace metal analysis, or equivalent. When used to filter any sample in a preparation batch or analytical batch, filters of the same type are also used to filter the method blank and the LCS in the batch. Acceptable results for the QC samples demonstrate that the filters neither add nor subtract analytes.

6.2.4 Syringes or equivalent filtration apparatus.

6.2.5 Repipettors or suitable reagent dispensers.

6.2.6 Calibrated automatic pipettes with pipette tips or Class A glass volumetric pipettes.

6.2.7 Class A volumetric flasks.

6.2.8 pH indicator strips (pH range 0 - 6).

6.2.9 Plastic digestate storage bottles.

7.0 Reagents and Standards

7.1 Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative method SOPs, e.g., DV-MT-0002, DV-MT-0018, and DV-MT-0022.

7.2 Laboratory control sample (LCS), and matrix spike and matrix spike duplicate (MS/MSD) spike solutions are purchased as custom TestAmerica Denver solutions. Standards are logged into the Reagents module of TALS and are assigned unique identification numbers that can be used to access traceability information. The TALS identification numbers are recorded on the metals prep bench sheet.

7.2.1 All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. These plastic bottles may be stored in a glass jar.

7.2.2 Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.2.3 See TALS for the list of spiking levels. A volume of 0.1 mL of each working spike solution is added to the 50-mL final sample volume.

7.3 Nitric Acid (HNO_3), concentrated, trace-metal grade or better.

NOTE: When preparing diluted acids, always add acid to water. If the water is added to the acid, the sudden increase in temperature may cause splashing.

7.4 Nitric Acid, 1:1

Dilute concentrated HNO_3 with an equal volume of reagent water.

7.5 30% Hydrogen Peroxide (H_2O_2), ultra pure grade.

7.6 Hydrochloric Acid (HCl), concentrated, trace metal grade or better.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Waters	HDPE Or Glass	500 mLs	HNO_3, pH < 2;	180 Days	40 CFR Part 136.3
Soils	Glass	4 oz	Cool 4 $\pm$ 2°C	180 Days	N/A

[1] Inclusive of digestion and analysis.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the TALS login, sample or method comments and/or program QAS to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, *Quality Control Program*.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, *QA/QC Requirements for Federal Programs*.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in TALS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified appropriately. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Table 2 provides a summary of quality control requirements, including type, frequency, acceptance criteria, and corrective action.

9.3 Initial Performance Studies

Before analyzing samples, the laboratory must establish a method detection limit (MDL). In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument he/she will be using. Ongoing

proficiency must be demonstrated by each analyst on an annual basis. See Section 12.1 for more details on detection limit studies, initial demonstrations of capability, and analyst training and qualification.

9.4 Preparation Batch

A preparation batch is a group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, an LCS, a matrix spike (MS), and a matrix spike duplicate (MSD). For samples logged in under Method 200.8, there must be two MS/MSD pairs for every batch containing more than ten samples. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify samples for the MS/MSD pair, then the batch may contain multiple MS/MSD pairs to accommodate client requests. Clients may also request a duplicate LCS (LCSD). In cases where the client has not provided sufficient sample to prepare an MS and MSD, an LCS and LCSD will be prepared instead.

9.5 Sample Count

Laboratory-generated QC samples (method blanks, LCSs) are not included in the sample count for determining the size of a preparation batch. The MS and MSD are usually not included in the sample count.

NOTE: For samples prepared under any AFCEE QAPP, all MSs and MSDs are included in the sample count.

9.6 Method Blank (MB)

The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. When samples are filtered in the laboratory for determination of dissolved metals, then the blank is filtered using a filter of the same type that was used for the samples. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false-positive data.

Acceptance Criteria: The method blank should not contain any analyte of interest at or above ½ the reporting limit (RL) or at or above 10% of the measured concentration of that analyte in associated samples, whichever is higher. In other words, the sample result must be a minimum of 10 times higher than the blank contamination level when the blank level is greater than ½ the RL. An exception is made for common laboratory contaminants (see section 16.1.1).

Corrective Action: If the method blank does not meet the criteria, the blank and all associated samples in the batch must be re-digested and reanalyzed. If the method blank is greater than ½ the RL and the samples have no detectable concentration of the

analyte of interest at or above the RL, the sample results may be reported with appropriate qualifiers if allowed by the project requirements. If allowed the PM must be notified and an NCM generated.

9.7 Laboratory Control Sample (LCS)

One aqueous LCS must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. When samples are filtered in the laboratory for determination of dissolved metals, then the LCS is filtered using a filter of the same type that was used for the samples. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

Acceptance Criteria: LCS recovery control limits are set at ± 3 standard deviations about the historical mean. These limits must not be wider than 85 - 115 % recovery for Method 200.8, or 80 - 120 % for Method 6020. The control limits are maintained in TALS.

Corrective Action: If the LCS % recovery falls outside of the control limits for any analyte, that analyte is judged to be out of control. All associated samples must be reprocessed for analysis. One possible exception is a recovery for a given element above the upper control limit with no detection for the same element in the samples. This latter case must be explained in the case narrative.

9.8 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client-specific data quality objectives (DQOs) may require the use of sample duplicates in place of or in addition to MS/MSDs. At least one MS/MSD pair must be processed for each preparation batch. Some client programs require a 10 % MS/MSD analysis frequency. If insufficient sample is available to process an MS/MSD pair, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria.

The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks, equipment blanks, or rinse blanks cannot be used for MS/MSD analysis.

Acceptance Criteria: The recovery for each analyte must fall within established limits. The relative percent difference (RPD) between the MS and MSD must be less than or equal to the established RPD limit. If any analyte recovery or relative percent difference (RPD) between the MS and MSD falls outside the

acceptance range, the recovery of that analyte must be in control for the LCS.

Corrective Action: If MS results fail to meet control limits, but the LCS results are within limits, then samples do not require re-preparation and reanalysis unless the results indicate that a spiking error may have occurred.

9.9 Quality Assurance Summaries

Certain clients may require specific project or program QC that may supersede the SOP requirements. Quality Assurance Summaries (QASs) are developed to address these requirements.

10.0 Procedure

Sample Preparation

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervisors to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

10.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

10.3 All samples are to be checked out of Sample Control with the Internal Chain of Custody in TALS properly completed.

10.4 Proper sample identification is extremely important in any preparation procedure. Labeling of beakers, digestion tubes, and bottles must be done in a manner to ensure connection with the proper sample.

10.5 Samples are typically logged in as either waters or soils. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating sample preparation, examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous, but it appears to be more like a waste (biphasic, oil, sludge-like, organic liquid, lots of sediment, etc.), then contact the project manager and the laboratory group leader for further instructions.

10.6 If possible, prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab, data review, and reporting groups.

10.7 Guidelines are provided in Appendix A on procedures to minimize contamination of

samples and standards.

10.8 All data shall be recorded directly on the described forms, logbooks, electronic forms, or directly in TALS at the time of data generation. It is not acceptable to record data on loose papers, scraps of paper, gloves, sample vials, or "Post-It" notes. Data may be recorded on paper bench sheets if the sheets are subsequently scanned and saved in a designated folder on the company server.

10.9 Aqueous Sample Preparation Setup

The following setup procedure must be followed for all aqueous samples prior to performing the specific digestion procedure:

10.9.1 Sample pH is verified during sample receipt. When a sample is received with improper/insufficient preservation, the sample is delivered with notification of the deficiency.

10.9.1.1 Measure the sample pH with pH paper using a separate aliquot of sample. Do not put the pH paper directly into to bottle. Record the pH on a copy of the internal chain of custody (ICOC). When all of the samples have been tested, initial and date the copy of the ICOC, scan it, and save it to the Metals folder on the G: drive.

10.9.1.2 If the pH>2 for a sample requiring acidic preservation, add 1-2 mL of conc. HNO_3 to the sample. Replace the lid and mix.

10.9.1.3 Recheck the pH of the sample. If the pH<2, record the sample in the Metals preservation logbook. If the pH>2, repeat 10.9.1.2 until pH<2 or 5mls has been added. If the sample still has a pH greater than 2 do not add any additional acid and create an NCM. Add the sample to the Metals preservation logbook

10.9.1.4 Allow the sample to sit for 8-16 hours following acidification.

10.9.1.5 After 8-16 hours, recheck the pH of the sample. If the pH<2, proceed with the appropriate digestion procedure. Note the date/time of this pH recheck in the Metals preservation logbook.

10.9.1.6 If after 8-16 hours the pH>2, repeat steps 10.9.1.2 through 10.9.1.5 until the pH remains <2 following the 8-16 hour period or 5mls of HNO_3 has been added.

Note: Acid must be added at least 24 hours before analysis.

10.9.2 Select the unfiltered fraction for a total or total recoverable analysis or the filtered fraction for a dissolved analysis. For SPLP select the proper

sample leachates.

NOTE: Samples requiring dissolved metals determination are either filtered and preserved in the field or are filtered and preserved by the laboratory as soon as possible after receiving the samples. When filtered in the laboratory, the filtration and preservation are recorded in the Laboratory Sample Filtration and Preservation Logbook, including the preservative type and lot number. Filter acceptability is demonstrated by using filters of the same type to filter samples and batch QC samples when preparation batches include samples that were filtered in the laboratory. The results of the analysis of the batch QC samples are used to demonstrate that the filtration process neither adds nor subtracts target analytes from samples.

10.9.3 Mix the sample by shaking the container.

10.9.4 Measure and transfer 50 mL of the sample into a digestion tube. When using calibrated digestion tubes, pour the sample into the tube to the 50-mL mark. Record the lot number of the digestion tubes in TALS.

10.9.5 Measure two extra aliquots of the sample that is selected for the MS/MSD analysis. Spike each aliquot with 0.1 mL of each spiking solution (see TALS). Record the standards and pipette identifications in TALS.

10.9.6 Measure and transfer 50 mL of reagent water into a digestion tube for the method blank. If a determination of dissolved metals is requested, use filtered reagent water for the method blank.

10.9.7 Measure and transfer 50 mL of reagent water into a digestion tube for the LCS and add 0.1 mL of spiking solution (see Table 2). Record the standards and pipette identifications in TALS. If determination of dissolved metals is requested (preparation method 3005A), and one or more samples were filtered in the laboratory, then filter the LCS using a filter of the same type that was used to filter the sample(s).

10.10 Proceed to the appropriate Section of this SOP for the desired preparation method as follows:

Preparation Method*	SOP Section	Analytical Method
3020A Total Metals	10.10	Method 6020
3005A Total Recoverable	10.11	Method 6020
3005A Dissolved Metals	10.11	Method 6020
200.8 Total Recoverable	10.12	Method 200.8

Metals		
200.8 Dissolved Metals	10.12	Method 200.8
3050B Special Sb prep	10.13	Method 6020

(See also WI-DV-017)

10.11 Method 3020A - Preparation for Total Metals Analysis by ICP-MS Method 6020 and 6020A

10.11.1 To the sample in a digestion tube, add 1.5 mL of concentrated HNO_3.

10.11.2 Heat at 90 - 95 °C until the volume is reduced to approximately 5 mL. Record the start time and the Hot Block temperature in TALS.

CAUTION: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be re-prepared and reanalyzed.

10.11.3 Allow the digestion tube to cool in a fume hood.

10.11.4 Add 1.5 mL of concentrated HNO_3. Cover and reflux gently.

10.11.5 Continue heating, adding additional acid as necessary in 1-2 mL increments to ensure a complete digestion. Record the start and stop times and the Hot Block temperature in TALS.

NOTE: Digestion is complete when the digestate is light in color and does not change in appearance with continued refluxing.

10.11.6 Evaporate to low volume, approximately 3 - 5 mL.

10.11.7 Allow the digestion tube to cool, then add about 10 mL of reagent water.

10.11.8 Replace the cover and continue warming for 10 to 15 minutes to allow additional solubilization of any residue to occur. Record the stop time in TALS.

10.11.9 Allow the sample to cool and rinse the watch glass into the digestion tube with reagent water.

10.11.10 Re-Volume to 50 mL with reagent water, cap and mix thoroughly.

10.11.11 The sample is now ready for ICP-MS analysis. Refer to SOP DV-MT-0018 or DV-MT-0022.

NOTE: If insoluble materials are present in a sample digestate, the ICP-MS analyst may filter the sample prior to analysis.

Refer to SOP DV-MT-0018 or DV-MT-0022 for additional details.

10.12 Method 3005A - Preparation for Total Recoverable and Dissolved Metals Analysis by ICP-MS Method 6020 and 6020A

10.12.1 To the sample in a digestion tube, add 2.0 mL of concentrated HNO_3.

10.12.2 Heat the sample to 90 - 95 °C and cautiously evaporate to a low volume of 15 - 20 mL, while ensuring that no portion of the sample container is allowed to go dry. Record the start and stop times and the Hot Block temperature in TALS.

CAUTION: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be re-prepared.

10.12.3 Allow the sample to cool in a fume hood.

10.12.4 Rinse the digestion tube with reagent water.

10.12.5 Re-Volume to 50 mL with reagent water, cap and mix thoroughly.

10.12.6 The sample is now ready for ICP-MS analysis. Refer to SOP DV-MT-0018.

NOTE: If insoluble materials are present in a sample digestate, the ICP-MS analyst may filter the sample prior to analysis. Refer to SOP DV-MT-0018 or DV-MT-0022 for additional details.

10.13 Method 200.8 - Preparation for Total Recoverable/Potentially Dissolved/Dissolved Metals Analysis by ICP-MS

10.13.1 To the sample, add 0.5 mL of concentrated HNO_3 and 0.25 mL of concentrated HCl.

10.13.2 Adjust the digestion block temperature so the solution in a covered container rises to approximately 90 - 95 ºC. Record temperature on bench sheet.

10.13.3 Heat the sample until it evaporates to approximately 10 mL, while ensuring that no portion of the bottom of the digestion tube is allowed to go dry.

CAUTION: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

10.13.4 Cover the sample and gently reflux for an additional 30 minutes. Avoid vigorous boiling to prevent the loss of the HCl-H_2O azeotrope. Record the start and stop times and the Hot Block temperature in TALS.

10.13.5 Allow the sample to cool in a fume hood.

10.13.6 Rinse the watch glass or cover into the container and re-volume to 25 mL with reagent water. Cap and mix thoroughly.

10.13.7 The sample is now ready for ICP-MS analysis. Refer to SOP DV-MT-0002.

NOTE: If insoluble materials are present in a sample digestate, the ICP-MS analyst may filter the sample prior to analysis. Refer to SOP DV-MT-0002 for additional details.

10.14 Method 3050B – Special Prep for Sb, Sn and Ag for Analysis by ICP-MS Method 6020

10.14.1 To 25 mL of sample in a digestion tube, add 2.5 mL of HNO_3 and 2.5 mL of HCl.

10.14.2 Heat at 90-95 °C until the sample has reduced to a volume of 10-15 mL ensuring that no portion of the sample container is allowed to go dry.

Record the start and stop times and the Hot Block temperature in TALS.

10.14.3 Remove the sample from the Hot Block and allow it to cool in a fume hood.

10.14.4 Add 1.0 mL of HCl to the digestion tube and cover with a ribbed watch glass.

10.14.5 Replace the watch glass and heat the sample for 15 minutes.

Record the start and stop times and the Hot Block temperature in TALS.

10.14.6 Remove the sample from the Hot Block and allow it to cool in a fume hood.

10.14.7 Re-volume to 100 mL with reagent water, cap and mix thoroughly.

10.15 Calibration

The digestion block temperature must be maintained between 90 and 95 °C. The temperature must be monitored continuously while in use and must be recorded on the metals preparation bench sheet. The temperature must be monitored by measuring the temperature of reagent water contained in a digestion tube that is placed in each digestion block. The thermometer used and the start and end time temperatures are recorded in TALS. The thermometer is calibrated in accordance with SOP DV-QA-0001, *Thermometer Calibration Procedures*.

11.0 Calculations / Data Reduction

11.1 Not applicable. See the determinative method SOPs, DV-MT-0002, DV-MT-0018 and DV-MT-0022 for data analysis and applicable calculations.

11.2 Documentation

11.2.1 All of the preparation information is recorded and stored in TALS.

11.2.2 The preparation information includes:

11.2.2.1 Batch number, job and sample numbers, preparation date, and analyst name;

11.2.2.2 Matrix and prep type;

11.2.2.3 Initial sample pH, Initial sample volume and final volume;

11.2.2.4 Reagent manufacturer and lot number for each reagent used;

11.2.2.5 Digestion tube lot information;

11.2.2.6 Standard identification number for each standard used;

11.2.2.7 Start and stop times for digestions;

11.2.2.8 Observed and corrected temperature readings during digestion;

11.2.2.9 Identification numbers of calibrated measuring equipment used (thermometers, balances, pipettes, etc.).

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL policy in DV-QA-005P. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency.

12.2 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. Ongoing proficiency must be demonstrated annually. IDOCs and ongoing proficiency demonstrations are conducted as follows.

12.2.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The

concentration of the QC check sample should be equivalent to a mid- level calibration.

12.2.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

12.2.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

12.2.4 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

12.3 Training Requirements

The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

13.0 Pollution Control

13.1 This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

13.2 Standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in Section 13, *Waste Management and Pollution Prevention*, of the Corporate Safety Manual, and DV-HS-001P, *Waste Management Plan*.

14.2 The following waste streams are produce when this method is carried out:

14.2.1 Expired Chemicals/Reagents/Standards: Contact Waste Coordinator

14.2.2 Acidic waste from sample digests: Waste Stream J.

NOTE: Radioactive, mixed waste and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

15.0 References / Cross-References

15.1 SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

15.1.1 Method 3005A, Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy, Revision 1, July 1992.

15.1.2 Method 3020A, Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy, Revision 1, July 1992.

15.1.3 Method 6020, Inductively Coupled Plasma - Mass Spectrometry, Revision 0, September 1994.

15.1.4 Method 3050B, Acid Digestion of Sediments, sludges and soils, Rev. 2, Dec. 1996.

15.2 Methods for the Chemical Analysis of Water and Waste (MCAWW), 1983.

15.3 Method 200.8, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectroscopy, Revision 5.4, May 1994.

16.0 Method Modifications:

16.1 Modifications and Interpretations Applicable to SW-846 Reference Methods

16.1.1 Chapter 1 of SW-846 states that the method blanks should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above one-half of the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

16.1.2 The referenced methods, as well as Table 3-1 of SW-846, refer to the use of a 100-mL aliquot for digestion. This SOP requires the use of a 50-mL sample size to reduce waste generation. The use of reduced sample volumes is supported in EPA's document "Response to Public Comments Background Document, Promulgation of the Second Update to SW-846, Third Edition", dated November 3, 1994. This document stated, "...flexibility to alter digestion volumes is addressed and 'allowed' by the table (3-1) and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples..."

EMSL-Ci has also taken the stance that "reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology." Additionally, in written correspondence from the Office of Solid Waste, Oliver Fordham stated. " As a 'representative sample' can be assured, scaling causes no loss of precision and accuracy in the analysis."

16.2 Modifications Specific to Method 3005A

An additional 1.0 mL of HNO_3 was included to replace the 5.0 mL of HCl. HCl was eliminated to reduce interferences from chloride.

16.3 Modifications and Interpretations Specific to Method 3020A

16.3.1 Section 10.11.6 of this SOP requires that the sample be reduced to a volume of 3 -5 mL. Section 7.2 of Method 3020A states that the volume should be reduced to 3 mL, but also states that no portion of the bottom of the digestion tube should go dry. The volume required by this SOP is a closer approximation of the volume required to provide an adequate covering of the bottom of the digestion tube so as to prevent the loss of critical analytes through volatilization.

16.3.2 The scope of 3020A has been expanded to include silver, based on comparison studies with 7760A. Method 3020A consistently demonstrated improved accuracy and precision over Method 7760A in the matrices tested (reagent water, surface water, and TCLP leachate) up to a concentration of 1 ppm silver.

17.0 Attachments

Table 1.TCLP Reporting Limits, Regulatory Limits, and Matrix Spike Levels

Table 2.Summary of Quality Control Requirements

Appendix A.Contamination Control Guidelines

18.0 Revision History

- Revision 7, Dated 30 June 2015
  - Updated Section 10.13.2 for temperature requirement of 90-95 for method 200.8
  - Updated Section 10.9.1.1 for proper technique when using pH paper.
  - Added new Section 10.8 reminding analysts to enter data directly at time of acquisition
  - Added Section 11.2 describing required data to be recorded
  - Removed Section 11.4

- Revision 6, Dated 29 September 2014
  - Annual review
  - Removed references to microwave procedure
  - Removed direct-shoot for dissolved analysis
  - Corrected section references
  - Replaced LIMS and Standards Log references with TALS
  - Clarified the number of MS/MSDs per prep batch based on method
  - Removed workflow diagrams Figures 1-4
  - Removed Tables 1 and 2

- Minor spelling and language corrections throughout

- Revision 5, Dated 30 September 2013
  - Reference to SOP DV-IP-0017 for preparation of organic waste
  - Formatting updates
  - Updated section 9, 12 & 14 to include more detail
  - Annual review
  - Updated sections 10.8.1.2 - 10.8.1.4 to removed reference to amount of HNO_3 acid added.
  - Added to Section 10.8.1.6 that a maximum of 5mls of HNO_3 can be added.
- Revision 4, Dated 28 September 2012
  - Annual review
  - Section 9.6 Updated method blank control limits to ½ the reporting limit.
  - Updated appendix B with revised Work Instruction.
- Revision 3.5, dated 23 September 2011
  - Annual Technical Review
  - Removed reference to Supplemental Metals Prep Sheets in Sections 10.10.8 and 10.13.5.1
  - Removed reference to Clouseau in Section 10.8.1.2
  - Removed references to LIMS codes in Appendix B

Earlier revision histories have been archived and are available upon request.

Table 1.

TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	RL (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

Table 2.

Summary of Quality Control Requirements

QC Parameter	Frequency	Acceptance Criteria	Corrective Action
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOP: DV-MT-0002	Re-digest and reanalyze samples associated with the method blank.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOP: DV-MT-0002	Re-digest and reanalyze all samples associated with the LCS.
Matrix Spike (MS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOP: DV-MT-0002	Re-prep not required unless preparation error suspected.
Matrix Spike Duplicate (MSD)	See Matrix Spike	Refer to determinative SOP: DV-MT-0002	See Corrective Action for Matrix Spike.

Appendix A.

Contamination Control Guidelines

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or latex gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX E
EXAMPLE COC

TestAmerica Savannah
5102 LaRoche Avenue

Savannah, GA 31404-6019
phone 912.354.7858 fax 912.352.0165

Chain of Custody Record

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

Regulatory Program: ☐ DW ☐ NPDES ☐ RCRA ☐ Other:

TestAmerica Laboratories, Inc.

Client Contact	**Project Manager: Jonathan Colomb**	**Site Contact: Patricia Beckley**		COC No:
Weston Solutions, Inc.	**Tel/Fax: 773-947-4064**	**Lab Contact: Sheila Hoffman**	**Carrier: Fed Ex**	___1___ of ___1___ COCs
70 N.E. Loop 410; Suite 600	**Analysis Turnaround Time**			Sampler:
San Antonio, TX 78216-5842	☑ CALENDAR DAYS ☐ WORKING DAYS			**For Lab Use Only:**
(703) 724-0544 Phone	TAT if different from Below _____			Walk-in Client:
(xxx) xxx-xxxx FAX	☐ 2 weeks			Lab Sampling:
Project Name: Gold King Mine - Region 9	☐ 1 week			
Site: Region 9	☐ 2 days			Job / SDG No.:
P O # 20406.016.002.0010.08	☐ 1 day			

Sample Identification	Sample Date	Sample Time	Sample Type (C=Comp, G=Grab)	Matrix	# of Cont.	Filtered Sample (Y / N)	Perform MS / MSD (Y / N)	Total Metals; including HG*	Dissolved Metals; including Hg**	pH (SM4500H)	Alkalinity (SM2320B)	TSS (SM2540D)	TDS (SM2450C)	Hardness	Sample Specific Notes:
SJBB-081615-11	8/16/15	1400	G	SW	5	Y	N	X	X	X	X	X	X	X	
SJBB-081615-12	8/16/15	1400	G	SW	5	N	N	X	X	X	X	X	X	X	
SJMH-081615-11	8/16/15	1245	G	SW	5	Y	N	X	X	X	X	X	X	X	

Preservation Used: 1= Ice, 2= HCl; 3= H2SO4; 4=HNO3; 5=NaOH; 6= Other _____

Possible Hazard Identification:
Are any samples from a listed EPA Hazardous Waste? Please List any EPA Waste Codes for the sample in the Comments Section if the lab is to dispose of the sample.

☐ Non-Hazard ☐ Flammable ☐ Skin Irritant ☐ Poison B ☑ Unknown

Sample Disposal (A fee may be assessed if samples are retained longer than 1 month)

☐ Return to Client ☐ Disposal by Lab ☐ Archive for _____ Months

Special Instructions/QC Requirements & Comments:
*** (200.7: Al, Ca, Fe, K, Mg, Na) (200.8: Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, Ag, Se, Tl, V, ZN) (245.1 Hg) (SM2340B)**
**** EPA 200.7, 200.8, 245.1**
Dissolved metals samples have been field filtered

Custody Seals Intact: ☐ Yes ☐ No | Custody Seal No.: | Cooler Temp. (°C): Obs'd:_____ Corr'd:_____ Therm ID No.:_____

Relinquished by: Patricia Beckley	Company: Weston Solutions	Date/Time: 8/17 16:00	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received by:	Company:	Date/Time:
Relinquished by:	Company:	Date/Time:	Received in Laboratory by:	Company:	Date/Time: