SUPPORT FOR THE EPA NATIONAL CONTRACT FOR LEAD ANALYSIS

Contract No. EP-BPA-15-D-0004

2015

Quality Assurance Project Plan
Category 1

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2015 Quality Assurance Project Plan, Category 1
National Contract for Lead Analysis (Contract No. EP-BPA-15-D-0004)

Approved by:

U.S. EPA Project Officer: _____ Date: 12/10/15

U.S. EPA QA Manager: _____ Date: 12/10/15

U.S. EPA Delivery Order Manager: _____ Date: 12/10/15

ERG Program Manager: _____ Date: 12/21/15

ERG Program QA Officer: _____ Date: 12/21/15

DRI Project Manager: _____ Date: 12/15/15

DRI Project QA Officer: _____ Date: 12/15/2015

DISCLAIMER

This Category 1 Quality Assurance Project Plan has been prepared specifically to address the operation and management of the U.S. EPA National Contract for Lead Analysis for the National Ambient Air Quality Standards (NAAQS). The contents have been prepared in accordance with Level 1 Specifications of the EPA Guidance for Quality Assurance Project Plans, EPA QA/G-5.

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SYMBOLS AND ABBREVIATIONS

AMTIC	Ambient Air Monitoring Technical Information Center
AQS	Air Quality Subsystem
BPA	Blank Purchase Agreement
BS/BSD	Blank Spike/Bland Spike Duplicate
CAR	Corrective Action Report
CCB	Continuing calibration blank
CCV	Continuing calibration verification
COC	Chain of Custody
CSN	Chemical Speciation Network
CV	Coefficient of Variation, precision
DOC	Demonstration of Capability
DPR	Daily Performance Report
DQOs	Data Quality Objective(s)
DRI	Desert Research Institute
DUP	Duplicate (used for Replicate Analysis)
EAF	Environmental Analysis Facility
EPA	U.S. Environmental Protection Agency
ERG	Eastern Research Group, Inc.
EDXRF	Energy Dispersive X-ray Fluorescence
FACA	Federal Advisory Committee Act
FEM	Federal Equivalency Method
FRM	Federal Reference Method
HSV	High standard verification
IC	Initial Calibration Standards (ICP-MS)
ICB	Initial Calibration Blank
ICP-MS	Inductively Coupled Plasma/Mass Spectrometer
ICSA	Interference Check Standard A
ICSAB	Interference Check Standard B
ICV	Initial calibration verification
ISTD	Internal Standard
LCV	Low Calibration Verification
LIMS	Laboratory Information Management System
LOQ	Limit of Quantitation
LQL	Lower Quantifiable Limit

LRB	Laboratory Reagent Blank
MS/MSD	Matrix Spike/Matrix Spike Duplicate
MB	Method Blank
MDLs	Method Detection Limit(s)
mm	Millimeter
MQOs	Measurement Quality Objective
µg/L	Micrograms per liter
$\mu g/m^3$	Microgram per cubic meter
NAAQS	National Ambient Air Quality Standard
NAREL	National Air and Radiation Environmental Laboratory
NELAC	National Environmental Laboratory Accreditation Conference
NELAP	National Environmental Laboratory Accreditation Program
ng/L	Nanogram per liter
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
OSHA	Occupational Safety and Health Administration
Pb-TSP	Lead for Total Suspended Particles
Pb-PM_{10}	Lead for PM_{10}
PDS	Post digestion spike
PE	Performance Evaluation
POC	Parameter Occurrence Code
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RB	Raw Blank
RD	Raw Data
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SOPs	Standard Operating Procedure(s)
SRD	Serial dilution
SRM	Standard Reference Material
TCEQ	Texas Commission on Environmental Quality
TSAs	Technical System Audits
TSP	Total Suspended Particles
XRF	X-ray Fluorescence

DISTRIBUTION LIST

Copies of this plan and all revisions will be provided to:

- Jeff Yane, Work Assignment Manager, U.S. EPA, C404-02, RTP, NC
- Laurie Trinca, Project Manager, U.S. EPA, C304-06, RTP, NC
- Greg Noah, AT QA Coordinator, U.S. EPA, C304-06, RTP, NC

U.S. EPA Regional contacts may obtain a copy of the QAPP by contacting the ERG Program Manager. It is the responsibility of each Regional contact to make copies of the plan for appropriate State personnel or to refer them to ERG Program Manager.

PROJECT MANAGEMENT
SECTION 1
PROJECT/TASK ORGANIZATION

1.1 Assignment of Program Personnel

Table 1-1 presents the program organization for each aspect of the Environmental Protection Agency (EPA) Analysis for Lead in TSP and PM_{10} Filters. The program organizational chart is presented in Figure 1-1. All Eastern Research Group (ERG) and Desert Research Institute (DRI) staff working on this contract are provided access to a current electronic copy of this signed, EPA approved Quality Assurance Project Plan (QAPP).

ERG's primary support on this contract includes analysis for lead for Total Suspended Particles (Pb-TSP) or PM_{10} (Pb-PM_{10}) by Inductively Coupled Plasma/Mass Spectrometer (ICP-MS). DRI's primary support includes analysis for Pb-PM_{10} filters by X-ray Fluorescence (XRF) analysis.

ERG is responsible to the client for the work of the subcontractor, DRI. The subcontractor will meet the Data Quality Objectives (DQOs) requirements for the appropriate method. ERG shall maintain a record of subcontractor compliance, including documentation of subcontractor's Method Detection Limits (MDLs).

1.1.1 Program Manager

Ms. Julie Swift, an ERG Vice President, is the Program Manager for this contract and will serve as the primary contact. In this role, she has the primary responsibility for understanding EPA's and their clients' (i.e., State, local, and tribal agencies) needs at the program level. Ms. Swift coordinates with the ERG Quality Assurance (QA) Officer and metal's Task Lead to provide EPA client perspective and communicate technical issues and needs. As the Program Manager, Ms. Julie Swift is responsible for the technical operation and the quality

of the program on a day-to-day basis. She leads the analytical tasks and provides technical direction and support. She assists in the resolution of technical issues and serves as a resource for the Task Lead regarding any project issues. Ms. Swift also performs an overall review of the data that is reported.

1.1.2 Program QA Coordinator

Ms. Donna Tedder, the Program and Laboratory QA Coordinator, is responsible for ensuring the overall integrity and quality of project results. Ms. Tedder, or her designee, will do a 10 percent QA review for all sample analyses delivered for reporting to the Program Manager. In the case of subcontracted work, 20 percent of data from subcontractor will be reviewed. The lines of communication between management, the Program QA Coordinator, and the technical staff are formally established and allow for discussion of real and potential problems, preventive actions, and corrective procedures. On major quality issues, Ms. Tedder reports independently to Ms. Mary Willett, ERG's corporate QA Officer.

1.1.3 Task Leaders

Ms. Jennifer Nash, ERG's Metals Task Lead, is responsible for meeting the project objectives, meeting report schedules, and directing the technical staff in execution of the technical effort for their respective task(s). She will review 100 percent of all sample analyses and will deliver 10 percent of sample analyses that the QA Coordinator requests for review prior to data reporting by the Program Manager. Ms. Nash will assess and report on the project's progress and results (e.g., recordkeeping, data validation procedures, sample turnaround time) and ensure timely, high-quality services that meet the requirements in this QAPP.

ERG will subcontract the analysis for the XRF analysis of PM_{10} filters to DRI. Dr. Richard Tropp will serve as DRI's Principal Investigator and Project Manager while Steve Kohl, from DRI, will be the DRI Task Leader responsible for leading the XRF analysis of PM_{10} filters. Dr. Tropp will serve as primary contact at DRI, with Mr. Kohl as secondary. Dr. Tropp

will also be responsible for overseeing the project and Quality Assurance/Quality Control (QA/QC) of the Energy Dispersive X-ray Fluorescence (EDXRF) data and its reporting to ERG. Mr. Kohl will be responsible for overseeing the receipt, EDXRF analysis, data processing, data validation and reporting for the Teflon PM_{10} samples.

Table 1-1
Program Organization

Program Assignment	Program Personnel Assigned	Phone Number	Email Address
ERG Program Manager	Julie Swift	(919) 468-7924	julie.swift@erg.com
Task Lead – ERG ICP-MS Analysis	Jennifer Nash	(919) 468-7881	jennifer.nash@erg.com
DRI Project Manager	Richard Tropp	(775) 674-7094	Richard.Tropp@dri.edu
Task Lead – DRI XRF Analysis	Steve Kohl	(775) 674-7056	Steve.Kohl@dri.edu
Program QA Coordinator	Donna Tedder	(919) 468-7921	donna.tedder@erg.com
Project Administrator	Kerry Fountain	(919) 468-7962	kerry.fountain@erg.com

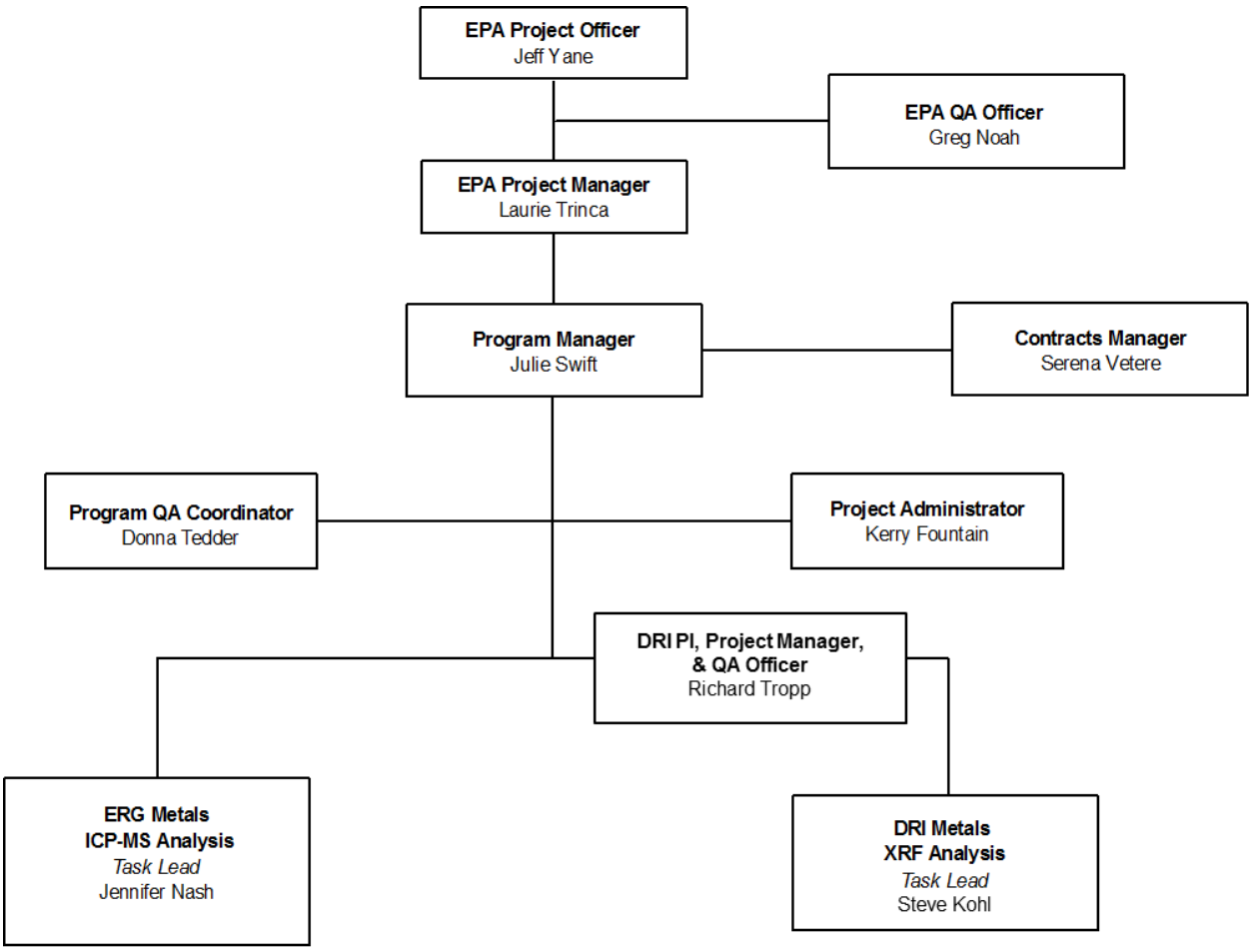

Figure 1-1. Lead Analysis Organizational Chart

SECTION 2
PROBLEM DEFINITION/BACKGROUND

On November 12, 2008, the EPA issued a rule strengthening the primary and secondary National Ambient Air Quality Standards (NAAQS) for lead and associated monitoring requirements (Federal Register Volume 73, Number 219, (73 FR 66964) [(1)] to provide necessary protection for public health and welfare. The EPA revised various elements of the primary standard to provide increased protection for children and at-risk populations against adverse health effects, most notably including neurological effects in children. EPA revised the primary (health-based) standard from 1.5 micrograms per cubic meter ($\mu g/m^3$) to 0.15 $\mu g/m^3$, as total suspended particles (TSP). EPA is revising the secondary (welfare-based) standard to be identical in all respects to the revised primary standard.

The EPA also promulgated a new Federal Reference Method (FRM) for the sampling and analysis of Pb-PM_{10} as Code of Federal Regulations Title 40 Part 50 (40 CFR Part 50), Appendix Q[(2)]. The averaging time was revised to a rolling 3-month period with a maximum (not-to-be-exceeded), evaluated over a 3-year period.

EPA revised the data handling procedures, including allowance for the use of Pb-PM_{10} data in certain circumstances, and the treatment of exceptional events, and ambient air monitoring and reporting requirements for Pb, including those related to sampling and analysis methods, network design, sampling schedule, and data reporting. Depending on specific circumstances outlined in the rule, States have the option of monitoring for Pb-TSP or Pb-PM_{10} following approved FRMs or Federal Equivalent Methods (FEMs) to meet the monitoring requirements.

SECTION 3
PROJECT/TASK DESCRIPTION

This section describes the activities performed under the national contract for the analysis of Pb-TSP and Pb-PM_{10} for state, local, and tribal monitoring agencies. Sampling and analysis schedules are prepared when a Blank Purchase Agreement (BPA) is provided by EPA.

3.1 NAAQS for Lead Analysis

The NAAQS national contract for the analysis of Pb-TSP and Pb-PM_{10} was created so that the State, Local and Tribal monitoring agencies could access a laboratory to provide their analysis following EPA approved FRM/FEM analysis specifications. The filters are supplied by the state/local agencies for this program. The EPA provides the agencies, through their Regional Coordinators, access to this contract to provide the analysis. A list of the analyses, EPA FRM/FEM, and laboratory Standard Operating Procedures (SOP) are listed in Table 3-1. ERG can prepare the data in the Air Quality Subsystem (AQS) database format for quarterly upload if requested.

Table 3-1
List of Analytical Services

Analysis	Method	SOP
ICP-MS • Pb-TSP • Pb-PM_{10}	 EQL-0512-201[3] EQL-0512-202[4]	 ERG-MOR-084 ERG-MOR-085
XRF • Pb-PM_{10}	40 CFR Part 50, Appendix Q[2]	DRI SOP #2-209

SECTION 4

DATA QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

Because ERG performs analysis services only, DQOs for defining a network program are not identified in this QAPP. This section will discuss the Measurements Quality Objectives (MQOs) of ERG and DRI laboratory analyses, emphasizing the levels of uncertainty the decision maker is willing to allow/accept from the analytical results.

Once a sampling DQO is established, the quality of the data must be evaluated and controlled to ensure that data quality is maintained within the established acceptance criteria. MQOs are designed to evaluate and control various phases (sampling, preparation, analysis) of the measurement process to ensure that the total measurement uncertainty is within the range prescribed by the DQOs. MQOs can be defined in terms of the following data quality indicators:

Precision - a measure of mutual agreement among individual measurements of the same property usually under prescribed similar conditions. This is the random component of error.

Bias - the systematic or persistent distortion of a measurement process that causes error in one direction. Bias is determined by estimating the positive and negative deviation from the true value as a percentage of the true value.

Detectability - the determination of the low range critical value of a characteristic that a method-specific procedure can reliably discern.

Comparability - a measure of the level of confidence with which one data set can be compared to another.

Bias has been the term frequently used to represent closeness to “truth” and includes a combination of precision and bias error components. The MQOs listed will attempt to separate measurement uncertainties into precision and bias components. Bias will be assessed in the quarterly EPA audits which will be reported into AQS.

Analytical Precision is calculated by comparing the differences between replicate analyses (two analyses of the same sample) from the arithmetic mean of the two results as shown below. Replicate analyses with low variability have a lower Relative Percent Difference (RPD) (better precision), whereas high variability samples have a higher RPD (poorer precision).

$$RPD = \frac{|X_1 - X_2|}{\bar{X}} \, x \, 100$$

Where:

X_1 = Ambient air concentration of a given compound measured in one sample;

X_2 = Concentration of the same compound measured during replicate analysis;

$\overline{X}$ = Arithmetic mean of X_1 and X_2.

Table 4-1 lists the MQOs for Pb-TSP and Pb-PM_{10} using ICP-MS and XRF.

Table 4-1

Measurement Quality Objectives for the National Lead Analysis Program

Analyte/ Instrument	Reporting Units	Precision from analysis of Replicate Samples (RPD)*	Precision from collection of Collocate Samples*	Comparability/ Based on Method	Minimum Detection Limit
Pb-TSP ICP-MS	µg/filter	± 10%	± 20%	EQL-0512-201	See Table 11-4
Pb-PM10 ICP-MS	µg/filter	± 10%	± 20%	EQL-0512-202	See Table 11-4
Pb-PM10 XRF	µg/filter	± 10%	± 20%	40 CFR Part 50, Appendix Q	See Table 11-4

* Sample value is ≥ 10 times the MDL

SECTION 5
SPECIAL TRAINING REQUIREMENTS/CERTIFICATION

The activities of EPA's National Contract for Lead Analysis is performed using accepted EPA, National Institute for Occupational Safety and Health (NIOSH), and Occupational Safety and Health Administration (OSHA) analytical protocols for the analytical laboratory staff.

5.1 ERG Analytical Laboratory Personnel

ERG analytical laboratory personnel involved in this project have been trained in their tasks and have up to 28 years of experience in the duties they will be performing in the analytical laboratory. Training of ERG laboratory personnel is recorded in ERG Training Records in an Excel® database and filed as a hardcopy. Technical training includes general techniques and specific training based on the appropriate SOP, method, and program QAPP. After training, an initial demonstration of each personnel's ability to perform the analytical task involves repeated measurements of a standard. These records are kept by the ERG QA staff. Currently, no special certifications are needed for the analysis of the ambient samples received for this programs. Health and Safety training is performed annually. The laboratory personnel will adhere to the ERG Corporate Health and Safety manual.

ERG maintains appropriate SOPs for each analytical method. These SOPs are presented in Appendix A. All SOPs document equipment and/or procedures required to perform each specific laboratory activity. Laboratory staff will be subject to on-site surveillance by the Quality Assurance staff and quarterly audit samples.

5.2 DRI Analytical Laboratory Personnel

DRI Environmental Analysis Facility (EAF) personnel involved in this project have an education background and up to 35 years of experience in the duties they will be performing at DRI EAF. The DRI Project Manager, Dr. Tropp, has been overseeing sampling and analysis

projects for over 35 years, including the QA/QC of XRF analysis results. DRI's EAF Analysis Task Leader, Mr. Kohl, has been performing EDXRF analysis of PM samples for more than 20 years. All laboratory personnel performing tasks according to EAF SOPs have passed a demonstration of capability (DOC) initially then annually according to *DRI SOP for Demonstration of Capability*, DRI SOP #6-0015r1 in Appendix B. These records are kept by the EAF QA Manager. DRI EAF personnel are subject to periodic internal QA audits by the EAF QA Manager. In addition, DRI EAF personnel will perform periodic PE sample analyses as required. All DRI EAF personnel are required to undergo DRI laboratory safety training annually and adhere to the Institute's health and safety plans.

SECTION 6
DOCUMENTATION AND RECORDS

The EPA National Contract for Lead analysis generates a number of documents and records that need to be retained/archived. The PM will provide all staff working on this contract access to a current electronic copy of this signed, EPA approved QAPP. In this QAPP, ERG's reporting package (defined as the information required to support the data reported) includes all data required to be collected as well as support data deemed important by ERG and/or DRI.

6.1 Data Management

ERG has a structured records management retrieval system that allows for the efficient archive and retrieval of records. The analytical information that is collected by the laboratory will be managed in this system. The laboratory paper copies of all analyses are stored on site in a secured temperature-controlled laboratory area for up to five years after the close of the contract. Data obtained from DRI will be imported into the LIMS data server so that the same reports will be generated for all samples submitted for analysis. ERG also archives the data in the Laboratory Information Management System (LIMS) data server which is backed up weekly, monthly, and biannually. The backed-up data is stored at an off-site ERG facility. Data Storage and Retrieval is discussed in more detail in Section 15.6. The Program Manager has final authority for the storage, access to, and final disposal of all records kept for this program.

6.2 Data Reports

Data reports, sent in Adobe and Excel formats to EPA and appropriate state/local/tribal agencies, will include the sample name, filter ID number, collection date, received date, analysis date, analytical method, analytical data reported in µg/filter, MDL, and qualifiers. This report will be submitted within 30 days from the receipt of the samples. The data reports will include analytical results for individual samples as well as associated QC samples, associated MDLs, and qualifiers.

6.3 Records and Supporting Data

Data used for the measurement of lead and the associated QA/QC data are collected electronically or on data forms. Table 6-1 presents the location of the data records for laboratory operations stored at the ERG and DRI laboratories.

Table 6-1
Data Documentation and Records

Item	Record	Short Term Location Storage	Long Term Location Storage
Field Operations			
Chain of Custody (COC)	ERG COCs	In Laboratory with Samples	Copy scanned and stored on ERG LIMS
Laboratory Records - ERG			
Sample Prep Data	Bench sheets	Hardcopy filed, LIMS	Hardcopy archived, LIMS
Sample Management Records (sample receipt, handling, storage, etc.)	COCs	LIMS, with bench sheets	LIMS, with bench sheets
Test Methods	SOPs	Hardcopy filed, shared network drive	Shared network drive
QA/QC Reports (General QC records, MDL information, calibration, etc.)	Individual records for each analysis	Hardcopy filed, shared network drive	Hardcopy archived, shared network drive
Corrective Action Reports	Individual records for each analysis	Original copy filed, copy in data package	All copies archived
Laboratory Records - DRI			
Sample Management Records (sample receipt, handling, storage, etc.)	COCs	Shipping & Receiving	Hard Copy Archiver
Test Methods	SOPs	Analytical; Lab	LAN & QA Files
QA/QC Reports (General QC records, MDL information, calibration, etc.)	Individual records for each analysis	Analytical Lab	LAN
Corrective Action Reports (CAR)	Individual records for each analysis	Analytical Lab	LAN and EAF QA Manager *
Data Reduction, Verification, and Validation			
Electronic Data (used for AQS data entry if requested)	Excel® and Access®	Shared network drive	Shared network drive

* Archive for formal CARs

6.3.1 Notebooks

ERG issues laboratory notebooks to each laboratory division upon request. This notebook is uniquely numbered and associated with the laboratory personnel. Although LIMS data entry forms are associated with all routine environmental data operations, the notebooks can be used to record additional information about these operations. All notebook entries are filled out in indelible ink. Corrections are made by inserting one line through the incorrect entry, initialing the correction (ERG and DRI maintain a signature log), and placing the correct entry alongside the incorrect entry, if this can be accomplished legibly, or by providing the information on a new line.

Field Notebooks - Field notebooks are the responsibility of the EPA, States, local or tribal agencies as ERG is not responsible for the collection of samples.

Laboratory Notebooks - Notebooks are associated with general procedures such as temperature records for the refrigerators, calibration of analytical balances, sample preparation logs, calibration of analytical instruments, preventive maintenance and repairs, receipt of standards and other supplies, etc., used in this program.

Sample Shipping and Receipt - ERG's LIMS system is used to record samples received. Hard copies of COC records are also stored for one year; however, electronic copies are scanned and stored in LIMS and on a shared network drive.

6.3.2 Electronic Data Collection

In order to reduce the potential for data entry errors, automated systems are utilized (where appropriate) and record the same information that is found on data entry forms. Whenever possible, DRI utilizes barcode-based hardcopy forms, data processing routines to process data from sampling and analytical instruments directly, and standardized data processing routines. Information available from multiple sources (e.g., hardcopy forms, sampler files, and

analytical instruments) are cross-checked for consistency and revised or flagged when questions arise. Instrument and laboratory environmental data are stored on instruments and computers in the laboratories and transferred to a database on the EAF LAN.

6.4 Data Reporting Package Archiving and Retrieval

In general, all the information listed above will be retained for at least 5 years from the date of the end of the closed contract with EPA. If any litigation, claim, negotiation, audit or other action involving the records has been started before the expiration of the 5-year period, however, the records will be retained until completion of the action and resolution of all issues which arise from it. The long-term storage at ERG is located in the laboratory in a locked climate-controlled file room with limited access. The project secretary keeps a record of documents entering and leaving long-term storage. Access to the facility storage area is limited to authorized personnel only.

DRI EAF uses a phased approach for long-term storage of hard-copy records. Recently archived records are located in a hardcopy storage area at DRI with limited access and checkout logs. Older records, generally more than five years old after project completion, may be moved to a climate-controlled offsite storage facility. It also has limited access and checkout logs. For electronic records, DRI EAF laboratory computers house raw data stored on a RAID 1 (Mirror) system. Raw data is automatically backed up to a virtual file and database server, which is run on a physical clustered RAID 1 (Mirror) server, once a day. Once data is on the server it is stored in an instantly accessible, un-modifiable directory for 35 days and an instantly accessible, modifiable directory for 10 days. All data in these locations begin as exact copies of data that was on each individual laboratory computer. After data is safely in those locations, the raw data is extracted from the files and imported to the database server for possible modification. After data has been on the server for 35 days, it is automatically written to tape and stored indefinitely. Daily e-mails are automatically generated to confirm backups and notify computer personnel of data processing and data management issues. All hard drives and tape, once filled, are stored in a special media storage room. The room is secure, accessible only by assigned personnel, with

entry through a security system. The room has no windows, no drop ceilings, and is buried in the side of a hill in the lower section of the DRI building. It also contains UV filters on the lights to prevent damage to media. In addition, there are separate keyed lockers for each DRI laboratory. As part of an Institute-wide disaster recovery plan, data stored on networks at DRI's Reno campus are backed up to DRI's Las Vegas campus and vice versa.

6.5 Quality System Document Control

To ensure the use of the most current version of quality system documents, all quality documents (QAPP, SOPs, etc.) generated at the ERG Laboratory must be uniquely identified. Original documents shall include the date of issue, revision number, page number, total number of pages, and appropriate signatures. Copies of quality documents shall be controlled and include the date of issue, revision number, page number, total number of pages, and copy control number. When an original quality document is updated, the QA Coordinator or designee will ensure that the copy documents are also updated and old versions are disposed. During the course of the project, revised QAPPs will be circulated to the EPA and to ERG's laboratory staff. For copies of documents out of the laboratory's control, a stamp or watermark stating "Uncontrolled" or "Draft", if applicable, will be applied. Each approved QAPP will be posted on EPA's Ambient Air Monitoring Technical Information Centers (AMTIC) Website.

MEASUREMENT DATA ACQUISITION
SECTION 7
SAMPLING PROCESS DESIGN

ERG is not responsible for the collection of samples nor the design of the samplers used in the NAAQS program. Pb-TSP sampling that meets the requirements of Appendix B to Part 50, Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method)[5] is acceptable as a FRM sampler. Low-volume PM_{10} samplers that meet the requirements (as described in Appendix O of Part 50[6]) can be used for Pb-PM_{10} monitoring intended to meet NAAQS comparison objectives. ERG is responsible only for the analysis of the samples it receives from the sites.

SECTION 8

SAMPLING METHOD REQUIREMENTS

Because ERG is not responsible for actual execution of the field sampling in this program, the method support for the site's samplers are not discussed in this QAPP.

SECTION 9
SAMPLE HANDLING AND CUSTODY REQUIREMENTS

ERG's Shipping and Receiving Task Leader will ensure that sample media that is received in the laboratory follow all of the procedures listed in this QAPP and the individual SOPs. The Task Leader will also advise the Project Manager of any issues or obstacles regarding sample receipt, login and storage. The sample custodian working under the Shipping and Receiving Task Leader will receive custody of samples, complete COC receipt information, document sample receipt, and enter COC information into LIMS to create a work order. Samples for XRF analysis will be received and logged in at ERG's laboratory before they are sent to DRI for analysis.

9.1 Analysis Chain of Custody Forms

Field testing personnel will record data on the COC forms (Figure 9-1). The COC form documents time, date, location, and other field parameters. Because the sites supply the filters used for metal analysis, COC forms are generated by the State, local or tribal agency for these samples. If needed, however, the COC forms provided on the AMTIC website at: http://www3.epa.gov/ttn/amtic/pb-monitoring.html. Samples are received at ERG's laboratory as presented in the *SOP for Sample Receipt at ERG Chemistry Laboratory*, ERG-MOR-045, in Appendix A.

The sample specific information from the COC is then entered into the LIMS (example login page is shown in Figure 9-2). The sample is logged into the LIMS database following the *SOP for Sample Login to the Laboratory Information Management System*, ERG-MOR-079 found in Appendix A. The sample is given a unique LIMS identification number.

The LIMS ID number is recorded on all ERG copies of the COC. The COC is scanned (the PDF is stored in the LIMS system) and is kept with the samples until analysis is complete.

Chain of Custody TSP/PM_{10} Lead Analysis (EP-BPA-15-D-0004)

601 Keystone Park Drive, Suite 700, Morrisville, NC 27560

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SITE						Relinquished by:			
AQS Code						Date/Time:			
Submitter:			ANALYSES			Received by:			
						Date/Time:			
#	Filter ID	Date	TSP (ICP	PM10 (ICP	PM10 (XR	Sample Volume (m^3)	Comments	ERG LIMS ID (Lab use only)	
1									
2									
3									
4									
5									
6									
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Figure 9-1. Metals COC

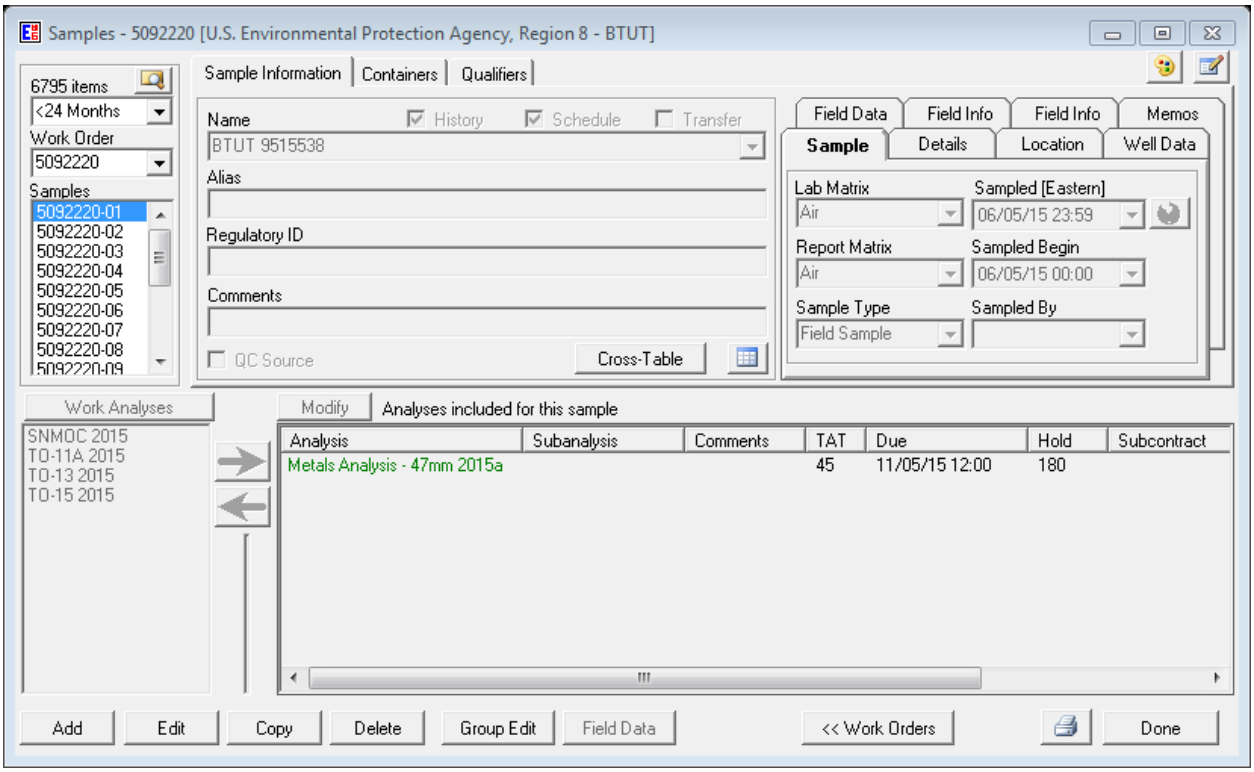


Figure 9-2. Example ERG LIMS Login Page

9.2 Invalid Samples

The sample can be determined invalid at the site or in the laboratory. SOP ERG-MOR-045 describes the sample receiving procedure and sample acceptance. Individual sites will be contacted if there are any questions about the samples upon receipt. When a sample is designated as invalid, the assigned LIMS ID number is notated as a void and the sample is invalidated on the individual respective COC form. The sites will also be notified of any invalid samples in the analytical data reports.

9.3 Analytical Data

All laboratory electronic records will be stored for archive on shared network drive which is backed-up daily, weekly, and monthly. The back-ups are stored off-site for added safety. Raw data will be included in the project archive files stored in an ERG long-term storage location.

DRI EAF laboratory computers house raw data stored on a RAID 1 (Mirror) system. Raw data is automatically backed up to a virtual file and database server, which is run on a physical clustered RAID 1 (Mirror) server once a day. Once data is on the server it is stored in an instantly accessible, un-modifiable directory for 35 days and an instantly accessible, modifiable directory for 10 days. All data in these locations begin as exact copies of data that was on each individual laboratory computer. After data is safely stored in those locations, the raw data is extracted from the files and imported to the database server for possible modification. After data has been on the server for 35 days, it is automatically written to tape and stored indefinitely. Daily e-mails are automatically generated to confirm backups and notify computer personnel of data processing and data management issues. All hard drives and tape, once filled, are stored in a special media storage room.

All records generated are signed or initialed by the person performing the work and reviewed by an appropriate Task Leader. Measurement results become part of a project report, of which 10 percent is chosen and reviewed by the QA Coordinator or a reviewer designated by the QA Coordinator.

9.4 Sampling Monitoring Data

All COC forms from the monitoring sites will be stored with the extraction bench sheet. The COC forms will be reviewed by the Analysts, Task Leaders and Program Manager. The original field data for all the samples, TSP by ICP-MS, PM_{10} by ICP-MS and PM_{10} by XRF will remain in ERG custody and eventually will be stored on file until 5 years after the end of the contract. DRI will receive a copy of the COC forms from the sites with the ERG LIMS ID number added. ERG will contact the individual site if necessary information is not completed on the COC forms.

SECTION 10
ANALYTICAL METHODS REQUIREMENTS

Analytical procedures are laboratory-specific because of the different methods being used at ERG and DRI. The ERG analytical methods for of Pb-TSP and Pb-PM_{10} uses ICP-MS. The analytical method used at DRI utilizes the XRF for the analysis of Pb-PM_{10}. All analytical method SOPs are provided in Appendix A for ERG and Appendix B for DRI. Corrective action for analytical system failures realized at time of analysis is initiated by the Analyst, supported by the Task Leader for that method.

The SOPs for these analytical methods are reviewed annually and updated as necessary. The QA Coordinator, Program Manager and Writer/Editor will review, sign and date it before distributing to the particular laboratories satellite file areas. The previous copies will be replaced with the revised edition. The original, and all previously revised edits, are stored in a historical file maintained by ERG's Document Administrator.

10.1 Lead Analysis Using an ICP-MS Analytical System

Sample preparation and analysis procedures are based on NAAQS FEM for the analysis of Lead (EQL-0512-201[3] for TSP and EQL-0512-202[4] for PM_{10}) using ICP-MS analysis techniques. Upon receipt from the field, the samples are checked against the COC forms and then logged into the LIMS system. Each sample component is examined to determine if damage occurred during travel. Color, appearance, and other particulars of the samples are noted. A complete description of the preparation and analytical procedures for glass fiber (8x10") filters (ERG-MOR-084) and for Teflon® 47mm filters (ERG-MOR-085) are presented in Appendix A. Analysis hold time for metals filters is 180 days.

The ICP-MS consists of an inductively coupled plasma source, ion optics, a quadrupole mass spectrometer, a recirculator and an autosampler. The mass spectrometer will be mass calibrated and resolution checked. Resolution at low mass is indicated by magnesium isotopes

24, 25, and 26. Resolution at high mass is indicated by lead isotopes 206, 207, and 208. Instrument stability must be demonstrated by running a tuning (daily performance check) solution (1 nanograms per liter (ng/L) of barium, bismuth, cerium, cobalt, indium, lead, lithium, and uranium; and 10 ng/L of magnesium) five times with the resulting Relative Standard Deviation (RSD) of absolute signals for all analytes of less than 3 percent. Sample and waste disposal procedures are outlined in ERG-MOR- 033, the *SOP for Hazardous Waste*.

10.2 Lead Analysis Using an X-Ray Fluorescence Analytical System

DRI will analyze the PM_{10} filters for Pb by XRF. Upon receipt from ERG, the samples are checked against the COC forms. EDXRF analysis will be performed on Teflon-membrane filters for Pb PM_{10}, although the system may be used for up to 51 elements including the 33 elements currently reported to AQS for EPA's Chemical Speciation Network (CSN). XRF analyses are performed on a PANalytical Epsilon 5 EDXRF analyzer. Seven XRF conditions are normally used by the PANalytical instrument on each sample to optimize the detection limits for the specified elements. However, since Pb has no significant interferences from other elements that are accounted for in the deconvolution software for the condition used, if EPA and ERG agree, DRI will modify its normal multi-element procedure to use only the one condition for Pb and increase the condition's analysis time by a factor of four to improve the Pb detection limit by a factor of two.

Two types of EDXRF standards are used for calibration, performance testing, and auditing: (1) vacuum-deposited thin-film elements and compounds from Micromatter Co. (Vancouver, BC), and (2) polymer films. The vacuum deposit standards cover most elements and are used as calibration standards. The polymer film and NIST standards are used as QC standards. During EDXRF analysis, filters are removed from their Petri slides and loaded into holders for entry into the x-ray analysis chamber. The vacuum in the x-ray chamber and the heat induced by the absorption of x-rays may evaporate some materials, such as ammonium nitrate. A QC standard and a replicate from a previous analysis will be analyzed with each set of 10 filters. When a QC value differs from specifications by ± 10% or more, or when a replicate

value differs from the original value (where values exceed 10 times the detection limits) by ±10% or more, the problem is identified and filters may be reanalyzed. If further tests of standards show that the system calibration has changed by more than ±5%, the instrument is recalibrated. In addition, DRI will maintain a set of laboratory blanks that will be analyzed periodically (~1 blank for every 20 filters analyzed) to test for baseline shifts in blank values.

After EDXRF analysis, the Teflon-membrane filters are returned to their Petri slides and stored until the XRF data validation is completed and indicates that the runs are acceptable.

Detailed information on the EDXRF analysis of Teflon-membrane filters is given in DRI *SOP for for X-Ray Fluorescence (XRF) Analysis of Aerosol Filter Samples (PANalytical Epsilon 5)*, DRI SOP #2-209.8, in Appendix B.

SECTION 11
QUALITY CONTROL REQUIREMENTS

This section describes the quality control requirements for each of the analytical methods. The MDLs presented in this section were performed in 2015.

11.1 Standard Traceability

The standards used for all analytes are vendor-supplied National Institute of Standards and Technology (NIST) standards or vendor-supplied referenced to a NIST standard. All analytical methods are also certified by comparison to a second source NIST-traceable standard. The ERG-MOR-022, *SOP for the Preparation of Standards in the ERG Laboratory*, provides direction for preparing standards (Appendix A).

11.2 Accuracy and Acceptance

Because ambient air measurements encompass a range of compounds and elements whose individual concentrations are unknown, defining absolute accuracy is not possible. Instead, accuracy is determined by comparing the analysis of standards of known concentration. The criteria for the analysis of collocate samples and their replicate analyses are found in Section 4. Each instrument calibration is discussed by method in Section 13 of this QAPP. Accuracy of analysis is based on the accuracy of the calibration, including the accuracy of the calibration standards. Accuracy is monitored throughout the program using QC and quarterly audit (or proficiency) samples. Routine analysis of proficiency lead test strips/filters for TSP by ICP-MS, PM_{10} by ICP-MS and PM_{10} by XRF is discussed in Section 16.1.3. Required QC samples and their criteria and corrective actions are discussed by the methods listed below.

11.2.1 Lead Analysis by ICP-MS

Daily, the mass spectrometer used for metals analysis must have an acceptable daily performance check using the tuning solution. Performance specifications are presented in Table 11-1. Analysis of lead will be performed by ICP-MS. Bismuth and Holmium are the internal standard used for the analysis of lead. Internal standard responses must be evaluated for stability. Daily calibration, using a calibration blank and a minimum of 4 non-zero standards prepared from NIST-traceable stock solutions, is performed to ensure that the analytical procedures are in control. To be considered acceptable, the calibration curve must have a correlation coefficient ≥ 0.998. After calibration, an Initial calibration Verification (ICV), Initial Calibration Blank (ICB), Low Standard Verification (LCV), High Standard Verification (HSV) to ensure quality by verifying the initial calibration before the analysis of the samples and throughout the day. Interference Check Standard A (ICSA), and Interference Check Standard B (ICSAB) are also analyzed daily to ensure the accurate measurement of lead.

Table 11-1.

ICP-MS Instrument Performance Specifications

Mass Number	Sensitivity/Ratio	RSD
KED Mode		
24Mg 25Mg 26Mg	> 3,000 cps > 500 cps > 600 cps	< 5% RSD
59Co	> 30,000 cps	< 2% RSD
115In	> 30,000 cps	< 2% RSD
206Pb 207Pb 208Pb	> 60,000 cps > 50,000 cps > 80,000 cps	< 2% RSD
238U	> 80,000 cps	< 2% RSD
140CeO/140Ce	< 0.01	N/A
59Co/35Cl.16O	< 18.0	N/A
Background	< 0.5 cps @ Mass 4.5 < 2.0 cps @ Mass 220.7	N/A

*cps – Counts per second

If the initial calibration checks do not meet criteria, a second calibration check analysis is performed. If the second set does not pass, or if one or more of the daily QC checks do not meet criteria, a new calibration curve is prepared and analyzed. All samples analyzed with the unacceptable QC check will be reanalyzed or flagged appropriately when necessary. During the analysis of the samples, the Continuing Calibration Verification (CCV) and Continuing Calibration Blank (CCB) are analyzed immediately before the analysis of samples, every ten samples, and at the end of every analysis batch. The ICSA and ICSAB are analyzed every eight hours and at the end of every analysis. The LCV is analyzed at the end of every analysis. Quality procedures for metals analysis by ICP-MS are shown in Table 11-2.

Table 11-2
Summary of Quality Control Procedures for ICP-MS Analysis

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Daily Performance Check (DPR)	Daily, prior to samples	See Table 11-1 for acceptance criteria.	1)Repeat analysis of DPR 2)Re-optimize instrument tuning parameters 3) Reprepare DPR standard 4) Perform instrument maintenance
Initial Calibration Standards (IC)	Daily, at least 5 calibration points (blank included as one calibration point)	Correlation coefficient ≥ 0.998 & %RSD ≤ 10. RSDs > 10 are acceptable for the CAL2 standard.	1) Repeat analysis of calibration standards 2) Reprepare calibration standards and reanalyze
ICV	Immediately after calibration	Recovery 90-110%	1) Repeat analysis of ICV 2) Recalibrate ICV standard 3) Recalibrate and reanalyze
ICB	Immediately after ICV	Absolute value must be < MDL	1) Locate and resolve contamination problems before continuing 2) Reanalyze or recalibrate or flag failing elements for the entire analysis when appropriate
HSV	After ICB and before ICS	Recovery from 95-105%	1) Repeat analysis of HSV 2) Reprepare HSV
ICSA/IFA	Following the HSV, every 8 hours and at the end of each run	Within ±3 times Limit of Quantitation (LOQ) from zero or from the standard background contamination when present	1) Repeat analysis of ICSA 2) Reprepare ICSA and analyze 3) Adjust correction equation(s) and reprocess entire analysis

Table 11-2, Continued
Summary of Quality Control Procedures for ICP-MS Analysis

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
ICSAB/IFB	Following each ICSA	Recovery 80-120% of true value plus standard background contamination when present	1) Repeat analysis of ICSAB 2) Reprepare ICSAB and analyze 3) Adjust correction equation(s) and reprocess entire analysis
CCV	Analyze before samples, after every 10 samples, and at the end of each run	Recovery 90-110%	1) Reanalyze CCV 2) Reprepare CCV 3) Recalibrate and reanalyze samples since last acceptable CCV
LCV	At the beginning and end of each analysis, between the CCV and the CCB	Recovery 70-130%	1) Reanalyze LCV 2) Reprepare LCV 3) Recalibrate and reanalyze samples since last acceptable LCV
CCB	Analyzed after each CCV	Absolute value must be < MDL	1) Reanalyze CCB 2) Reanalyze samples since last acceptable CCB
LRB/BLK1	1 per 20 samples, a minimum of 1 per batch	Absolute value must be < MDL	1) Reanalyze 2) If > MDL, but < 5x MDL, sample results for that element must be flagged for the entire analysis 3) If > 5x the MDL then sample results for that element must be blank subtracted
MB/BLK2	1 per 20 samples, a minimum of 1 per batch	Absolute value must be < MDL. Note: The MB is used only for the purpose of MDL generation	This standard is not required by the method and there is no corrective action
Standard Reference Material (SRM)	1 per 20 samples, a minimum of 1 per batch	Recovery 80-120%	1) Reanalyze 2) Flag sample data 3) Re-extract batch
LCS/BS (and BSD for 47mm Teflon® filters only)	1 per 20 samples, a minimum of 1 per batch	Recovery 80-120%	1) Reanalyze 2) Flag data if recovery for only one or two elements fail criteria 3) Reprepare sample batch if recovery for most elements fail criteria, if possible

Table 11-2, Continued
Summary of Quality Control Procedures for ICP-MS Analysis

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Replicates (DUP) (Replicate Analysis)	1 per 20 samples, a minimum of 1 per batch	≤ ±10% RPD for 47 mm Teflon filters and 20% RPD for 8x10" Quartz filters values ≥ 10 times the MDL	1) Check for matrix interference in the case of DUP1 2) Repeat replicate analysis 3) Flag data
Collocated Samples (C1/C2)	10% of samples annually, if applicable	≤ ±20% RPD for sample and collocate values ≥ 10 times the MDL	1) Flag C2 data if associated replicate analysis are within criteria 2) Repeat analysis if replicate analysis fail
Matrix Spike (MS) and Matrix Spike Duplicate (MSD) for 8x10" Quart filters only	1 per 20 samples per sample batch	Recovery 75-125%	1) Flag data if recovery for only one or two elements fail criteria, or when a matrix interference is confirmed by SRD and/or PDS results 2) Reanalyze 3) Reprepare sample batch if recovery for most elements fail criteria or contamination is evident
Post Digestion Spike (PDS)	1 per 20 samples, minimum of 1 per batch	Recovery 75%-125%	1) Flag failed elements for parent sample and PDS 2) Reprepare PDS if preparation issue is suspected reason for failure
Serial Dilution (SRD)	1 per batch	Recovery 90-110% of undiluted sample if the element concentration is minimally a factor of 50 above the MDL in the original sample	1) Reprepare dilution if preparation issue is suspected reason for failure 2) Flag failed analytes
Internal Standards (ISTD)	Every Calibration, QC and Field Sample	Recovery 60-125% of the measured intensity of the calibration blank	1) If drift suspected, stop analysis and determine cause, recalibrate if necessary 2) Reprepare sample 3) If recovery > 125% due to inherent ISTD, dilute sample and reanalyze

11.2.2 Lead Analysis by XRF

Table 14-1 summarizes the QC measures for elemental analysis by EDXRF.

Two types of EDXRF standards are used for calibration, performance testing, and auditing: (1) vacuum-deposited thin-film elements and compounds from Micromatter Co. (Deer Harbor, WA), and (2) polymer films. The vacuum deposit standards cover all elements except for Ir, Ta, Zr, and Hf (which may be determined by interpolation) and are used as calibration standards. The polymer film and NIST standards are used as QC standards. During EDXRF analysis, filters are removed from their Petri slides and loaded into the carousel for entry into the x-ray analysis chamber.

The vacuum in the x-ray chamber and the heat induced by the absorption of x-rays may evaporate some materials, such as ammonium nitrate. Two QC standards are run once per day. Ten percent replicates are also analyzed. When a QC value differs from specifications by ± 10% or more, or when a replicate value differs from the original value (where values exceed 10 times the detection limits) by ±10% or more, the previous filters are reanalyzed. If further tests of standards show that the system calibration has changed by more than ±5%, the instrument is recalibrated. In addition, DRI will maintain a set of laboratory blanks that will be analyzed periodically (~1 blank for every 20 filters analyzed) to test for baseline shifts in blank values.

More detailed information on the QC measures for elemental analysis by EDXRF may be found in DRI SOP #2-209.8, in Appendix B.

Table 11-3
Summary of Quality Control Procedures for XRF Analysis

Requirement	Frequency	Calibration Standard	Performed By	Acceptance Criteria	Corrective Action
Multipoint Calibrations	Annually	QC standards	XRF lab supervisor	± 5%	Recalibrate
Minimum Detection Limit (MDL)	Initially, then quarterly or after major instrument change	Lab blanks	XRF lab supervisor, Project Manager	Within ± 10% of previous limits	Troubleshoot instrument and check filter lots
Lower Quantifiable Limit (LQL)	Quarterly	Field blanks	XRF lab supervisor, Project Manager	Within ± 10% of previous limits	Troubleshoot instrument and check filters
QC Samples					
Lab blanks	1/20 samples	N/A	Analyst	Within 3 σ of MDLs	Check instrument and filter lots
QC standards	Daily	Micromatter thin films	Analyst	± 10%	Samples before QC standard and previous standards reanalyzed
NIST-traceable standards	Annually	Micromatter thin films	Analyst	± 10%	Samples before QC standard and previous standards reanalyzed
Replicates	10% of samples	N/A	Analyst	± 10% when value >10*MDL	Reanalysis of previous samples
Level 1 Review	Every sample	N/A	XRF lab supervisor	Per SOP	Reanalysis of problem samples or flagging per SOP

11.3 Precision

Analytical precision is estimated by repeated analysis of approximately 10 percent of the samples. The second analysis is performed in the same analytical batch as the first analysis. Precision estimates are calculated in terms of absolute percent difference. Because the true concentration of the ambient air sample is unknown, these calculations are relative to the average sample concentration. The precision criteria for all parameters were listed previously in Table 4-1.

Precision is determined as the RPD using the following calculation:

$$RPD = \frac{|X_1 - X_2|}{\overline{X}} \times 100$$

Where:

X_1 is the ambient air concentration of a given compound measured in one sample;

X_2 is the concentration of the same compound measured during duplicate/collocate/replicate analysis; and

$\overline{X}$ is the arithmetic mean of X_1 and X_2.

11.4 Sensitivity (Method Detection Limits)

MDLs are determined different ways for each analytical system. For the ICP-MS, one MDL is determined for glass fiber filters, and another for Teflon® filters. The detection limits for metals by ICP-MS is determined by the FACA[7] method using compiled method blank data. The XRF MDLs are determined by DRI as three times the standard deviation of laboratory blanks. They are updated periodically, usually quarterly. The MDLs are shown in Table 11-3 and are based on an average sampling volume of 2000 m^3 for the glass fiber filters and 24.04 m^3 for the Teflon® filters.

Table 11-4. 2015 Method Detection Limit

Element	47 mm Teflon MDL (ng/m^3)	8x10" Glass Fiber Filter MDL (ng/m^3)
Lead – ICP-MS	0.029	0.089
Lead – XRF	2.0*	

* If only the one condition for Pb is used and the analysis time in increased by a factor of four, the MDL could become 1.0 ng/m^3.

NOTE: For total metals: Assumes total volume of 24.04 m^3 for Teflon® filters and 2000 m^3 for Glass Fiber filters.

SECTION 12
INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE REQUIREMENTS

To ensure the quality of the analytical equipment, ERG and DRI conduct performance checks for all equipment used. The laboratories monitor the performance of the analytical instrumentation to ensure proper operation while maintaining a spare parts inventory to shorten equipment downtime. Table 12-1 details the maintenance items, how frequently they will be performed, and who is responsible for performing the maintenance. All checks, testing, inspections, and maintenance done on each instrument are recorded in the appropriate Maintenance Logbook or LIMS Instrument Maintenance Logs for each instrument. Following instrument maintenance, a calibration must be passed to ensure the instrument is performing properly prior to analyzing samples. Because ERG's instrument is under full service contracts, service is rendered swiftly and instrument down time is kept to a minimum. DRI does not have a full service contract for its XRF instrument but keeps a wide variety of spare parts on hand for most common maintenance issues and make our own repairs. Historical maintenance on worst case instrument failure (multiple components), it has taken less than 2 weeks to get parts and repair and recalibrate the instrument. There is also a mutual aid agreement with UC Davis for analyzing XRF samples in case of XRF instrument failure.

12.1 ICP-MS

For ICP-MS analysis, preventive maintenance is performed by competent technical service representatives as needed. ERG personnel perform minor maintenance, such as detector maintenance, on an as-needed basis. Spare pump tubing, autosampler probes, nebulizers, spray chambers, torches, and cones should all be kept in reserve in the lab for the ICP-MS. More procedures, checks, and scheduled maintenance checks are provided in ERG's SOP ERG-MOR-084 and -085 for metals analysis by ICP-MS, in Appendix A.

Table 12-1
Preventive Maintenance in ERG & DRI Laboratories

Item	Maintenance Frequency	Responsible Party
ICP-MS Instrument		
Computer Backup	Daily	Manufacturer Service Contractor/Analyst
Change Roughing Pump Oil	Annually	Manufacturer Service Contractor/Analyst
Chiller Fluid Top-off and Cleaning	As Needed	Manufacturer Service Contractor/Analyst
Replace Peripump Tubing	Daily	Analyst
Clean/Replace Sample Introduction Components	As Needed	Analyst
Replace Autosampler Housing & Instrument Air Filters	Annually	Manufacturer Service Contractor/Analyst
XRF Instrument		
Run QC standards	Daily	Analyst
Fill LN2 container	Weekly	Analyst
Perform detector energy calibration	Weekly after LN_2 fill	Analyst
Check/fill x-ray tube cooling water vessel	As needed	XRF Lab Supervisor
Check/change pump oil	As needed	XRF Lab Supervisor
Multipoint calibrations	Annually or after certain equipment replacement or repair	XRF Lab Supervisor

12.2 XRF

For XRF analysis, most preventive maintenance is performed by competent analysts while the multipoint calibration is performed by the XRF Laboratory Supervisor. The instrument tends to run with minimal maintenance and major components tend to operate for years before needing replacement. Additional procedures and checks are described in DRI's SOP #2-209 for lead analysis by XRF in Appendix B.

SECTION 13
INSTRUMENT CALIBRATION AND FREQUENCY

Because the requirements for analytical system calibrations differ, the laboratories are discussed separately in this section. Analytical instruments and equipment are calibrated when the analysis is set up, when the laboratory takes corrective action, following major instrument maintenance, or if the continuing calibration acceptance criteria have not been met. Appropriate standards are prepared by serial dilutions of pure substances, accurately prepared concentrated solutions. In preparing stock solutions of calibration standards, great care is exercised in measuring weights and volumes, since analyses following the calibration are based on the accuracy of the calibration.

DRI's three types of standards used with the DRI XRF are: (1) elemental thin film standards from μMatter; (2) multiple element thin film standards from μMatter; and (3) NIST certified standards. None of these standards require preparation; they are used as received from the supplier. The μMatter standards are stored in PetriSlides and kept in a cool dark cabinet when not in use to retard oxidation and loss of volatile elements. NIST standards are stored in the XRF room in the standards cabinet at ambient conditions. Certificates of elemental concentrations are provided by the manufacturer and are filed in the XRF lab. The DRI XRF system is recalibrated approximately every 12 months using the μMatter thin film standards. Recalibration is also performed whenever the QA standard indicate a drift of >±5% in calibration. Standards including elements from Na to U are analyzed in standard 47 mm filter holders under the filter analysis application (Filterxxxyy, where yyy = month and xx = year). Calibration factors in μg/cm2 per counts per second per milliamp are calculated for each element using linear regression analysis by the Epsilon 5 software package. The μMatter standards are accurate to ±5% relative, as stated by the manufacturer. The NIST standards are used to verify the multipoint calibration that is performed annually or after major component repairs or replacement.

Each calibration analysis is stored, electronically and hardcopy, with the samples analyzed using that calibration. All programs store the calibration information separately with all pertinent information (raw data, control charts, and/or any summary statistics) together with the analyzed samples.

13.1 ICP-MS Calibration

Calibration requirements for ICP-MS is shown in Table 13-1.

13.2 XRF Calibration

Calibration requirements for the XRF are also shown in Table 13-1.

Table 13-1
ICP-MS and XRF Analytical Calibration Requirements

Analytical Parameter	Quality Parameter	Method of Determination	Frequency	Acceptance Criteria
ICP-MS	Calibration – Quantitative	Initial analysis of a calibration blank plus 4 levels of standards	Prior to sample analysis	Correlation coefficient ≥ 0.998 & RSD ≤ 10. RSDs > 10 are acceptable for the CAL2 standard.
	ICV	Analysis of a second source standard	Immediately following calibration	Recovery 90-110%
	ICB	Analysis of an ASTM Type I water acidified with the same acid matrix as is present in the calibration standards.	Immediately following the ICV	Absolute value must be ≤ MDL
	HSV	Analysis of high concentration standard	Immediately following the ICB	Recovery 95-105%

Table 13-1, Continued
ICP-MS and XRF Analytical Calibration Requirements

Analytical Parameter	Quality Parameter	Method of Determination	Frequency	Acceptance Criteria
	ICSA	Analysis of blank solution containing interfering elements	Following the HSV, every 8 hours, and at the end of each run	Analyte must be ±3x the QL from zero or from the standard background contamination when present.
	ICSAB	Analysis of standards containing interfering elements	Immediately following each ICSA	Recovery 80-120% of true value plus standard background contamination when present
	CCV	Analysis of mid-range calibration standard to verify initial calibration	Analyze before the 1st sample, after every 10 samples and at the end of the run	Recovery 90-110%
	LCV	Analysis of low-range calibration standard	Analyze at the beginning and end of each analysis	Recovery 70-130%
	CCB	Analysis of an ASTM Type I water acidified with the same acid matrix as is present in the calibration standards.	Analyze after each CCV	Absolute value must be ≤ MDL
XRF Analysis	Accuracy	QC µMatter standards	Daily	± 5% of standard
	Detector Signal	Internal tungsten beam	Weekly	Internal automated adjustment

SECTION 14
INSPECTION/ACCEPTANCE FOR SUPPLIES AND CONSUMABLES

14.1 Purpose

The purpose of this element is to establish and document a system for inspecting and accepting all supplies and consumables that may directly or indirectly affect the quality of the data. By having documented inspection and acceptance criteria, consistency of the supplies can be assured. This section details the supplies/consumables, their acceptance criteria, and the required documentation for tracing this process.

14.2 Critical Supplies and Consumables

Table 14-1 details the various components for the laboratory operations.

14.3 Acceptance Criteria

Acceptance criteria must be consistent with overall project technical and quality criteria. It is the laboratory analyst's responsibility to update the criteria for acceptance of consumables. As requirements change, so do the acceptance criteria. Observation of damage due to shipping can only be performed once the equipment has arrived on site.

All supplies and consumables are inspected and either accepted or rejected upon receipt in the laboratory. The employees who ordered the supply are responsible for verifying that the order is acceptably delivered, stored and dispersed upon receipt in the laboratory. Some supplies or consumables listed in Table 14-1 have to be deemed acceptable, through testing or blanking, such as with the filters used for blank analysis. Any changes in standards and sample media must meet the acceptance criteria outlined in Section 11 for that particular method. Such testing and blanking data is kept with the sample data. Staff should not use supplies or consumables of different model numbers or from different vendors without first discussing it with the Program Manager and testing the supply or consumable.

Table 14-1
Critical Field and Laboratory Supplies and Consumables

Area	Item	Description	Vendor	Model Number
Laboratory Supplies and Consumables (Laboratories listed below)				
ICP-MS	Argon	Coolant Gas	Air Gas	LARS-65
ICP-MS	Helium	Collision Gas	Air Gas	HE R80A
ICP-MS	Acid	High Purity HNO_3 High Purity HCl High Purity HF	Fisher	A497-2 A466-500 A463-250
ICP-MS	Inorganic standards	Individual Metals Standards	High Purity Spex Inorganic Ventures	Various
ICP-MS	Nalgene 60oz. bottles	Sample containers	Fisher	16058-043
ICP-MS	Extraction consumables	Sample Vials FilterMate Filters Reflux Caps Autosampler Vials	SCP Science Environmental Express CPI	010-500-264 SC0408 SC506 P/N 4092-316
ICP-MS	Glass Fiber/ Teflon Filters	Filters	Whatman MTL	1822-866 PT47AN
XRF	Liquid Nitrogen	Detector coolant	Air Gas	NA
XRF	Mylar sheets	2”x 2” 3.6 µm thick	Somar Spectrofilm	3615-33
XRF	Tweezers	For handling filters	Millipore	62-000067
XRF	Kimwipes	Large & small	VWR	34255 & 34155
XRF	Methanol (in squeeze bottle)	Cleaning solvent for sample holders & filter loading area	Fisher Scientific (VWR)	A454-4 (16649-945)
XRF	Epsilon 5 XRF Analysis Logsheet	Analysis Logsheet	DRI	NA

Consumables and supplies with special handling and storage needs must be handled and stored as suggested by the manufacturer. Consumables with expiration dates, such as standards, must be labeled with a receipt date, date opened, and the initials of the person that opened the consumable and standard expiration dates must be entered into the standards section of LIMS. To decrease waste, the oldest supplies or consumables should be used first.

14.4 Tracking and Quality Verification of Supplies and Consumables

Tracking and quality verification of supplies and consumables have two main components. The first is the need of the end user of the supply or consumable to have an item of the required quality. The second need is for the purchasing department to accurately track goods received so that payment or credit of invoices can be approved. In order to address these two issues, at ERG the following procedures outline the proper tracking and documentation procedures to follow:

- Receiving personnel will perform a rudimentary inspection of the packages as they are received from the courier or shipping company. Note any obvious problems with a receiving shipment such as crushed box or wet cardboard.

- The package will be opened, inspected, and contents compared against the packing slip.

- If there is a problem with the equipment/supply, note it on the packing list and notify the Purchasing Agent who will immediately call the vendor.

- If the equipment/supplies appear to be complete and in good condition, sign and date the packing list and give it to the Purchasing Agent so that payment can be made in a timely manner.

- Notify appropriate personnel that equipment/supplies are available. For items such as filters, it is critical to notify the laboratory manager of the weight room so sufficient time for processing of the filters can be allowed.

- Stock equipment/supplies in appropriate pre-determined area.

Standards and reference materials are purchased from vendors who certify the purity and traceability of these standards. Certificates of analysis and/or purity are maintained in project files or in the LIMS standards log.

SECTION 15
DATA MANAGEMENT

15.1 Data Recording

Data management for sample data is presented in Figure 15-1. The sample data path is shown from sample origination to data reporting and storage. The LIMS allows the laboratory to manage and track samples, instrument workflow, and reporting. The LIMS stores the raw instrument data and performs the conversion calculations to put the data into final reporting units. These calculations are reviewed and documented annually by ERG's QA coordinator and kept in the QA files in Room 102. The main procedures are described in the *SOP for the Laboratory Information Management System* (ERG-MOR-099). The main functions of the LIMS system include, but are not limited to:

- Sample login;
- Sample scheduling, and tracking;
- Sample processing and quality control; and
- Sample reporting and data storage.

All LIMS users must be authorized by the LIMS Administrator and permitted specified privileges. The following privilege levels are defined:

- Data Entry Privilege – The individual may see and modify only data within the LIMS that he or she has personally entered.
- Reporting Privilege – Without additional privileges.
- Data Administration Privilege – Data Administrators for the database are allowed to change data as a result of QA screening and related reasons. The Data Administrator is responsible for performing the following tasks on a regular basis:
  - Merging/correcting the duplicate data entry files;
  - Running verification/validation routines, correcting data as necessary; and
  - Generating summary data reports for management.

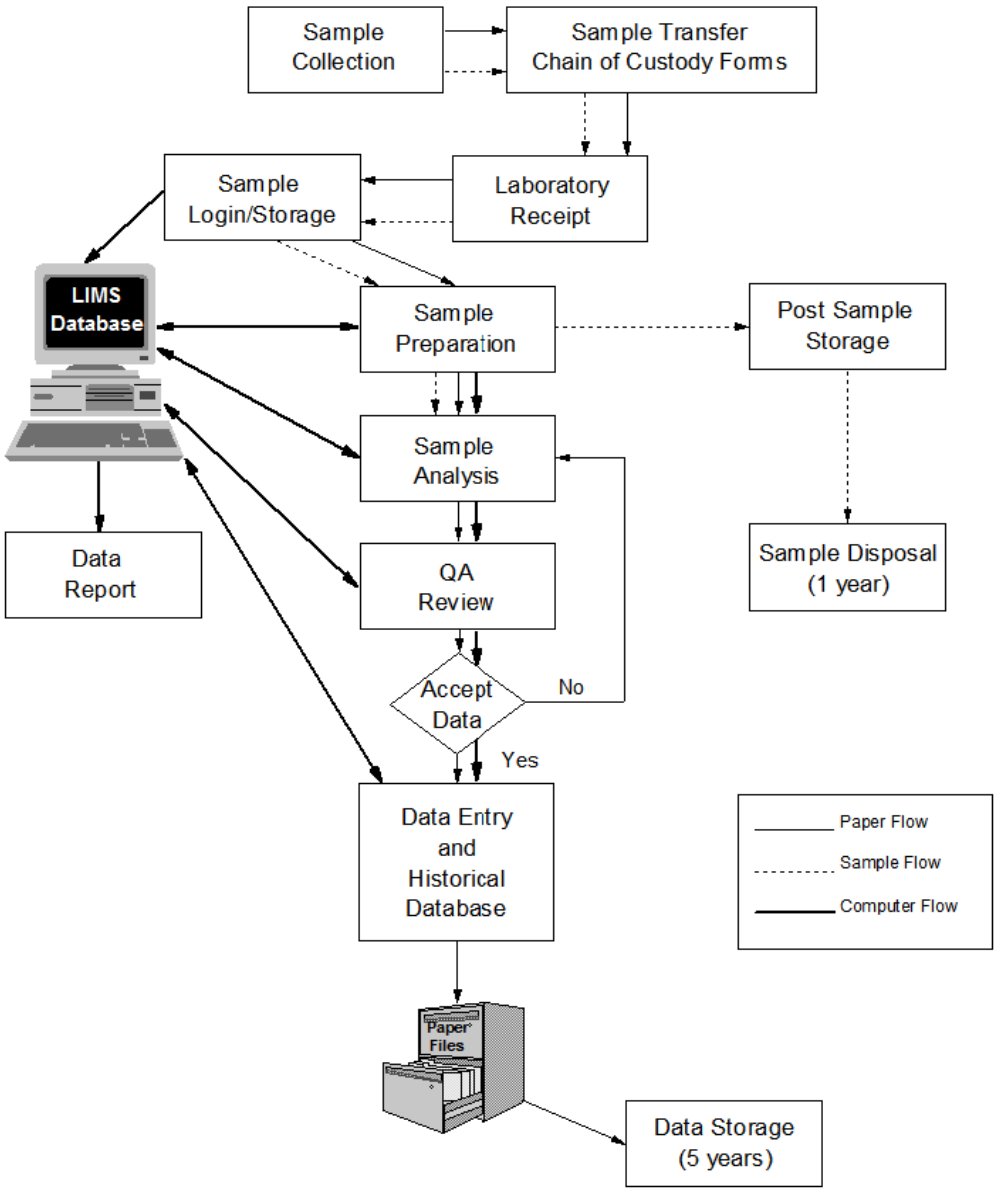


Figure 15-1. Data Management and Sample Flow Diagram

15.2 Data Validation

Data validation is a combination of checking that data processing operations have been carried out correctly and of monitoring the quality of the field operations. Operations checked include collection information on COCs, sample receipt entry into LIMS, sample volume entry

into bench sheets, and upload of data into LIMS. Data validation can identify problems in these areas. Once problems are identified, the data can be corrected or invalidated, and corrective actions can be taken for laboratory operations.

15.3 Data Reduction and Transformation

Calculations for transforming raw data from measured units to final concentrations use standardized procedures listed in the individual ERG or DRI SOPs. The equations for transforming raw data are set up to automatically calculate to final concentrations in the LIMS system. The initial units for ICP-MS Pb results are ng/L with final reporting units of µg/filter. The initial units for XRF Pb results are µg/cm^{2}with the final results in µg/m^3. For XRF Pb, the associated MDLS and uncertainties are reported along with the final concentrations. For ICP-MS, the associated MDLs are reported along with the final concentrations, and the MDLs are adjusted for dilution (for ICP-MS) and actual prep volumes before reporting.

The electronic data file is uploaded onto a network server (which is backed-up daily) and into the LIMS. DRI data files are imported onto the network server. Once the data is in LIMS, the ERG Task Leader reviews it following the checklists presented in Section 16 using instrument software and method specific controls set up in LIMS. Ten percent of the total data is reviewed by the QA Coordinator or designee following the checklist and method specific acceptance criteria in the summary quality control procedure tables outlined in Section 11. After the data has successfully completed both reviews and the checklists have been signed, it is available for reporting by the Program Manager.

The *SOP for Project Peer Review* uses manual calculations and visual verification to review all data reported to EPA and State/ local/tribal agencies following guidelines outlined in SOP ERG-MOR-057 (see Appendix A). *SOP for Developing, Documenting, and Evaluating the Accuracy of Spreadsheet Data*, presented in SOP ERG-MOR-017 (see Appendix A), is consulted in special cases where the calculations are performed via spreadsheets instead of the LIMS system.

Reporting formats are designed to fulfill the program requirements and to provide comprehensive, conventional tables of data. The LIMS data reporting format includes any required data qualifiers, footnotes, detection limits for each analyte, and appropriate units for all measurements. The LIMS can produce Adobe and Excel data reports, which is standard for this program. The report is reviewed by the Program Manager or designee before it is sent to the client. As mentioned in Section 15.5, a comprehensive annual data report is prepared including data statistics and characterization.

15.4 Data Transmittal

Data transmittal occurs when data are transferred from one person or location to another or when data are copied from one form to another. Some examples of data transmittal are copying raw data from a notebook onto a data entry form for keying into a computer file and electronic transfer of data over a computer network. Each individual SOP listed in Appendix A & B discusses the procedures for determining the calculations of concentrations as well as data entry.

If requested, ERG will report all ambient air quality data and information specified by the AQS User's Guide and other documents located at the website http://www.epa.gov/ttn/airs/airsaqs/manuals/ coded in the AQS format. Such air quality data and information will be fully screened and validated and will be submitted directly to the AQS via electronic transmission, in the format of the AQS, and in accordance with the annual schedule. The *SOP for the Preparation of Monitoring Data for AQS Upload* is presented in Appendix A (SOP ERG-MOR-098).

15.5 Data Tracking

The ERG LIMS database contains input functions and reports necessary to track and account for the status of specific samples and their data during processing operations. The following input locations are used to track sample and sample data status:

- Sample Control
  - Sample collection information (by Work Order);
  - Sample receipt/custody information;
  - Unique sample number (LIMS ID);
  - Storage location;
  - Required analyses;
  - Project due dates/hold times.

- Laboratory
  - Batch/bench assignment;
  - Sequence assignment;
  - Data entry/review;
  - Query/update analysis status;
  - Standards/calibration information.

15.6 Data Storage and Retrieval

Data archival policies are shown in Table 15-1.

All data are stored on the ERG LIMS server. This system has the following specifications:

- Operating System: Windows 2008 Server
- Memory: 6G RAM
- Hard Drives: Three drives of 450G each configured as RAID 5;
- Network card: Gigabit card (10/100/1000)
- Tape Drives for Backup: Two tape drives are daisy chained (Compaq SDLT 600 & HP SureStore DLT 818).
- Security: Network login password protection on all workstations; Additional password protection applied by application software.

Security of the data in the database is ensured by the following controls:

- Password protection on the data base that defines three levels of access to the data;
- Regular password changes (quarterly);
- Logging of all incoming communication sessions, including the originating telephone number, the user's ID, and connect times; and
- Storage of media, including backup tapes, in an alternate location that is at a locked, restricted access area.

Table 15-1. Data Archive Policies

Data Type	Medium	Location	Retention Time	Final Disposition
Laboratory notebooks	Hardcopy	Laboratory	5 years after close of contract	N/A
LIMS Database	Electronic (on-line)	Laboratory	Backup media after 5 years	Backup tapes retained indefinitely

ASSESSMENT/OVERSIGHT
SECTION 16
ASSESSMENTS AND RESPONSE ACTIONS

An assessment is defined as an evaluation process used to measure the performance or effectiveness of the quality system or the establishment of the monitoring network and sites and various measurement phases of the data operation.

The results of QA assessments indicate whether the control efforts are adequate or need to be improved. Documentation of all QA and QC efforts implemented during the data collection, analysis, and reporting phases are important to data users, who can then consider the impact of these control efforts on the data quality. Both qualitative and quantitative assessments of the effectiveness of these control efforts will identify those areas most likely to impact the data quality. ERG will perform the following assessments in order to ensure the adequate performance of the quality system.

The Response/CAR will be filed whenever a problem is found such as an operational problem, or a failure to comply with procedures that affects the quality of the data. A CAR is an important ongoing report to management because it documents primary QA activities and provides valuable records of QA activities. A CAR can be originated by anyone on the project, but must be sent to the Program QA Coordinator and Program Manager. Any problem that affects the quality of the overall program will be discussed with the EPA.

On the numbered CAR, the description of the problem, the cause of the problem, the corrective action, and the follow-up are documented. The follow-up assists the QA coordinator in determining if the corrective action was successful and if it was handled in a timely manner. ERG's CAR is recorded on a three-part form, the white copy goes into the project file, the yellow copy goes into the QA file (Room 102), and the pink copy goes to the facilitator. A copy of the ERG CAR Form is shown in Figure 16-1.

Corrective Action Report – 2015-01

Originator:	**Date:**	
Project Number:	**Corrective Action Number:**	
Is Immediate Stop of Work required?	Yes	No
Description of the Problem: (Provide date and time identified)		
State cause of Problem: (An investigation can reveal the cause, may fill after investigation, provide dates and time frame and if multiple approaches have been used to identify the cause)		
State Corrective Action Planned: (Include persons involved in action and date action is to be completed, include all approaches and dates)		
Close Out Details: (Fill when the corrective action successfully provides an effective long-term solution, include all approaches attempted)		

Signature and Date	Comments
QA Officer:	
Project Manager:	
Originator:	

Figure 16-1. ERG Corrective Action Report Form

DRI's process for dealing with corrective actions is governed by DRI *SOP for Corrective actions*, DRI SOP #6-017, and its CAR is shown in Figure 16-2.

EAF CORRECTIVE ACTION REQUEST

CAR No. _____ **Date** _____

To **From**	
How Identified	
Reported (Nonconformance) Conditions **Answer Due Date**	**Signature**
Root Cause	
Corrective Action (Give Steps & Expected Completion Dates)	
Preventive Action	
Completed by	**Date**
Accepted by	**Date**
Follow-up Results **Performed by**	**Date**
Closed Out (Y/N) _____	If not closed out on follow-up, issue a new CAR
New CAR No.	**Date**

Figure 16-2. DRI Corrective Action Report Form

Each recommendation addresses a specific problem or deficiency and requires a written response from the responsible party. Each also requires the Program QA Coordinator to verify that the corrective action has been implemented. A summary of the past years' CARs are discussed during the annual QA Management Systems Review.

The following actions are taken by the laboratory QA Coordinator and Program Manager when any aspect of the testing work, or the results of this work, does not conform to the requirements of the quality system or testing methods:

- Identify nonconforming work and take actions such as the halting of work, the withholding of test reports;
- Evaluate of the impact of nonconforming work on quality and operations;
- Take remedial action and make decision about the acceptability of the nonconforming work (resample, use as is with qualification, unable to use);
- Notify the client, and if necessary, recall the work; and authorize the resumption of work.

ERG and DRI are responsible for implementing the analytical phase of this program and are not responsible for the overall DQOs. Therefore, this QAPP tries to ensure that analytical results are of adequate quality to ensure the achievement of the various program DQOs.

16.1 Assessment Activities and Project Planning

16.1.1 External Technical Systems and Data Quality Audits

A Technical Systems Audit (TSA) is a thorough and systematic on-site qualitative audit, where facilities, equipment, personnel, training, procedures, subcontractor systems, and record keeping are examined for conformance to the QAPP. The TSAs will be performed by EPA or its designee at the ERG Laboratory. The TSAs of the contract are conducted approximately every five years. The EPA QA Office will implement the TSA either as a team or as an individual

auditor. ERG will participate in any data quality audits by EPA or designee at the discretion of the EPA QA Coordinator.

The EPA audit team will prepare a brief written summary of findings for the Program Manager and Program QA Coordinator. Problems with specific areas will be discussed and an attempt made to rank them in order of their potential impact on data quality. ERG will work with EPA to solve required corrective actions. As part of corrective action and follow-up, an audit finding response letter will be generated by the Program Manager and Program QA Coordinator. The audit finding response letter will address what actions are being implemented to correct the finding(s) of the TSA. This summary from EPA and the following response from ERG are filed in the QA/QC file in Room 102. The findings and the follow-up corrective actions are discussed in the annual QA Management Systems Review.

As part of ongoing National Environmental Laboratory Accreditation Conference (NELAC) certification, TSAs are performed at ERG by Florida Department of Health or designee every two years. A summary of findings is sent to ERG, specifically the QA Coordinator. The QA Coordinator sends its response of corrective actions which is either accepted or denied by Florida Department of Health. This documentation is stored in the QA/QC file in Room 102. The findings and the follow-up corrective actions are discussed in the annual QA Management Systems Review.

As a contractor laboratory performing analyses for EPA's $PM_{2.5}$ CSN, DRI has external TSAs performed roughly every three years by an audit team from EPA's National Air and Radiation Environmental Laboratory (NAREL). In addition, as part of its NELAP accreditation program through the Texas Commission on Environmental Quality (TCEQ), the EAF is audited roughly every three years by a TCEQ contractor.

16.1.2 Internal Technical Systems Audits

At ERG, an internal TSA is performed examining facilities, equipment, personnel, training, procedures, and record keeping for conformance to the individual SOPs and this QAPP. The TSAs will be performed by the Program QA Coordinator and will be conducted at least once per year. The checklists for the internal TSAs are based on the NATTS TSA or National Environmental Laboratory Accreditation Program (NELAP) checklists with additional areas addressing the individual SOPs and this QAPP. The content of the checklists vary episode to episode to ensure comprehensive in-depth coverage of procedures over time. Such elements will be included in the checklists:

- Criteria listed in Section 11 of this QAPP
- SOP specifications
- Method specifications
- Supporting equipment specifications
- Other laboratory wide QA systems in place (ex. Satellite SOP notebooks)

The Program QA Coordinator will report internal audit findings to the Program Manager within 30 days of completion of the internal audit in the form of a report. The EPA Delivery Order Manager will be informed if issues from the internal audit impact the quality of this program. The report is filed in the QA/QC file in Room 102. All corrective actions are addressed and implemented as soon as they are determined. The findings and the follow-up corrective actions are discussed in the annual QA Management Systems Review to assess effectiveness of the corrective actions.

At DRI, internal audits are conducted by the EAF QA Manager using the procedures contained in DRI *SOP for General EAF Internal Audit Procedures*, DRI SOP #4-117.1. The checklists for the internal TSAs are based on the EPA CSN TSA and NELAP checklists with additional areas addressing the individual SOPs, this QAPP, and the QAPPs for other projects.

16.1.3 Proficiency Testing

The PT is an assessment tool for the laboratory operations. Routine 'blind' samples (Pb Test strips/filters) are sent to the laboratory, where they follow the normal handling routines that any other sample follows. The results are sent to the Program Manager and Program QA Coordinator for final review and reporting to the auditing agency. The auditing agency prepares a PT report and sends a copy of the results to the Program Manager, Program QA Coordinator, and the EPA QA Office(s). Any results outside the acceptance criteria are noted in the PT report. Repeated analyte failures are investigated to determine the root cause and documented on a CAR. The PT reports are filed in the QA/QC file in Room 102. The performance on these audits is discussed in the annual QA Management Systems Review.

As a CSN contractor laboratory, DRI receives annual XRF PE samples from NAREL. However, these are ambient PM2.5 samples (of different sampling durations) and the XRF analysis is not exclusively for Pb. Pb one of several elements typically used for the annual inter-comparison. The results of these intercomparisons may be found at: http://www3.epa.gov/ttn/amtic/pmspec.html.

16.2 Documentation of Assessments

16.2.1 TSA, Data Quality Audit, and PT Documentation

All reports from EPA or designated contractors regarding ERG's performance on TSAs, Data Quality Audits, and PTs are filed in the QA/QC file in Room 102. PT reports are dispersed and discussed with contributing staff.

Reports from internal TSAs are prepared and discussed with the Program Manager, and filed in the QA/QC file in Room 102. A similar procedure is used by DRI for internal TSAs, external TSAs, and PE results and intercomparisons.

16.2.2 Internal Data Review Documentation at ERG

Internal data review is performed on 100 percent of the data by the Task Leader and 10 percent of the data by the Program QA Coordinator or designee against the criteria in the individual SOPs and this QAPP prior to being reported each month. The assessment is documented on the data review checklist, which is returned to the Task Leader for minor correction action and inclusion in the data package. The checklists used for analyses are shown in their respective SOPs (Appendix A) as follows:

- **Lead by ICP-MS** – ERG-MOR-084, *SOP for the Preparation and Analysis of High Volume Quartz Filters for Metals by ICP-MS using Method IO 3.5 and FEM Method EQL-0512-201* and ERG-MOR-085, *SOP for the Preparation and Analysis of 47mm Filters for Metals by ICP-MS using Method IO 3.5 and FEM Method EQL-0512-202.*

During the internal data review, major QC problems identified are brought to the attention of the Program Manager and are documented on a CAR. The final project report also addresses QA considerations for the whole project.

16.2.3 Internal Data Review Documentation at DRI

The procedures used at DRI are similar to those used by ERG. The SOP used for these analysis are presented in Appendix B.

- **Lead by XRF** – DRI *SOP #2-209.8, X-Ray Fluoresence (XRF) Analysis of Aerosol Filter Samples (PANalytical Epsilon 5), IO 3.3, and 40 CFR Part 50, Appendix Q.*

SECTION 17
REPORTS TO MANAGEMENT

This section describes the quality-related reports and communications to management necessary to support monitoring network operations and the associated data acquisition, validation, assessment, and reporting. Important benefits of regular monthly reports to EPA provide the opportunity to alert EPA to data quality problems, to propose viable solutions to problems, and to procure necessary additional resources.

Effective communication among all personnel is an integral part of a quality system. Regular, planned quality reporting provides a means for tracking the following:

- Adherence to scheduled delivery of data and reports;
- Documentation of deviations from approved QA and test plans, and the impact of these deviations on data quality; and
- Analysis of the potential uncertainties in decisions based on the data.

Frequency, content and distribution of reports for monitoring are shown below.

17.1 Data Reports

Analytical data reports prepared by the Program Manager are sent to EPA, State, Local and Tribal agencies within 30 days after the samples are received at ERG's laboratory. These reports include the monthly analytical data for each sample collected includes sample results, sample information (sample information, sample volume, etc.) and a QA data.

17.2 Internal Technical System Audit Reports

The Program QA Coordinator or designee performs an internal technical system audit at least once a year. The findings are listed in reports which are presented to the Program Manager

and filed in the QA/QC storage file cabinet located in Room 102. These reports are available to EPA personnel during their TSA. More detail on internal TSAs is provided in Section 16.

DATA VALIDATION AND USABILITY

SECTION 18

DATA REVIEW AND VERIFICATION

Data verification is a two-stage process to determine if the sampling and analytical data collection process is complete, consistent with the DQOs discussed in this QAPP and associated SOPs, and meets the program requirements. First the data is reviewed for completeness, accuracy, and acceptability. Then the data is verified to meet the quality requirements of the program.

18.1 Data Review Design

Information used to verify air toxics data, includes:

- Sample COCs, holding times, preservation methods.
- Multi-point calibrations – the multipoint calibrations are used to establish proper initial calibration and can be used to show changes in instrument response.
- Standards – certifications, identification, expiration dates.
- Instrument logs – all activities and samples analyzed are entered into the LIMS logs (batches, sequences, etc.) to track the samples throughout the measurements procedures.
- Supporting equipment – identification, certifications, calibration, if needed.
- Blank, CCVs, replicate and spike results – these QC indicators can be used to ascertain whether sample handling or analysis is causing bias in the data set.
- Review Checklists – these record monthly data quality review performed on all data by Task Leader and on 10 percent of the data by the QA Coordinator or designee. Data is reviewed using the checklists derived from the SOPs and this QAPP.
- Summary Reports – data reports present the data to the EPA and respective State/local/tribal representatives including data qualifiers.

The reliability and acceptability of environmental analytical information depends on the rigorous completion of all the requirements outlined in the QA/QC protocol. During data analysis and validation, data are filtered and accepted or rejected based on the set of QC criteria listed in the individual SOPs included in Appendix A (ERG) and B (DRI).

The data are critically reviewed to locate and isolate spurious values. A spurious value, when located, is not immediately rejected. All questionable data, whether rejected or not, are maintained along with rejection criteria and any possible explanation. Such a detailed approach can be time-consuming but can also be helpful in identifying sources of error and, in the long run, save time by reducing the number of outliers.

18.2 Data Verification

Data verification confirms by examination that specified requirements have been fulfilled. The specific requirements are QC checks, acceptable data entry limits, etc. as presented in Section 4 and Section 11. The analytical procedures performed during the monitoring program will be checked against those described in the QAPP and the SOPs included in Appendix A (ERG) and B (DRI). Deviations from the QAPP will be classified as acceptable or unacceptable, and critical or noncritical. During review and assessment, qualifiers will be applied to the data as needed; data found to have critical flaws (such as low spike or surrogate recoveries, contaminated blanks, etc.) will be invalidated and a CAR filled out and implemented, if needed. All of the data management guidelines followed for this contract are presented in Section 15.

18.3 Data Review

The chain of custody forms are checked to ensure accurate transcription. The results are double-checked by the Task Lead and a 10% check is performed by the QA Coordinator. The collected data are reviewed by the Analyst and the Task Leader. The data are scrutinized daily to eliminate the collection of invalid data. Invalid samples are discussed in more detail in Section 9.2. The analyst records any unusual circumstances during analysis (e.g., power loss or

fluctuations, temporary leaks or adjustments, operator error) on the LIMS bench sheet and notifies the analytical Task Leader.

QC samples and procedures performed during the monitoring program will be checked against those described in Section 4 of the QAPP. If QC is found unacceptable by these criteria, corrective actions described in the same section are implemented. Prior to reporting, 100 percent of the data is reviewed by the Task Leader. To verify accuracy, at least 10 percent of the database is checked by the QA Coordinator or designated reviewer. Items checked include original data sheets, checks of all calculations (from calibration to sample analysis), and data transfers. As the data are checked, corrections are made to the database as errors or omissions are encountered. If major errors are found, all of the data is checked to verify data quality. The Program Manager reviews all of the data before it is reported to EPA or the State/local/tribal agencies.

18.4 Data Reduction, Validation, and Reporting

Data validation is confirmed by examination of objective evidence that the particular requirements for a specific intended use are fulfilled. Intended use deals with data of acceptable quality to permit making decisions at the correct level of confidence. This section outlines data validation and usability requirements.

All samples received are given a LIMS ID number that corresponds to that sample's information. An analysis logbook is maintained to detail pertinent sample information at the time of analysis. Entries include site code, sample date, analysis date, LIMS ID, and electronic file names. Electronic copies of the data are stored on the ERG LIMS server.

Data summaries are distributed to the participating EPA technical staff, administrators, and to the administrators of the State/local/tribal agencies involved in the study. Each report is prepared within 30 days from receipt of the samples at ERG's laboratory. Cumulative listings are periodically generated upon request. Any changes made in the data as a result of subsequent

data validation processes performed by EPA and/or State/local/tribal agencies are noted in the cumulative project data summaries for each specific sampling site. The data summaries include:

- Site code;
- Sample identifications;
- Sample dates;
- Target compound list;
- Final concentrations; and
- Method detection limits.

Data summaries are emailed to the program participants. The Program Manager reviews all data before they are reported to EPA and/or the State/local/tribal agencies.

18.5 Air Quality System

ERG can submit the data collected for the Lead Analysis to the AQS database if requested by the sites. This data can be either submitted by ERG or by the State, Local or Tribal Agency.

Prior to ERG's submittal of data to AQS, the State/local/tribal agency would have to submit, at a minimum, Basic Site Information transactions (Type AA) for each sampling site, and Site Street Information (Type AB) and Site Open Path Information (Type AC), if necessary. ERG then submits monitor transactions to prepare the AQS database for data upload. Data that are uploaded into AQS include Raw Data (RD) transactions, QA transactions and Raw Blank (RB) transactions.

The submittal process involves the following steps:

- The raw data are formatted into pipe-delimited (|) coding that is accepted by the AQS. Raw data, data generated by single sample episodes, by the primary sample

(D1) of a duplicate episode, or by collocates (C1 and C2) are submitted using RD transactions. Precision data, data generated by duplicate and replicate samples (R1, D2, and/or R2) are submitted using QA transactions, specifically duplicate and replicate transactions. Accuracy data, generated for lead-FEM audit results, are submitted using Pb Analysis Audit transactions.

- The RD, QA (specifically duplicate, replicate and Pb Analysis Audit), and RB coding is generated and reviewed following guidelines listed in the *SOP for the Preparation of Monitoring Data for AQS Upload (ERG-MOR-098)* to ensure that the proper monitor ID (including state, county, site, parameter, and Parameter Occurrence Code [POC] codes), sampling interval, units, method, sample date, start hour, and sample values are correct. The transactions are stored as text files for upload into the AQS database.

- The transaction files are loaded under the appropriate screening group.

- The transactions are edited to remove any errors found by AQS and then are resubmitted. This step is repeated until the transactions are free of errors.

- AQS performs a statistical check on the data submitted to validate the data and determine if there are any outliers based on past data.

- The data transactions are then posted into the AQS database.

18.5.1 AQS Flagging and Reporting

Air toxics data submittals may be submitted with flags to indicate additional information related to the sample. There are two qualifier flag types that may be applied: Null codes and Qualifier codes.

- **Null Code —** assigned when a scheduled sample is not usable (e.g., damaged filter, improper sampling time, etc.).

- **Qualifier Code —** used to note a procedural or quality assurance issue that could possibly affect the uncertainty or concentration of the value.

Qualifier Codes can be used in combination, with up to 10 possible codes applied. If a Null code is used, no other flag should be used since no results are reported. Table 18-1 presents the Qualifier codes and Table 18-2 presents the Null codes available to AQS users. These flags

are applicable to the various steps of sample collection and analysis such as field operations, chain of custody, and laboratory operations.

Blank issue flags are qualifier flags used if reported blank values are above the limits set by the method SOPs or QAPP. If high blank values are associated with samples, the sample values are reported but appropriately flagged. Samples will not be invalidated due to high blank values. Blank issue flags are included in Table 18-1.

Table 18-1
Qualifier Codes

Qualifier Code	Qualifier Description
1	Deviation from a CFR/Critical Criteria Requirement
2	Operational Deviation
3	Field Issue
4	Lab Issue
5	Outlier
6	QAPP Issue
7	Below Lowest Calibration Level
9	Negative value detected - zero reported
CB	Values have been Blank Corrected
CC	Clean Canister Residue
CL	Surrogate Recoveries Outside Control Limits
DI	Sample was diluted for analysis
EH	Estimated; Exceeds Upper Range
FB	Field Blank Value Above Acceptable Limit
HT	Sample pick-up hold time exceeded; data questionable
IA	African Dust
IB	Asian Dust
IC	Chemical Spills & Industrial Accidents
ID	Cleanup After a Major Disaster
IE	Demolition
IF	Fire - Canadian
IG	Fire - Mexico/Central America
IH	Fireworks
II	High Pollen Count
IJ	High Winds
IK	Infrequent Large Gatherings
IL	Other
IM	Prescribed Fire
IN	Seismic Activity
IO	Stratospheric Ozone Intrusion
IP	Structural Fire

Table 18-1, Continued
Qualifier Codes

Qualifier Code	Qualifier Description
IQ	Terrorist Act
IR	Unique Traffic Disruption
IS	Volcanic Eruptions
IT	Wildfire-U. S.
J	Construction
LB	Lab blank value above acceptable limit
LJ	Identification Of Analyte Is Acceptable; Reported Value Is An Estimate
LK	Analyte Identified; Reported Value May Be Biased High
LL	Analyte Identified; Reported Value May Be Biased Low
MD	Value less than MDL
MS	Value reported is ½ MDL substituted
MX	Matrix Effect
ND	No Value Detected
NS	Influenced by nearby source
QX	Analyte does not meet QC criteria
SQ	Values Between SQL and MDL
SS	Value substituted from secondary monitor
SX	Does Not Meet Siting Criteria
TB	Trip Blank Value Above Acceptable Limit
TT	Transport Temperature is Out of Specs
V	Validated Value
VB	Value below normal; no reason to invalidate
W	Flow Rate Average out of Spec.
X	Filter Temperature Difference out of Spec.
Y	Elapsed Sample Time out of Spec.

Table 18-2
Null Codes

Null Code	Qualifier Description
AA	Sample Pressure out of Limits
AB	Technician Unavailable
AC	Construction/Repairs in Area
AD	Shelter Storm Damage
AE	Shelter Temperature Outside Limits
AF	Scheduled but not Collected
AG	Sample Time out of Limits
AH	Sample Flow Rate out of Limits
AI	Insufficient Data (cannot calculate)
AJ	Filter Damage
AK	Filter Leak
AL	Voided by Operator
AM	Miscellaneous Void

Table 18-2, Continued
Null Codes

Null Code	Qualifier Description
AN	Machine Malfunction
AO	Bad Weather
AP	Vandalism
AQ	Collection Error
AR	Lab Error
AS	Poor Quality Assurance Results
AT	Calibration
AU	Monitoring Waived
AV	Power Failure
AW	Wildlife Damage
AX	Precision Check
AY	Q C Control Points (zero/span)
AZ	Q C Audit
BA	Maintenance/Routine Repairs
BB	Unable to Reach Site
BC	Multi-point Calibration
BD	Auto Calibration
BE	Building/Site Repair
BF	Precision/Zero/Span
BG	Missing ozone data not likely to exceed level of standard
BH	Interference/co-elution/misidentification
BI	Lost or damaged in transit
BJ	Operator Error
BK	Site computer/data logger down
BL	QA Audit
BM	Accuracy check
BN	Sample Value Exceeds Media Limit
BR	Sample Value Below Acceptable Range
CS	Laboratory Calibration Standard
DA	Aberrant Data (Corrupt Files, Aberrant Chromatography, Spikes, Shifts)
DL	Detection Limit Analyses
FI	Filter Inspection Flag
MB	Method Blank (Analytical)
MC	Module End Cap Missing
SA	Storm Approaching
SC	Sampler Contamination
ST	Calibration Verification Standard
TC	Component Check & Retention Time Standard
TS	Holding Time Or Transport Temperature Is Out Of Specs.
XX	Experimental Data

ERG submits data to AQS using qualifier flags to show where the data are with respect to the detection level. A variety of terms and acronyms are used for defining the lowest level that can be detected for each analytical method. These terms and applications are presented below:

- **Quantitation Limits (QL) —** the lowest level at which the entire analytical system must provide a recognizable signal and acceptable calibration point for the analyte.

- **Detection Limits (DL) —** the minimum concentration of an analyte that can be measured above instrument background.

- **MDL —** the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte (Part 136, App. B).

- **SQL —** the lowest concentration of an analyte reliably measured within specified limits of precision and accuracy during routine laboratory operating conditions. Normally, the SQL is determined as a multiplier of the method detection limit (e.g., 3.18 times) and is considered the lowest concentration that can be accurately measured, as opposed to just detected.

The qualifier flags associated with quantitation and detection limits are also included in Table 18-1, while Table 18-3 summarizes how they are applied to the data. ERG and DRI MDLs will be uploaded into AQS to provide an accurate representation of the data.

Table 18-3
Summary of Quantitation and Detection Limit Flags and Applications

If Concentration is:	Value to Report	Flag Applied
> SQL	Value	None
> MDL ≤ SQL	Value	SQ
≤ MDL	Value	MD
Not Detected	0	ND

SECTION 19
DATA VALIDATION, VERIFICATION AND ANALYSIS

Many of the processes for verifying and validating the measurement phases of the data collection operation have previously been discussed in Section 18. If these processes as written in the QAPP are followed, and the sites are representative of the boundary conditions for which they were selected, one would expect to achieve the DQOs. However, exceptional field events may occur, and field and laboratory activities may negatively affect the integrity of samples. In addition, it is expected that some of the QC checks will fail to meet the acceptance criteria. This section will outline how ERG will take the data to a higher level of quality analysis by performing software tests, plotting, and other methods of analysis.

19.1 Process for Validating and Verifying Data

19.1.1 Verification of Data

For the analytical data, the entries are reviewed to reduce the possibility of entry and transcription errors. Once the data are transferred to the ERG LIMS database, the data will be reviewed for routine data outliers and data outside acceptance criteria. These data will be flagged appropriately. All flagged data will be "re-verified" to ensure that the values are entered correctly.

19.1.2 Validation

Records of all samples will be retained on file for 5 years, valid or invalid. Information will include a brief summary of why the sample was invalidated along with the associated flags. This record will be available on a network server. When the laboratory analyst reviews the COC forms, he/she will look for possible problems. Filters that have flags related to obvious contamination, filter damage, or field accidents will be examined immediately. Upon concurrence of the associated laboratory analyst and the Program Manager, these samples will be invalidated.

19.2 Data Analysis

Data analysis refers to the process of interpreting the data that are collected. This section will describe how the laboratories will begin to analyze the data to ascertain what the data illustrate and how the data should be applied. The analyst should note any data that needs flags (dilutions, collocate/replicate precision agreement). This is verified by the Task Leader, QA Coordinator, and the Program Manager. The Program Manager has the ultimate authority to invalidate any sample, given acceptable reasons.

19.2.1 Analytical Tests

ERG will employ software programs, described below, to help analyze the data.

Spreadsheet – Select ERG employees perform analysis on the data sets using Excel® spreadsheets (analysts, Task Leaders, and QA reviewers) and Access® databases (AQS data entry). Spreadsheets and databases allow the user to input data and statistically analyze, graph linear data. This type of analysis will allow the user to see if there are any variations in the data sets. In addition, various statistical tests such as tests for linearity, slope, intercept or correlation coefficient can be generated between two strings of data. Time series plots and control charts can help identify the following trends:

- Large jumps or dips in concentrations;
- Periodicity of peaks within a month or quarter; and
- Expected or unexpected relationships among species.

SECTION 20
RECONCILIATION WITH DATA QUALITY OBJECTIVES

The project management team, QA Coordinator, and sampling and analytical team members are responsible for ensuring that all measurement procedures are followed as specified and that measurements data meet the prescribed acceptance criteria. Prompt action is taken to correct any problem that may arise.

20.1 Conduct Preliminary Data Review

A preliminary data review will be performed as discussed in Section 16 to uncover potential limitations to using the data, to reveal outliers, and generally to explore the basic structure of the data. The first step is to review the quality assurance reports. The second step is to calculate basic summary statistics, generate graphical presentations of the data, and review these summary statistics and graphs.

ERG will review all relevant quality assurance reports, internal and external, that describe the data collection and reporting process. Particular attention will be directed to looking for anomalies in recorded data, missing values, and any deviations from standard operating procedures in a qualitative review.

20.2 Draw Conclusions from the Data

If the sampling design and statistical tests conducted during the final reporting process show results that meet acceptance criteria, it can be assumed that the network design and the uncertainty of the data are acceptable.

SECTION 21

REFERENCES

1. U.S. Environmental Protection Agency. Federal Register Volume 73, Number 219, (73 FR 66964). National Ambient Air Quality Standards for Lead; Final Rule. Rules and Regulations, November 12, 2008.
Can be found at: http://www.gpo.gov/fdsys/pkg/FR-2008-11-12/html/E8-25654.htm

2. U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40 CFR Part 50, Appendix Q. Reference Method for the Determination of Lead in Particulate Matter as PM10 Collected from Ambient Air. Office of the Federal Register, November 12, 2008.
Can be found at: http://www.ecfr.gov/cgi-bin/text-idx?SID=2c090408f6dc7f96eeb9e53b4acc8481&mc=true&node=ap40.2.50_118.q&rgn=div9

3. U.S. Environmental Protection Agency. Standard Operating Procedure for Determination of Lead in TSP by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with Hot Block Dilute Acid and Hydrogen Peroxide, Method EQL-0512-201.
Can be found at: http://www3.epa.gov/ttn/amtic/files/ambient/pb/EQL-0512-201.pdf

4. U.S. Environmental Protection Agency. Standard Operating Procedure for the Determination of Lead in PM10 by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with Hot Block Dilute Acid and Hydrogen Peroxide Filter Extraction, Method EQL-0512-202.
Can be found at: http://www3.epa.gov/ttn/amtic/files/ambient/pb/EQL-0512-202.pdf

5. U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40 CFR Part 50, Appendix B. Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High-Volume Method). Office of the Federal Register, April 22, 1983.
Can be found at: http://www.ecfr.gov/cgi-bin/text-idx?SID=2c090408f6dc7f96eeb9e53b4acc8481&mc=true&node=ap40.2.50_118.b&rgn=div9

6. U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40 CFR Part 50, Appendix O. Reference Method for the Determination of Coarse Particulate Matter as $PM_{10-2.5}$ in the Atmosphere. Office of the Federal Register, October 17, 2006.
Can be found at: http://www.ecfr.gov/cgi-bin/text-idx?SID=2c090408f6dc7f96eeb9e53b4acc8481&mc=true&node=ap40.2.50_118.o&rgn=div9

7. U.S. Environmental Protection Agency. Federal Advisory Committee Act (FACA).
Can be found at: *http://www.epa.gov/waterscience/methods/det/*

Appendix A

ERG Standard Operating Procedures

ENGINEERING AND SCIENCE DIVISION

TITLE: Standard Operating Procedure Developing, Documenting, and Evaluating the Accuracy of Spreadsheet Data	EFFECTIVE DATE: MAY 20 2015
REFERENCES: ERG-MOR-009	
SATELLITE FILES: N/A	
REVISIONS: Removed outdated statements, Added document control of spreadsheets	
WRITER/EDITOR: NAME/DATE Donna Tedder 5/20/15	PROJECT MANAGER: NAME/DATE Julie L. Smith 5/20/15
PROJECT QUALITY ASSURANCE MANAGER: NAME/DATE Donna Tedder 5/20/15	NEXT SCHEDULED REVIEW: 1/31/17

1.0 IDENTIFICATION AND PURPOSE

This standard operating procedure (SOP) describes the procedures to follow when developing spreadsheets that are intended to be a project deliverable, not spreadsheets used as a general check. It prescribes the minimum standards to be maintained to help ensure data quality and reproducibility. With the use of the laboratory information management system (LIMS), project deliverable spreadsheet use is somewhat limited.

2.0 MATRIX OR MATRICES

NA

3.0 METHOD DETECTION LIMIT

NA

4.0 SCOPE AND APPLICATION

This SOP applies to all spreadsheets developed during project work at the laboratory located in Morrisville, NC.

5.0 METHOD SUMMARY

To ensure the quality of data delivered to client in the form of a spreadsheet, the developer must consider multiple components of the spreadsheet, including the data, calculations, and presentation of the spreadsheet. The data, subsequent calculations and assumptions must be reviewed by another project team member before the spreadsheet can be finalized and sent to the client.

6.0 DEFINITIONS

Spreadsheet – An electronic table that is used to process or present data. A spreadsheet can be used to store and manipulate data, as well as present data in report-quality, tabular format.

Spreadsheet Developer (Developer) – The person responsible for the overall accuracy and quality of a spreadsheet. The Developer ensures that data are entered correctly and that mathematical functions are accurately executed.

Reviewer – The person not associated with the development of the spreadsheet that verifies the accuracy, completeness, and reasonableness of the data in the spreadsheet.

7.0 INTERFERENCES

NA

8.0 SAFETY

NA

9.0 EQUIPMENT AND SUPPLIES

NA

10.0 MATERIALS

NA

11.0 CHEMICALS, REAGENTS, AND STANDARDS

NA

12.0 COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

NA

13.0 CALIBRATION AND STANDARDIZATION

NA

14.0 PROCEDURE

14.1 Summary of Responsibilities

14.1.1 The Spreadsheet Developer:

- Ensures that all original data are transcribed (entered) to the spreadsheet correctly.
- Ensures that all equations used to generate results are entered correctly; ensures that all equations are used appropriately.
- Ensures that all conversion factors and constants used in equations are described.
- Ensures that all sources of original data are referenced in the spreadsheet.
- Ensures that all variables within equations are defined.
- Ensures that all spreadsheet tables are developed (content and format) according to the directions provided by the Project Manager or Task Leader, QAPP or SOP.
- If possible, keeps a log of spreadsheet revisions. If different versions of a spreadsheet are created, the Developer should maintain a log that describes the changes made to the different versions. With two or more people editing one spreadsheet, control can be hard to maintain. One approach is to allot a tab in the spreadsheet where it can be logged who edits the spreadsheet and what was done (short description), including the date of the edits.

14.1.2 The Project Manager or Task Leader:

- Determines when the use of spreadsheets (rather than database technology) are appropriate.
- Determines if a specific format must be used and specifies what information should be included in each spreadsheet.
- Ensures that methods and technical approaches used to produce a desired result are technically sound.
- Ensures that spreadsheet documentation is included in the project file or within the spreadsheet.
- Provides guidance on how to present data in the spreadsheet (based on client's needs, project goals and objectives and QAPP QC acceptance criteria if applicable).

14.1.3 The Reviewer:

- Verifies that the Developer's technical approach is reasonable and logical.
- Verifies that calculations and results are accurate.
- Verifies that documentation is complete and clear.
- Ensures that assumptions and procedures used are reasonable.
- Provides timely, constructive, and direct comments to the Developer.
- Assigns a document version control number (SOP ERG-MOR-009).

14.2 To maintain acceptable data quality, it is important to practice adequate QC measures during the development and review of spreadsheets. The information presented in a spreadsheet should be evaluated to determine if input data are transcribed correctly, calculated results are technically sound, and the final results are reported in a manner that will allow the data to be evaluated.

14.2.1 Spreadsheet Identification:

- Save the spreadsheet using a descriptive label and include the Work Assignment number or unique project number, if applicable, for example, "WA 1-09 Method Detection Limits".

- Include a title in the spreadsheet, at the beginning. Make the title descriptive enough to clearly identify the data presented and the project.

- All spreadsheets should contain a tab to log the person(s) making edits to the spreadsheet and a short description of the edits, including date of edits, labeled Version Control, or similar.

- Identify the reviewer and the date (month/day/year) the spreadsheet was reviewed in the log tab.

- As needed, include headers or footers that identify the name of the electronic spreadsheet file, the page number, and total number of pages (e.g., Page 1 of 2), and the date the spreadsheet was last revised. The name of the disk or drive on which the file is stored may also be included with the file name.

- Assign a unique name and number to the revised version of the spreadsheet.

- Include a footer or header in the spreadsheet (or a note at the top or bottom of the spreadsheet) that indicates the date the spreadsheet was generated and the revision number, not the date that printing occurred.

14.2.2 Spreadsheet Development:

- Describe all equations, using footnotes or a comments field, where appropriate. (e.g., if gram/kilogram are being converted to pound/ton, the equation performing the calculation should be explained as: "Convert g/kg to lb/ton: 1 g/kg x 1 lb/453.59 g x 1 kg/1,000 g x 453.59g/lb x 2,000 lb/ton, which is equivalent to multiplying by 2"). If detailed descriptions exist in project notebooks, then a reference to that notebook (e.g., notebook and page number) should be made in the comments field.

- Identify any constants or conversion factors used.

- Avoid using specific values in equations, except for easily recognizable conversion factors or constants. Enter values within a cell. Equations that use the value should reference the cell.

- Hand (manually) verify equation cells.

- Protect verified equation cell regions of spreadsheet to avoid accidentally over writing.

14.2.3 Supporting Data Requirements

The original raw data used in the spreadsheet should be retained in the project file and in the project archive.

14.2.4 Project Data File Requirements

Maintain an electronic backup copy at an identified location on the network and in hard copy in the project file.

15.0 CALCULATIONS

NA

16.0 QUALITY CONTROL

Spreadsheet Quality Control Responsibilities

16.1 The Spreadsheet Developer:

- Checks the accuracy of data transcriptions.

- If the spreadsheet is being given to someone who will make revisions or enter data, data cells that should not be changed should be locked. Locking data cells in this manner will help prevent inadvertent changes to the spreadsheet.

16.2 The Project Manager or Task Leader:

- Determines the level of QC necessary. For example, the Project Manager or Task Leader must decide if all data points and all calculations should be checked, or if only a percentage should be checked. It may be appropriate to initially check a percentage and, based on the number of discrepancies identified, decide if additional QC is required.

16.3 The Reviewer:

- Verifies at least one calculation for each equation or combination of equations used.
- Verifies the accuracy of total values, means, and statistical evaluations of the data.
- With the Project Manager or Task Leader, determines the amount of data to check; the number of errors found will dictate the amount of data evaluated for accuracy. The higher the error rate, the more data points to be checked. If numerous errors are found, the spreadsheet should be returned to the data generator with a note that includes a description of the review procedure and percentage of errors found. The error rate is a good indicator of the accuracy of all of the information in the spreadsheet. If needed, the site QA Coordinator should be consulted for guidance in determining the most effective way to determine which and how many values to recalculate.
- Verifies that original data were input correctly.
- Evaluates the technical soundness of methods and approaches used.
- Ensures that equations in the spreadsheet produce the correct result and that equations were entered into the spreadsheet accurately.
- Ensures that adequate documentation is included in the spreadsheet and that the documentation supports the data in the spreadsheet.
- Discusses all discrepancies with the Developer and Project Manager or Task Leader, as appropriate. Actual spreadsheet errors identified by the Reviewer should be corrected by the Developer.
- Summarizes the review, inputs their findings in the Version Control tab and comments on how to make changes to calculations in the Description tab indicating the errors or problems found, and the recommendations for revisions. The summary should also include the reviewer's name, data of QC review (month/day/year), name of file, type of data reviewed, and the percentage of each type reviewed in the Version Control tab.
- Assigns a document version control number (SOP ERG-MOR-009).

17.0 PREVENTION

NA

18.0 CORRECTIVE ACTION

NA

19.0 WASTE MANAGEMENT

NA

20.0 MAINTENANCE

NA

21.0 SHORTHAND PROCEDURE

1. Label a tab as Version Control and enter name, date and description of what was done
2. Label a tab as Description and include information about the project, the source of the raw data and what calculation are to be included in the spreadsheet. Define constants and equations here
3. In the working tab add a title on top of the page that includes a description of the table content
4. Ensure all raw data was entered correctly
5. Hand calculate some data points to review the spreadsheet results
6. Pass the spreadsheet to Technical Reviewer
7. The Technical reviewer will enter any comments or changes to the Control Version tab and provide a revised version to the Developer and Manager

22.0 DOCUMENTATION AND DOCUMENT CONTROL

All relevant information concerning Version Control, Description of calculations, should be included in separate tabs within the spreadsheet. However, accompanying documentation can be used such as hand calculations, more in detailed project descriptions and raw data collection comments. A separate tab within the spreadsheet will contain information about the edits to the spreadsheet contents, indicating editor's name, date, short description of edits including reviews. Once reviewed the spreadsheet is assigned a document version control number (SOP ERG-MOR-009).

23.0 REFERENCES

Food and Drug Administration (FDA) Good Laboratory Practice (GLP) standards, 40 CFR Part 58.81(a), Subpart E – Testing Facility Operation, Standard Operating Procedures

Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) GLP standards, 40 CFT Part 160.81(a), Subpart E – Testing Facility Operation, Standard Operating Procedures

Toxic Substance Control Act (SCA) GLP standards, 40 CFR Part 792.81(a), Subpart E – Testing Facility Operation, Standard Operating Procedures

24.0 TABLES, DIAGRAMS, FLOWCHARTS, VALIDATION DATA

NA

ENGINEERING AND SCIENCE DIVISION

TITLE: Standard Operating Procedure for the Preparation of Standards in the ERG Laboratory	EFFECTIVE DATE: May 21, 2012
REFERENCES: ERG-MOR-031, ERG-MOR-033, ERG Health and Safety Manual	
SATELLITE FILES: All	
REASON FOR REVISION: Update to increase applicability	
DATE OF LAST REVIEW:	NEXT SCHEDULED REVIEW:
WRITER: NAME/DATE Donna Tedder 5/16/12	TECHNICAL DIRECTOR: NAME/DATE Julie L. Swift 5/27/12
QUALITY ASSURANCE COORDINATOR: NAME/DATE Donna Tedder 5/16/12	MANAGER: NAME/DATE Julie L. Swift 5/27/12

1.0 IDENTIFICATION AND PURPOSE

This standard operating procedure (SOP) presents the procedure to be followed when preparing standards for use in the Sample Preparatory Laboratories. This procedure should be followed to ensure that only high-quality data are generated in the laboratory.

2.0 MATRIX OR MATRICES

This SOP addresses procedures used to prepare liquid standards/stocks from solid or liquid chemicals.

3.0 METHOD DETECTION LIMIT

NA

4.0 SCOPE AND APPLICATION

This SOP is a general guidance to standard preparation. Some procedures may not be applicable to all analyses preformed at this location. The SOP was originally intended for use in the Organic Sample Preparation Laboratory however, the general procedures outlined in this SOP can be applied to preparing standards for any method.

The calibration standards are used to establish or verify the instrument calibration which is used to calculate the concentrations of the analytes.

The internal standard solution is used to measure the relative responses of analytes (and surrogates). When used, internal standards are added to all samples, standards, and quality control (QC) samples at the same concentration.

The matrix spiking solution is added to a matrix prior to processing and is used to assess the efficiency of the preparative technique and analysis methodology.

The surrogate spiking solution containing one or more compounds, different from the method analytes but similar in physical and chemical behavior, that can be used to measure extraction and analysis efficiency without interfering with the analysis.

5.0 METHOD SUMMARY

NA

6.0 DEFINITIONS

COA	certificate of analysis
g	gram
ID	identification
LIMS	laboratory information management system
µg	microgram
µL	microliter
mg	milligram
mL	milliliter
ng	nanogram
QA	quality assurance
QC	quality control

7.0 INTERFERENCES

To ensure the standards are free from interfering contaminants, all glassware should be cleaned according to the glassware cleaning SOP (ERG-MOR-031). Syringes should be

cleaned by rinsing the plunger and the cylinder at least 10 times with the solvent to be used.

8.0 SAFETY

Follow normal laboratory safety procedures as outlined in the ERG Health and Safety Manual. The appropriate personal protection should be used during the preparation of standards/stocks.

9.0 EQUIPMENT

NA

10.0 MATERIALS

The following equipment should be obtained: volumetric glassware, including volumetric flasks and pipettes, and syringes in the appropriate size(s). All volumetric glassware should be class A. A balance should be used that is appropriate to the degree of precision desired. In most cases, either a four- or a five-place balance should be used. Document the calibration check in the balance notebook prior to using the balance.

11.0 CHEMICALS, REAGENTS, AND STANDARDS

All reagents used to prepare standards should be reagent grade or better and be identified by their manufacturer and lot number. Solvents should be "high purity" or "pesticide residue grade." If chemicals used in standards are less than 96% pure, then the percentage of purity must be factored into the calculations. All chemicals should be logged into the laboratory following the chemical inventory SOP (ERG-MOR-037). As chemicals are depleted, the chemical inventory should be updated so that chemicals can be replaced as needed. If a chemical has an expiration date, it should not be used past that date.

12.0 COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

Store the standard/stocks as recommended by the vendor, or by the method.

13.0 CALIBRATION AND STANDARDIZATION

NA

14.0 PROCEDURE

14.1 Standards Preparation - Stock Solutions

This section gives a general explanation of how to prepare standards.

14.1.1 For small amounts of liquids or solids, the chemicals should be measured by weight. Tare a small vial. Add the desired amount of chemical to the vial. Record the final weight of the vial with the chemical.

14.1.1.1 For solids, the desired chemical can be added with a small spatula. Calculate the amount needed to obtain the desired concentration using the following equation:

Final Concentration * Total Volume = Weight Added

Example: A final concentration of 1000 µg/mL is required for a standard. 100 mL of the solution is to be made up.

1000 µg/mL * 100 mL = 100,000 µg (100mg)

14.1.1.2 For liquids, the desired chemical can be added with a syringe, a pipette, or can be weighed. If the liquid is to be added with a syringe or pipette, calculate the volume needed with the following equation:

Density (µg/mL) * X mL Neat/Final Volume (mL) = µg/mL

Example: A final concentration of 1000 ng/µL is required for a standard. 100 mL of the solution is to be made up. The density of the liquid is 0.500 g/mL.

The approximate amount of liquid required is shown below.

500,000 µg/mL * X mL Neat/1 mL = 1000 µg/mL

X = 0.002 mL (2 µL)

14.1.2 Dissolve each of the weighed chemicals in the appropriate solvent. Some chemicals may not dissolve readily and may require sonication to promote dissolution.

14.1.3 Fill a clean, solvent-rinsed volumetric flask approximately ½ to ⅔ full of the solvent to be used for the standard. Add the dissolved chemicals from Step 14.1.2 to the volumetric flask. Rinse each vial three times with the solvent to make sure that all of the dissolved chemical is transferred to the volumetric flask.

14.1.4 Carefully fill the volumetric flask up to the final desired volume with the solvent. The bottom of the meniscus should be at the volume line on the volumetric flask. Stopper the volumetric flask with a ground glass stopper and invert the flask 10 to 15 times to make sure that the solution is well mixed.

14.1.5 Transfer the stock standard to a vial with a Teflon®-lined screw cap lid for storage in the standards refrigerator.

14.2 Working Standards Preparation - Dilutions of Stock Solutions

This section gives a general explanation of how to prepare dilutions of standard solutions.

14.2.1 When the concentration of a chemical is lower than can be obtained using the methods described above, dilutions of the stock solutions can be made. Initially, a calculation must be done to determine what dilution is needed using the equation below:

14.2.2 Fill a solvent-rinsed volumetric flask approximately ½ to ⅔ full with the solvent to be used for the standard. Measure the amount of the stock solution needed with a volumetric pipette or with a syringe. Add the stock solution to the solvent in the volumetric flask, and dilute to the volume needed with the solvent required.

14.2.3 Transfer the working standard to a vial with a Teflon®-lined screw cap lid for storage in the standards refrigerator.

15.0 CALCULATIONS

Many of the necessary calculations are presented in Section 14.0.

Final Concentration = Weight Added/Total Volume

Final Concentration = (Volume Added * Concentration)/Total Volume

In all calculations, check the units carefully to make sure that the final concentration is given in the proper units.

Note: If a chemical used was less than 96% pure, the final concentration should be multiplied by the purity to obtain the actual concentration. For example, if a chemical used in a stock solution is 95% pure, the final calculated concentration of the stock solution should be multiplied by 0.95.

To calculate the molarity of a standard solution:

Molarity = Number of Moles/Total Volume (liters)

Note: If solute is a percentage solution, the weight percentage must be taken in account.

16.0 QUALITY CONTROL

16.1 The preparation of all standards and stocks must be documented including the identification (ID) number, type, concentration, amount of solute, total volume, preparer, preparation dates, expiration dates, stock or chemical lot numbers, and solvent lot numbers.

16.2 When preparing a standard with calculations out of the normal for that analysis, the calculations must be validated by Task Lead or quality assurance (QA) staff before proceeding.

16.3 The following expiration dates should be used for prepared standards/stocks if one is not indicated in the associated method:

- Stock solutions: 1 year from date of preparation;
- Standard solutions: 6 months from date of preparation;
- Standard solutions expiration dates cannot extend past the expiration date of the stock solution from which they were prepared.

17.0 PREVENTION

When possible, minimize the amount of chemicals used in the preparation of the standards/stocks. Prepare the smallest volume of standard/stock that can be used before the expiration date.

18.0 CORRECTIVE ACTION

NA

19.0 WASTE MANAGEMENT

Hazardous waste disposal is discussed in SOP ERG-MOR-033.

20.0 MAINTENANCE

NA

21.0 SHORTHAND PROCEDURE

NA

22.0 DOCUMENTATION AND DOCUMENT CONTROL

On each standard vial, a label must be affixed with the standard name (e.g., base, neutral, acid, or BNA surrogate), identification (ID) number, the standard expiration date, and the initials of the person who made the standard.

The preferred method of standards documentation is the laboratory information management system (LIMS). The LIMS system has a Standards section to document ID number, type, concentration, amount of solute, total volume, preparer, preparation dates, expiration dates, lot numbers of chemical and solvent, and link the information to the appropriate QC samples. For commercial standards or stocks, the certificate of analysis (COA) can be scanned, imported, and linked with the appropriate standard/s. A sample Standards page from the LIMS system is presented in Figure 1.

A notebook can be used for standards and stocks. Write the standard number and description so they are clearly visible, preferably at the top of a page in the notebook. Follow this with a short description of how the standard was made, including the amounts added, the glassware used, and the solvent(s) used. If a solid compound was used, note how it was dissolved. The brand and lot numbers of all chemicals, including the solvents, must be recorded as well as the equations used to calculate the final concentrations. If a stock solution was used, also record the concentration. Lastly, record the final concentrations of the chemicals in the standard solution.

23.0 REFERENCES

NA

24.0 TABLES, DIAGRAMS, FLOWCHARTS, VALIDATION DATA

Figure 1. Sample LIMS Standards Page

Analytical Standard Record

Eastern Research Group

2D27011

Description:	IO3.5 Teflon Calibration Standard 1	Expires:	08/03/12
Standard Type:	Calibration Star	Prepared:	04/27/12
Solvent:	0.3% HCl, 1.11% HNO3, 0.1% HF	Prepared By:	Randy Mercurio
Final Volume (mls):	500	Department:	Inorganics
Vials:	1	Last Edit:	04/27/12 11:27 by RJM

Analyte	CAS Number	Concentration	Units
Yttrium	NA	0.07	ug/mL
Scandium		0.11	ug/mL
Indium		0.07	ug/mL
Gold	NA	5	ug/mL
Gallium	na	0.2	ug/mL
Bismuth	NA	0.07	ug/mL

Parent Standards used in this standard:

Standard	Description	Prepared	Prepared By	Expires	Last Edit	(mls)
1A25002	Fisher Optima Hydrofluoric Acid; E01/25/11		** Vendor **	03/31/13	02/21/11 12:52 by RM	0.5
1H22003	10,000 mg/L Gold Stock; Expires 208/22/11		** Vendor **	02/18/13	08/22/11 13:48 by RM	0.25
1I19003	J.T. Baker Ultrex II Nitric Acid; E09/19/11		** Vendor **	09/17/12	09/19/11 14:58 by RM	5.55
1I29009	Aristar Ultra Hydrochloric Acid; E09/29/11		** Vendor **	05/21/13	09/29/11 14:47 by RM	1.5
2A04003	ICP-MS IO3.5 Internal Standard; E01/04/12		Randy Mercurio	08/03/12	01/04/12 11:17 by RM	1

Reviewed By _____ Date _____

Page 1 of 1

ENGINEERING AND SCIENCE DIVISION

TITLE: Standard Operating Procedure for Hazardous Waste	EFFECTIVE DATE: 2/4/13
REFERENCES: 40 CFR Parts 260 through 299; ERG-MOR-037, ERG-MOR-038, Hazardous Waste Management Plan	
SATELLITE FILES: GC, GC/MS, ICP-MS, Prep	
REASON FOR REVISION: Updated to agree with Hazardous Waste Management Plan updates	
WRITER: NAME/DATE Tracey Foote 2/4/13	PROJECT MANAGER: NAME/DATE Julie L. Swift 2/5/13
QUALITY ASSURANCE COORDINATOR: NAME/DATE Donna Tedder 2/4/13	NEXT SCHEDULED REVIEW: 1/31/14

1.0 IDENTIFICATION AND PURPOSE

The purpose of this SOP is to provide guidelines for the correct handling and disposing of hazardous waste at the ERG analytical laboratory located at 601 Keystone Park Drive, Suite 700, Morrisville, NC. ERG's analytical laboratory is licensed as a small-quantity hazardous waste generator (SQG). ERG will maintain the SQG status as specified by our Environmental Management System (EMS). These guidelines have also been developed to ensure compliance with federal and North Carolina hazardous waste regulations. A description of the overall program is contained in the Hazardous Waste Management Plan. Also included in the Hazardous Waste Management Plan are the emergency procedures listed in the Emergency Preparedness and Response Plan section (Appendix C).

2.0 MATRIX OR MATRICES

N/A

3.0 METHOD DETECTION LIMIT

N/A

4.0 SCOPE AND APPLICATION

This document presents procedures for personnel who generate, handle, or are involved in the disposal of waste.

5.0 METHOD SUMMARY

N/A

6.0 DEFINITIONS

A hazardous waste handler is an individual who regularly transfers hazardous waste from the satellite accumulation points (SAPs) to the 180-day storage room.

A hazardous waste generator is any laboratory personnel who generates hazardous waste.

The health and safety coordinator (HSC) is responsible for managing health and safety programs at the ERG laboratory.

A satellite accumulation point (SAP) is a designated location near the point of generation where waste is temporarily stored.

A small-quantity generator (SQG) is a facility that generates less than 1,000 kg (2,200 lbs) of hazardous waste and less than 1 kg (2.2 lbs) of acutely hazardous waste in a calendar month.

7.0 INTERFERENCES

N/A

8.0 SAFETY

Proper personal protective equipment (PPE), as outlined in the Hazardous Waste Management Program, the SOP for PPE (ERG-MOR-038), and/or Section 14.2.3 of this document, is required to be worn when handling hazardous waste.

9.0 EQUIPMENT

N/A

10.0 MATERIALS

N/A

11.0 CHEMICALS, REAGENTS, AND STANDARDS

N/A

12.0 COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

Because waste disposal contractors are not currently permitted to accept dioxin-containing wastes, there are no disposal options for the dioxin-containing chemicals that ERG has archived. The following criteria define dioxin waste. The dioxin waste categories described below are subject to the RCRA regulations contained in 40 CFR Parts 261, 264, 265, 270, and 271:

- Waste containing tetra- and pentachloro-dibenzo-*p*-dioxins and -dibenzofurans;
- Process wastes from the manufacturing use of tetra-, penta-, or hexachlorobenzenes under alkaline conditions;
- Wastes from the production and manufacturing of tri-, tetra-, and pentachlorophenols and their chlorophenoxy derivatives;
- Discarded, unused formulations containing tri-, tetra-, and pentachlorophenols or formulations containing compounds derived from these chlorophenols; and
- Soil contaminated with any of the wastes listed above.

The dioxin-containing analytical standards that ERG has on-site are to remain segregated and stored in the refrigerator in the 180-day storage room, which requires a key for entry.

13.0 CALIBRATION AND STANDARDIZATION

N/A

14.0 PROCEDURE

Any chemical or item contaminated with a chemical, including samples, should be initially considered hazardous waste until the Project Manager and/or HSC determines otherwise.

14.1 Determination, Classification, and Packaging of Hazardous Waste

14.1.1 Determination

Not all waste is hazardous by EPA's definition. Project Managers, with the help of the HSC or designee, must determine whether generated waste is hazardous. Section 24.1 has a summary of questions to help determine the applicability of the regulations from Title 40 CFR 262.11.

14.1.2 Classification

The Morrisville facility typically generates the following classifications of hazardous wastes:

- F = from non-specific sources;
- U = hazardous compounds from discarded commercial products;
- D = characteristic (toxic, corrosive, ignitable, or reactive) wastes; and
- P = acutely hazardous from discarded commercial products.

The waste disposal contractor uses these classification codes to correctly group and dispose of the waste. The HSC or designee, while reviewing the hazardous waste manifests, ensures that the correct classification codes are used for waste generated at ERG laboratory.

14.1.3 Packaging

Hazardous waste generated by ERG is disposed of in two major packaging categories:

- Bulked wastes are produced routinely in relatively large volumes. This waste group includes spent solvents, aqueous acids, discarded environmental samples (large volumes), and contaminated sample vials. Approved hazardous waste handlers bulk these wastes every 4-6 weeks. Note: although these are considered bulked wastes for our purposes, for DOT purposes, these are still non-bulk containers (49 CFR 171.8)

- Lab pack wastes are chemical reagents contained in jars, vials, jugs, bottles, and cans. This waste is best disposed of in its primary container. Lab packs are 20- or 30-gal fiber drums that hold individual containers of chemically compatible waste. Individual containers are packed in a fiber drum surrounded by layers of

absorbent vermiculite material, which prevents shifting or breakage of small containers during transport.

Hazardous Waste Handlers should use the following list to determine which types of wastes can be bulked or lab-packed. The waste types with an asterisk (*) are typical wastes generated by the ERG facility.

- Bulked Waste
  - Halogenated flammable solvents*
  - Nonhalogenated flammable solvents*
  - Inorganic acids*
  - Organic acids
  - Aqueous waste contaminated with hazardous waste
- Lab-Packed Waste
  - Glass and metal contaminated with hazardous waste*
  - Paper and plastic contaminated with hazardous waste*
  - Poison A (poisonous gases)
  - Flammable gases
  - Non-flammable gases
  - Flammable liquids (i.e., those that cannot be bulked with solvents)
  - Oxidizers
  - Flammable solids
  - Corrosive liquids
  - Corrosive solids
  - Irritants
  - Combustible liquids

When determining whether to group the waste as either bulked or lab-packed waste, Hazardous Waste Handlers should consider the following factors:

- Bulk whenever possible (it is less expensive.). Use the same drum of an appropriate size for compatible wastes until it is full (it is less expensive.).
- For lab-packed waste, set the waste aside, generally in the chemical storage (Room 139) or a designated location in the labs. The waste disposal contractor packages these wastes at the time of pick-up.

- Do not mix wastes that can be bulked with lab-packed wastes. If the two are mixed, all the waste will need to be lab-packed.

- Never mix non-hazardous waste with hazardous waste. The result is a larger quantity of hazardous waste.

14.2 Hazardous Waste Collection and Storage Procedures

ERG is allowed to store hazardous waste for up to 180 days, provided safe storage practices, as defined by the state and federal governments, are followed. The dedicated storage area is Room 139, the 180-day storage area. The 180-day counting begins when the first drop of waste is transferred to the 180-day storage area.

14.2.1 Collection and storage of in-laboratory waste

Hazardous Waste Generators must follow these steps to store waste properly in the SAPs:

- Label all containers with Hazardous Waste labels, including the constituents or at least the process generating the wastes (i.e., TO-13 waste) on the bottles;

- All containers of hazardous waste must be sealed except when pouring;

- A maximum of 55 gal of hazardous waste and 1 kg acutely toxic waste is allowed at any one SAP; and

- If waste storage presents a clutter problem in the laboratory hoods, contact a Hazardous Waste Handler to transfer the waste to the 180-day storage area.

The following are additional requirements for properly storing specific types of wastes in the SAP and 180-day storage area:

- Glass and Metal Waste

  - All contaminated glass and metal waste will be collected in closed containers labeled Waste Glass and Metal. These containers must be stored in the SAP. A Hazardous Waste

Handler will periodically dispose of these in fiber drums located in the 180-day storage area.

- Place uncontaminated broken pipettes, test tubes, and other items of broken glass in the designated Broken Glass bins or containers, not in the regular trash cans. This practice will prevent the janitorial staff from cutting themselves on broken laboratory glassware.

- Solvent Waste

  - All organic solvent wastes are collected in 4 liter amber glass bottles in designated SAP areas. These are often transferred from the hood to a flammables or vented cabinet in the same SAP area when full before being bulked in the 180-day storage area.

- Contaminated Paper and Plastic Storage

  - Paper and plastic waste material that is contaminated with chemicals (hazardous or nonhazardous) will be placed inside thick plastic bags and stored inside the fume hood until the bag is transported to the 180-day storage area by a Hazardous Waste Handler.

- Aqueous Waste and Environmental Samples

  - If possible, environmental samples and other aqueous wastes should be stored in the original glass sample containers. NOTE: No Aqueous/Acid waste will be put in the solvent waste drum.

  - When storing liquid waste, an adequate supply of spill materials (vermiculite and/or absorbent padding) must be on hand to control and clean up potential spills. Refer to the Hazardous Waste Management Program for proper spill procedures.

- Acids and Corrosives

  - All acids and other corrosives must be stored in a separate area with adequate secondary containment to ensure that if

the chemical spills or leaks, it will not come into contact with containers of organic chemicals.

- When not in use or considered waste the acids or corrosives are stored in segregated and labeled storage areas under the laboratory hood in the storage cabinets or in vented flammables cabinets.

14.2.2 Collection of Field-Generated Hazardous Waste

Project Managers are responsible for planning the collection, storage, and transportation of hazardous waste generated in the field. Typical field wastes will include:

- Discarded PPE; and
- Chemicals used on site (e.g., glassware rinsate).

Prior to the start of the job, Project Managers shall arrange for the client to accept the waste or contract with a waste disposal firm to pick up hazardous waste from the site.

NOTE: Because ERG does not have the necessary DOT license, employees are not allowed to transport hazardous wastes.

14.2.3 Bulking waste in the 180-day storage area

- General Requirements

  General Requirements for the Hazardous Waste Handlers to transfer the waste to 180-day storage area are:

  - All containers must be approved hazardous waste containers.

  - Use a dolly or cart to transport accumulated waste from the SAPs to the 180-day storage area. If one is not available, carry all liquid waste inside secondary containers. Paint cans, buckets, and plastic tote bottles are acceptable secondary containers.

- Prior to pouring waste materials, all flammable waste drums must be grounded with a clip wire to a grounding rod located in the area.

- For all hazardous waste delivered to the 180-day storage area, the following information must be recorded in the disposal logbook (Refer to Section 24.2 for a sample page):

  - Date;
  - Quantity of waste;
  - Waste description;
  - Date disposed;
  - Initials of personnel disposing of waste.

- Proper Packaging and Labeling

All wastes placed in the same container must be compatible with each other and the material with which the drum is constructed. The container must be labeled with a yellow hazardous waste label and the information on the label completed to include:

- Description of waste;
- Generator's name and address;
- EPA identification number (found in 40 CFR); and
- Accumulation start date.

All containers and boxes of chemical waste to be disposed of in a lab pack must be marked with the following information:

- Name of the generator (ERG employee responsible for waste);
- Project or process description (i.e., TO-13 waste); and
- Date that the waste was placed into the 180-day storage area.

- Proper Handling Procedures

  The Hazardous Waste Handlers disposing of hazardous waste must use proper personal protection. PPE required for pouring liquid wastes are defined below:

- Pouring acids: Face shield (or full-face respirator), gloves, lab coat, long pants, and closed-toe shoes must be worn at all times.

- Pouring solvents: Respiratory protection, eye protection (unless full-face respirator is worn), lab coat, long pants, and protective gloves must be worn at all times.

Hazardous Waste Handlers should never dispose of waste alone; always dispose of the waste with two people ("buddy system") in case of an emergency. An alarm system is installed and tested annually to notify other laboratory personnel if a problem occurs.

14.3 Disposal of Non-Hazardous Waste

Only limited types of waste may be poured down the sanitary sewer or placed in municipal waste dumpsters. If a laboratory employee has any doubt on proper disposal of any type of waste, the employee should check with the one of the Project Managers.

The Morrisville laboratory routinely disposes and recycles glass containers. The containers are first allowed to dry under a laboratory hood to evaporate remaining chemical residues, and then are triple rinsed with water. The glass bottles are then either recycled (if they are reagent bottles) or disposed of in the dumpster (if the bottles previously contained solvent waste or acids).

15.0 CALCULATIONS

N/A

16.0 QUALITY CONTROL

16.1 Performance

Hazardous waste regulations require that the dedicated storage room (the 180-day storage room) is inspected on a weekly basis by the HSC or designee. This inspection has historically been performed every Tuesday. In addition, the HSC or designee also inspects the SAPs on a weekly basis to verify safe waste storage practices and track waste accumulation levels. Periodic inspections performed by Lab Managers are held to ensure the procedures are followed. Periodic training is held to ensure personnel remain familiar with the procedures.

16.2 Data Assessment

All waste storage procedures in the ERG laboratory will be reviewed by the ERG Hazardous Waste Specialist and periodically subject to inspection by an inspector from the North Carolina Division of Solid Waste Management.

17.0 PREVENTION

N/A

18.0 CORRECTIVE ACTION

N/A

19.0 WASTE MANAGEMENT

19.1 Waste Minimization

ERG will maintain the SQG status as required by our EMS. To minimize waste, ERG maintains a chemical inventory database which must be consulted prior to the purchase of any chemical. The database was created to minimize waste and to track materials that are in stock to prevent duplicate orders, and thus avoid unnecessary chemical storage and waste generation. See ERG-MOR-037 for more information on the chemical inventory procedures.

19.2 Waste Management Organization

The waste management program involves the following personnel, each with a set of specific responsibilities:

19.2.1 Project Manager Responsibilities

- Adequately plan and budget for hazardous waste management; and
- Ensure the laboratory is in compliance with all applicable regulations.
- Project Manager is responsible for ensuring that project and lab personnel:
  - Correctly label hazardous waste;

- Segregate, collect, and store waste properly in the laboratory and in the field;
- Have access to and wear appropriate PPE; and
- Are ready to respond to emergencies.

- Give accurate records to project secretary that document worker training in hazardous waste handling procedures; and

- Ensure that adequate supplies are available and procedures are in place for prompt emergency response.

19.2.2 Health and Safety Coordinator (or designee) Responsibilities

- Conduct weekly inspections of both the SAPs and the 180-day storage area to ensure that employees are disposing of hazardous waste in a timely manner to prevent excess and unsafe accumulation; complete and maintain inspection logs.

- Compile an inventory list of wastes to be picked up and coordinate with the hazardous waste disposal contractor;

- Review and sign manifests prepared by the hazardous waste disposal contractor prior to off-site shipment of hazardous waste and ensure the signed manifests are returned within 60 days after the disposal of the wastes;

- Conduct periodic hazardous waste training for all personnel working with hazardous waste;

- Complete and file all reports with the State of North Carolina, any disposal States as required, and EPA; and

- Retain all records.

19.2.3 Waste Generator Responsibilities

Waste generators are responsible for:

- Disposing of waste in a timely fashion, labeling each type of waste as it is generated;

- Segregating waste, placing in appropriate containers, and storing in designated storage locations (SAPs);

- Being familiar with emergency response procedures, including containment and clean-up of hazardous waste spills and the location of emergency flushing facilities; and

- Notifying the hazardous waste handler when waste needs to be moved to the 180-day storage area.

19.2.4 Hazardous Waste Handler Responsibilities

In addition to having all the Hazardous Waste Generator responsibilities (Section 19.2.3), Hazardous Waste Handlers are responsible for:

- Safely transferring hazardous waste from the SAPs to the 180-day storage area (see Section 14.2.3), including using the "buddy system" and wearing appropriate PPE during waste bulking/transfer operations;

- Labeling each container in the 180-day storage area;

- Entering all wastes transferred to the 180-day storage area into the Waste Disposal Log;

- Notifying the HSC when one month remains before disposal is required of the waste in the 180-day storage area;

- Notifying the disposal contractor to order additional disposal containers and spill cleanup supplies for the 180-day storage area as needed; and

- Cleaning up any spills in the 180-day storage area.

20.0 MAINTENANCE

N/A

21.0 SHORTHAND PROCEDURE

N/A

22.0 DOCUMENTATION AND DOCUMENT CONTROL

The Waste Disposal Log is located in the 180-day storage room (Room 139). All 180-day and SAP inspection logbooks currently in-use are stored in the Supply Room (Room 102). Archives of these logbooks are kept indefinitely in the Data Archives Room (Room 137). Signed hazardous waste manifests are stored in the Supply Room (Room 102) in a white binder labeled "ERG's Hazardous Waste Records," as instructed in SOP 089, "SOP for Hazardous Waste Inspections and Recordkeeping".

23.0 REFERENCES

N/A

24.0 TABLES, DIAGRAMS, FLOWCHARTS, VALIDATION DATA

24.1 Determination of Hazardous Waste

24.2 Waste Disposal Logbook

SECTION 24.1
Determination of Hazardous Waste

In Title 40 CFR 262.11, the regulations provide the following list of questions for proper identification of waste:

- Is the waste excluded from regulation under Title 40 CFR 261.4?
- Is the waste listed in Subpart D (40 CFR 261.30 through 261.35)?
- If the waste is not listed, does it exhibit any of the characteristics listed in Subpart C, Characteristics of Hazardous Wastes (40 CFR 261.20 through 261.24)?

See the referenced regulations for more hazardous waste determination details.

SECTION 24.2
Waste Disposal Logbook

Eastern Research Group, 601 Keystone Park Drive
Waste Disposal Logbook

Date	Operator Intitals	Waste Type	Volume Added (gal)	Cumulative Volume (gal)	Waste Type	Volume Added (gal)	Cumulative Volume (gal)	Waste Type	Volume Added (gal)	Cumulative Volume (gal)	Waste Type	Volume Added (gal)	Cumulative Volume (gal)
Drum #													

Date Started:_____ Date Waste Picked up:_____ Initials:_____

ENGINEERING AND SCIENCE DIVISION

TITLE: Standard Operating Procedure for Sample Receipt at the ERG Chemistry Laboratory	EFFECTIVE DATE: APR 28 2015
REFERENCES: ERG-MOR-079	
SATELLITE FILES: Shipping/Receiving	
REASON FOR REVISION: Minor Updates	
WRITER/EDITOR: NAME/DATE Donna Tedder 4/27/15	PROJECT MANAGER: NAME/DATE Julie L. Swift 4/28/15
QUALITY ASSURANCE MANAGER: NAME/DATE Donna Tedder 4/27/15	NEXT SCHEDULED REVIEW: 1/31/2016

1.0 PURPOSE

The purpose of this standard operating procedure (SOP) is to formalize the laboratory procedures for sample receiving and sample log-in. This procedure also documents the sample acceptance policy.

2.0 MATRIX OR MATRICES

This SOP applies to samples of any matrices received at the ERG Research Triangle Park Laboratory. Sample acceptance policies are included for the common sample matrices.

3.0 METHOD DETECTION LIMIT

Not applicable.

4.0 SCOPE AND APPLICABILITY

All samples received in the shipping/receiving area of the ERG Research Triangle Park Laboratory must be handled and distributed following these procedures. In most cases, the samples are collected on/in media that was prepared, labeled and shipped to the site

by the ERG Research Triangle Park Laboratory. If samples are received that do not meet these requirements appropriate corrective action must be taken.

5.0 METHOD SUMMARY

When samples arrive, they are unpacked, inspected, accepted or voided and logged-in into the Laboratory Information Management System (LIMS). The information from the chain-of-custody (COC) forms for each batch of samples received at ERG is entered into the LIMS according to its respective project number (ERG-MOR-079). Information relative to the samples (number, type, collocated or duplicate sample number, analysis to be performed) should be provided prior to arrival by the Task Leader (TL) or Project Manager (PM).

6.0 DEFINITIONS

COC	Chain-of-Custody
C	Collocated
D	Duplicate
FB	Field Blank
Hg	Mercury
IR	Infrared
LIMS	Laboratory Information Management System
NIST	National Institute of Standards and Technology
P	Primary
PM	Project Manager
PUF	Polyurethane Foam
SOP	Standard Operating Procedure
SVOC	Semivolatile Organic Compounds
TL	Task Leader

7.0 INTERFERENCES

Samples should be handled in a way to avoid contamination of samples.

8.0 SAFETY

8.1 The TL or PM should provide information on samples prior to their arrival so that the proper safety precautions can be taken.

8.2 Liquid samples should be handled with gloves; if a sample container is broken, it should be transferred immediately to a fume hood for proper handling and disposal.

9.0 EQUIPMENT

9.1 Heiss Gauge – capable of being zeroed and reading the vacuum or pressure of canister samples; or Weiss Gauge – capable of reading the vacuum or pressure of canister samples and calibrated annually by manufacturer.

9.2 IR Thermal sensor gun – calibrated annually by manufacturer and capable of measuring temperatures from 4 to -25 °C.

10.0 MATERIALS

Not applicable.

11.0 CHEMICALS, REAGENTS, AND STANDARDS

Not applicable.

12.0 COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

12.1 Canister samples are stored at room temperature in the air toxics laboratory.

12.2 Carbonyl cartridge samples are stored in refrigerator R-11.

12.3 PUF/XAD cartridge samples are stored in refrigerator R-7.

12.4 Hexavalent chromium filter samples are stored in freezer F-11.

12.5 Metals filter samples are stored at room temperature in the inorganic laboratory.

12.6 Other media should be stored according to the procedures described in the appropriate method or analysis SOP.

12.7 The cold packs must be stored in the freezer in the shipping and receiving area in time to refreeze prior to the next media shipment.

13.0 CALIBRATION AND STANDARDIZATION

13.1 The Weiss vacuum/pressure gauge is sent to the manufacturer annually for National Institute of Standards and Technology (NIST) traceable calibration.

13.2 The Omegascope® thermometers are sent to the manufacturer annually for calibration. The calibration and subsequent testing of the devices are performed using instrumentation and standards that are traceable to NIST.

14.0 RECEIVING and LOG-IN PROCEDURE

14.1 Visually inspect each sample and each sample COC upon receipt. COC must include full, proper, and complete documentation (including but not limited to sample identification, collection site, time and date of sample collection, collector's initials, and any comments regarding the sample). The sample acceptance criteria are listed in Section 16.0. Pay particular attention to the contents of coolers. Remove all items from coolers (including icepacks) to assure that no sample is left in the cooler.

14.1.1 Verify that the site code, collection date, any sample designation (Primary (P), Duplicate (D), Collocated (C) 1 or 2, Field Blank (FB)), and container number (container number or canister number, if it is a canister, hexavalent chromium, or PUF/XAD sample) on COC are same as sample/sample container. If one of these parameters does not match, notify the PM.

14.1.2 If the sample falls outside of acceptable criteria stated in the program instructions, or in Section 16.0 of this SOP (e.g., sample not at the proper temperature, sample container is broken, etc.), document on COC and immediately notify the PM so that a decision can be made whether to invalidate the sample.

14.1.3 The receiver shall initial the COC and record the date of receipt. The condition of the sample upon receipt (such as temperature, canister pressure, color) should also be recorded on the COC.

- In the case of a carbonyl cartridge, hexavalent chromium filter, or PUF/XAD cartridge sample, the receiver checks and records the sample temperature and the thermometer ID upon receipt on COC.

- In the case of a canister sample, the receiver records the canister pressure upon receipt.

14.2 Invalidated samples are listed as VOID on the COC and in the LIMS. The reason for invalidation is recorded in the LIMS and on the COC if not already there.

14.3 The LIMS log-in person assigns the next available unique number in the ERG LIMS. Samples are logged-in as they are listed on the COC forms.

14.4 Following LIMS log-in, each sample COC is labeled with its unique LIMS ID number. Copies of each COC are to be separated (or, if not multiple copies, copied). Original COCs go with sample, copies of each COC are scanned and either given to PM or put into a centralized location by the person logging in the samples.

14.5 Also following LIMS log-in, the original COC is paired with each sample. Labels with a unique LIMS ID and sample date are printed for each carbonyl, metals, and canister sample. Once paired with their original COCs, the samples are placed in the appropriate storage area as listed in Section 12.

14.6 After the log-in of samples is complete, work orders are printed so the PM or their designee must verify that the samples were logged-in correctly according to the copies of each COC.

14.7 Sample hold times vary by method; refer to appropriate analysis SOPs for required hold times. Those listed is this SOP refer to extraction hold times from the day of collection or analysis hold time when there is no associated extraction for that method. Adherence to specified hold times is documented by the LIMS and conveyed to the TL via LIMS Hold Time Alerts. Turnaround times are conveyed via program instructions and/or scheduled project meetings.

14.8 Any special procedures which apply to a set of samples should be made known to the analysts by the TL or PM.

15.0 CALCULATIONS

Not applicable.

16.0 QUALITY CONTROL

The PM or their designee verifies that the sample information has been logged into the LIMS correctly. The COC must be filled out in ink and include full, proper, and complete documentation (including but not limited to, time and date of sample collection, collector's initials, and any comments regarding the sample). Listed below is a summary of the **sample acceptance criteria**, specific to common sample media.

16.1 Special Projects Sample Acceptance Criteria

16.1.1 When samples are received for a new or special project, notify the PM and the recipient immediately. Follow the PM's direction for sample acceptance if method is unknown.

16.2 Canister Sample Acceptance Criteria

16.2.1 If the canister valve is open upon arrival, the sample is invalid.

16.2.2 The site, collection date, and canister ID number (written in indelible ink) must match the accompanying chain of custody.

16.2.3 The canister pressure upon receipt:

- If the gauge needle doesn't move (stays on zero), the sample may be void. If the canister vacuum is zero, there is a possibility that the canister leaked during transport. Notify the PM so that a decision can be made whether to invalidate the sample;
- If the canister vacuum is greater than 15" Hg, notify the PM so that a decision can be made whether to invalidate the sample. Depending on the collection time (3 hour vs. 24 hour), the sample may be valid;
- If the canister vacuum is more than 3 inches Hg different from the final field vacuum, notify the PM so that a decision can be made whether to invalidate the sample. This does not apply to positive pressure readings, in psig. Note: canisters from sites at higher elevations may have larger pressure differences, check with PM;
- There is no maximum positive pressure, psig, for a valid canister sample.

16.2.4 The sample is invalid if the sampling duration is less than 22 or greater than 26 for a 24 hour sample. Add a comment about the sample in LIMS if it has a sampling duration between 22-23 hours or between 25-26 hours, so that the PM can make the decision whether to invalidate the sample.

16.2.5 The sample is flagged in LIMS if the sample is received out of hold time of 30 days or the duration between cleaning and sampling is greater than 30 days.

16.3 Carbonyl Cartridge Sample Acceptance Criteria

16.3.1 The cartridge envelope must be labeled in indelible ink with sample identification that includes the collection site ID and time/date of sample collection. This information is checked to make sure it matches the accompanying COC.

16.3.2 If the sample cartridge and envelope is visibly damaged, the sample is invalid. Sample cartridges are not removed from the envelope for inspection unless the envelope is damaged.

16.3.3 If the sample is received above room temperature the sample should be flagged in LIMS. Note: As stated in the Note in Section 10.12 of Method TO-11A, if samples are to be shipped to a central laboratory for analysis, the duration of the non-refrigerated period should be kept to a minimum, preferably less than two days.

16.3.4 The sample is invalid if the sampling duration is less than 22 or greater than 26 for a 24 hour sample.Add a comment about the sample in LIMS if it has a sampling duration between 22-23 hours or between 25-26 hours, so that the PM can make the decision whether to invalidate the sample.

16.3.5 The sample is flagged in LIMS if the sample is received out of hold time of 14 days.

16.4 PUF/XAD Cartridge Sample Acceptance Criteria

16.4.1 If the site operator has noted the glass thimble is broken on the COC, the sample is invalid. Glass thimbles are not inspected in the shipping/receiving area unless there is visible damage to the plastic canister.

16.4.2 Likewise, if XAD has escaped from the cartridge, the sample is invalid.

16.4.3 The collection site, time/date of sample collection, , and container number must be written on the plastic canister label in indelible ink. This information is checked to ensure it matches the accompanying COC.

16.4.4 If the cartridge is received at a temperature > 21 °C the sample is flagged in LIMS.

16.4.5 The sample is invalid if the sampling duration is less than 22 or greater than 26 for a 24 hour sample. Add a comment about the sample in LIMS

if it has a sampling duration between 22-23 hours or between 25-26 hours, so that the PM can make the decision whether to invalidate the sample.

16.4.6 The sample is flagged in LIMS if the sample is received out of hold time of 14 days.

16.5 Hexavalent Chromium Filter Sample Acceptance Criteria

16.5.1 If the site operator has noted a tear, hole or water damage to the filter on the COC, the sample is invalid. Hexavalent chromium filters are not inspected in the shipping/receiving area unless there is visible damage to the plastic canister.

16.5.2 The collection site, time/date of sample collection, and container number must be written on the plastic canister label in indelible ink. This information is checked to ensure it matches the accompanying COC.

16.5.3 If the cartridge is received at a temperature > 15 °C the sample must be flagged in LIMS.

16.5.4 The sample is invalid if the sampling duration is less than 22 or greater than 26 for a 24 hour sample. Add a comment about the sample in LIMS if it has a sampling duration between 22-23 hours or between 25-26 hours, so that the PM can make the decision whether to invalidate the sample.

16.5.5 The sample is flagged in LIMS if the sample is received out of hold time of 21 days.

16.6 Metals Filter Sample Acceptance Criteria

16.6.1 If the site operator has noted water damage or a tear/hole to the filter that occurred prior to or during sampling, the sample is invalid. Metals filters are not inspected in the shipping/receiving area unless there is visible damage to the sample container.

16.6.2 The filter container or envelope must be labeled with a collection site and, time/date of sample collection written in indelible ink. This information must be checked against the accompanying COC to be sure it is correct and that all samples were received. Flow rate information must be included on either the sample COC or the sample container.

16.6.3 If no COC is present (e.g. Oklahoma metals filters), create a COC listing each sample received.

16.6.4 The sample is invalid if the sampling duration is less than 22 or greater than 26 for a 24 hour sample. Add a comment about the sample in LIMS if it has a sampling duration between 22-23 hours or between 25-26 hours, so that the PM can make the decision whether to invalidate the sample.

16.6.5 The sample is flagged in LIMS if the sample is received out of hold time of 180 days.

16.7 Other Media, Aqueous Sample Acceptance Criteria

16.7.1 If the sample container is broken or leaking, the sample is invalid.

16.7.2 If the sample is received at a temperature higher than the method requirements or out of method specified hold time, notify the PM. The sample may be invalid.

16.7.3 The sample identification, collection site, and time/date of sample collection and container number must match the accompanying COC.

16.8 Other Media, Solid Sample Acceptance Criteria

16.8.1 If the container is broken or the sample has spilled from an open or broken container, the sample is invalid.

16.8.2 If the sample is received at a temperature higher than the method requirements or out of method specified hold time, notify the PM. The sample may be invalid.

16.8.3 The sample identification, collection site, and time/date of sample collection and container number must match the accompanying COC.

17.0 PREVENTION

Not applicable.

18.0 CORRECTION ACTION

If samples are received that are not valid or acceptable based on this SOP, the PM for the project is informed of the samples involved and the issues. The PM contacts the client

and/or resolves the issue and all data related to the samples are flagged with the appropriate caution regarding use and applicability.

19.0 WASTE MANAGEMENT

Not applicable.

20.0 MAINTENANCE

Not applicable.

21.0 SHORTHAND PROCEDURE

Read the entire SOP before following the shorthand procedure, as quality control is not thoroughly covered in this section.

21.1 Special Projects

21.1.1 Notify the PM and the recipient immediately upon receiving samples for a new or special project.

21.1.2 Follow the directions of the PM for proper receiving of the samples.

21.2 Canister Samples

21.2.1 Verify the site code, collection date, any sample designation (P, D, C 1 or 2, FB), and canister number;

21.2.2 Initial and date COC;

21.2.3 Check and document pressure on COC;

21.2.4 Notify the PM if at a vacuum > 15 inches Hg;

21.2.5 Notify the PM if at a vacuum of zero inches Hg;

21.2.6 Invalidate if canister valve is open or partially open;

21.2.7 Invalidate and notify PM if sampled less than 22 or greater than 26;

21.2.8 Flag in LIMS if past hold time or time between canister cleaning and sampling is greater than 30 days;

21.2.9 Store in Air Tox Lab.

21.3 Carbonyl Cartridges

21.3.1 Verify the site code, collection date, any sample designation (P, D, C 1 or 2, FB);

21.3.2 Initial and date COC;

21.3.3 Check and document receipt temperature and thermometer ID on COC;

21.3.4 Invalidate if cartridge is damaged;

21.3.5 Invalidate and notify PM if sampled less than 22 or greater than 26;

21.3.6 Flag in LIMs if past hold time;

21.3.7 Store in refrigerator R-11 with the accompanying COCs.

21.4 PUF/XAD Cartridges

21.4.1 Verify the site code, collection date, any sample designation (P, D, C 1 or 2, FB), and container number;

21.4.2 Initial and date COC;

21.4.3 Check and document receipt temperature and thermometer ID on COC;

21.4.4 Flag in LIMS if cartridge is > 21°C;

21.4.5 Invalidate if glass thimble is broken;

21.4.6 Invalidate and notify PM if sampled less than 22 or greater than 26;

21.4.7 Flag in LIMs if past hold time;

21.4.8 Store in refrigerator R-7; COCs are clipped to the refrigerator door.

21.5 Hexavalent Chromium Filters

21.5.1 Verify the site code, collection date, any sample designation (P, D, C 1 or 2, FB), and container number;

21.5.2 Initial and date COC;

21.5.3 Check and document receipt temperature and thermometer ID on COC;

21.5.4 Flag in LIMS if cartridge is > 15°C;

21.5.5 Invalidate if filter is torn;

21.5.6 Invalidate and notify PM if sampled less than 22 or greater than 26;

21.5.7 Label the accompanying COC with the LIMS ID and attach COC to the container with the sample inside.

21.5.8 Flag in LIMs if past hold time;

21.5.9 Store in freezer F-11.

21.6 Metals Filters

21.6.1 Verify the site code, collection date, any sample designation (P, D, C 1 or 2, FB);

21.6.2 The receiver initials and dates the COC, if present (if no COC present, create a COC listing each sample received). COC should also be labeled with the LIMS IDs;

21.6.3 Invalidate if filter is torn;

21.6.4 Invalidate and notify PM if sampled less than 22 or greater than 26;

21.6.5 Flag in LIMs if past hold time;

21.6.6 Store in Inorganic Lab.

21.7 Other Media

21.7.1 Verify the site code, collection date, any sample designation (P, D, C 1 or 2, FB), and container number (as needed);

21.7.2 Initial and date COC;

21.7.3 Check and document receipt temperature and thermometer ID on COC;

21.7.4 Invalidate and notify PM if temperature exceeds method requirements; if sampled less than specified collection time; if container is broken or leaking;

21.7.5 Flag in LIMs if past hold time;

21.7.6 The LIMS ID is recorded on COC and a label with the LIMS ID is affixed to the sample container.

21.7.7 Store according to PM instructions.

22.0 DOCUMENTATION AND DOCUMENT CONTROL

The need for proper and complete documentation is essential. The documentation is the most reliable resource the laboratory has for knowing how to deal with the multitude of samples that come into a laboratory. If a sample is received with incomplete documentation, every effort should be made to complete the information necessary for the analysis of a sample.

23.0 REFERENCES

Datasystem User's Manual, Promium, LLC.

24.0 TABLES, DIAGRAMS FLOWCHARTS, AND VALIDATION DATA

Not applicable.

ENGINEERING AND SCIENCE DIVISION

TITLE: Standard Operating Procedure for Project Peer Review	EFFECTIVE DATE: APR 25 ~~2010~~ 2011 KY
REFERENCES: ERG-MOR-017	
SATELLITE FILES: All Labs	
REASON FOR REVISION: Update procedures and update to NELAC format	
DATE OF LAST REVIEW:	NEXT SCHEDULED REVIEW:
WRITER: NAME/DATE Donna Tedder 4/18/11	TECHNICAL DIRECTOR: NAME/DATE Quita C. Swift 4/19/11
QUALITY ASSURANCE COORDINATOR: NAME/DATE Donna Tedder 4/25/11	MANAGER: NAME/DATE Donna Tedder 4/25/11

1.0 IDENTIFICATION AND PURPOSE

The purpose of this standard operating procedure (SOP) is to present the guidelines for selecting a project peer reviewer and conducting the peer review function as it relates to projects conducted at the Morrisville office. This document is not intended to supersede any corporate-level peer review SOP; rather, it is intended to supplement other such documents.

2.0 MATRIX OR MATRICES

NA

3.0 METHOD DETECTION LIMIT

NA

4.0 SCOPE AND APPLICATION

This SOP covers general peer review requirements and does not cover project-specific requirements. Project-specific peer review requirements will be incorporated in project instructions or work plans.

This SOP describes how to select a peer reviewer and the required involvement of the peer reviewer throughout the course of a specific project.

5.0 METHOD SUMMARY

NA

6.0 DEFINITIONS

DQO	data quality objective
PE	professional engineer
PM	project manager
QAPP	quality assurance project plan
QC	quality control
SOP	standard operating procedure
TL	task leader

7.0 INTERFERENCES

NA

8.0 SAFETY

NA

9.0 EQUIPMENT

NA

10.0 MATERIALS

NA

11.0 CHEMICALS, REAGENTS, AND STANDARDS

NA

12.0 COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

NA

13.0 CALIBRATION AND STANDARDIZATION

NA

14.0 PROCEDURE

14.1 Selection of a Peer Reviewer

The selection of the peer reviewer is critical to maintaining proper project quality control (QC) of technical work. At project inception, the Project Manager (PM) and the Task Leader (TL) must evaluate the requirements of the specific project to assess the level of experience needed for assignment of a peer reviewer. The peer reviewer must be qualified to understand the technical aspects of the project and to comprehend the client's expectations of the project. Other requirements include an understanding of the priorities, needs, and constraints to complete the project. It is also necessary for the peer reviewer to be aware of ERG's contractual commitments and potential areas of liability and/or exposure.

Normally, the choice of peer reviewer will be governed by the type of work conducted. Experience in a subject area is desired most often, but is not always a necessity.

For those engineering projects requiring final approval by a registered professional engineer (PE), the Coordinating Professional Engineer for the office will guide the selection of the appropriate peer reviewer. For such projects, peer reviewer selection will be based upon knowledge of the subject area, level of experience, and availability throughout the duration of the project.

14.2 Responsibilities

This section describes the various responsibilities of the peer reviewer throughout the duration of a project. The peer reviewer should be involved in project planning, kick-off, routine progress meetings, results, and reports (preliminary, draft, and final).

14.2.1 Project Initiation

At project initiation, the peer reviewer selected must be qualified to understand the technical aspects of the project and the technical content

and quality needs and expectations from the client's perspective. The peer reviewer must understand the timing and scope of his or her duties during the course of the project. Further, the peer reviewer must make the commitment of time and resources to perform proper peer review.

14.2.2 Project Instructions

Project instructions should be peer reviewed carefully before they are distributed to the project team to ensure the following:

- Project objectives are clearly stated, are appropriate, and are realistic.

- All information is clearly communicated. The project instructions should clearly communicate expectations of all project team members with regard to budget, schedules, individual responsibilities, and milestones.

14.2.3 Review of Technical Work Products

All technical work products should be subjected to peer review. These documents include, but are not limited to:

- Technical notes;
- Test plans;
- Quality Assurance Project Plans (QAPPs);
- Preliminary reports;
- Draft reports;
- Final Reports;
- Calculations;
- Field data; and
- Laboratory data.

The areas to be covered in reviewing the technical work products include:

- The project objectives should be clearly stated, as in the QAPP data quality objectives (DQOs). Of equal importance in the peer review is whether the project met its stated objectives. This should be documented on a data review checklist if pertinent to the project.

- Where applicable, all national or local codes, standards, methods, SOPs, and/or contractual constraints should be employed and cited.

As above, the report must be technically defensible in the light of all relevant regulatory or codified requirements.

- The work products must be reviewed to ensure that proper documentation (appendices containing information generated during the course of the project) has been included and that assumptions and supplemental data sources are properly referenced.

- The peer reviewer must consider carefully the conclusions and recommendations made in work products. The conclusions and recommendations must address the client's needs, must be complete, must be supported by the data and work, and should be implementable.

Adequate time should be budgeted for each peer reviewer to ensure that proper review is conducted and that peer review is not compromised as a result of schedule constraints.

All peer review comments should be retained as a part of the project files. Peer review comments must be addressed by the PM or project team. It is recommended that the PM review how the peer review comments were addressed with the peer reviewer(s) prior to completing the subsequent draft of the work product.

14.2.4 Routine Project Data Review

At a minimum, 10% of laboratory data must be reviewed. However, if a systematic or large number of errors are found in the 10% review, more than 10% of the technical work products should be reviewed. As an option, an additional 1% of the technical work products can be reviewed by a second peer reviewer designated by quality staff or PM. The review should be documented on a data review checklist, located in the SOP if pertinent to the project. All peer review comments should be retained as a part of the project files. Peer review comments must be addressed by the PM or project team.

Most projects involve calculations of some form; the selected peer reviewer will ensure that these calculations are adequately reviewed for mathematical accuracy. The selected peer reviewer will check a random number of these calculations personally to ensure that the proper review is being conducted. See SOP ERG-MOR-017 for evaluating the accuracy of spreadsheet data.

14.3 Problem Resolution

The peer reviewer is charged with providing comments and insights into the project throughout the course of the project. Any feedback on project progress or staff performance should be directed to the PM/TL, as appropriate. Any changes made or actions taken to address the concerns should be communicated to the peer reviewer, as well as reviewer concerns that will not be addressed and the reason the comments or concerns will not be addressed.

15.0 CALCULATIONS

NA

16.0 QUALITY CONTROL

As noted in Section 14.1, peer review is critical to proper QC of technical work. The responsibilities of peer reviewers throughout the duration of a project are detailed in Sections 14.2.1 through 14.2.4. In addition, Section 14.2.4 refers to SOP ERG-MOR-017 for evaluating the accuracy of spreadsheet data.

17.0 PREVENTION

NA

18.0 CORRECTIVE ACTION

NA

19.0 WASTE MANAGEMENT

NA

20.0 MAINTENANCE

NA

21.0 SHORTHAND PROCEDURE

NA

22.0 DOCUMENTATION AND DOCUMENT CONTROL

As noted in Section 14.2.3, all peer review comments should be documented on appropriate data review checklists and retained as part of project files.

23.0 REFERENCES

NA

24.0 TABLES, DIAGRAMS, FLOWCHARTS, VALIDATION DATA

NA

ENGINEERING AND SCIENCE DIVISION

TITLE: Standard Operating Procedure for Sample Login to the Laboratory Information Management System	EFFECTIVE DATE: MAY - 6 2015
REFERENCES: ERG-MOR-045, Element Datasystem User's Manual, Promium LLC., Promium website, www.promium.com	
SATELLITE FILES: N/A	
REASON FOR REVISION: Updated procedure	
WRITER/EDITOR: NAME/DATE Jennifer Nash 5/4/15	PROJECT MANAGER: NAME/DATE Rachel Swift 5/6/15
PROJECT QUALITY ASSURANCE MANAGER: NAME/DATE Donna Tedder 4/29/15	NEXT SCHEDULED REVIEW: 11/31/16

1.0 IDENTIFICATION AND PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to introduce the reader to procedures for entering sample information into the Laboratory Information Management System (LIMS) after receiving samples at the laboratory.

2.0 MATRIX OR MATRICES

N/A

3.0 METHOD DETECTION LIMIT

N/A

4.0 SCOPE AND APPLICATION

The instructions provided in the SOP are applicable to the login of all samples received from clients at ERG's laboratory facilities. This SOP assumes that a user has some familiarity with the Element Datasystem LIMS software.

5.0 METHOD SUMMARY

All samples received at the ERG Laboratory are logged into the LIMS database. The LIMS generates a unique identification (ID) number for each sample, and maintains the pertinent collection information and data for each sample.

6.0 DEFINITIONS

COC - Chain of Custody
Element - The name of the LIMS software used by ERG and sold by Promium, Inc.
ID - Identification
LIMS - Laboratory Information Management System
QC - Quality Control
SOP - Standard Operating Procedure
TAT - Turnaround Time

7.0 INTERFERENCES

N/A

8.0 SAFETY

N/A

9.0 EQUIPMENT

9.1 Desktop computer connected to ERG's Laboratory Intranet server BART (Y://).

9.2 Promium Element Software.

10.0 MATERIALS

N/A

11.0 CHEMICALS, REAGENTS, AND STANDARDS

N/A

12.0 COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

N/A

13.0 CALIBRATION AND STANDARDIZATION

N/A

14.0 PROCEDURE

14.1 Run the Element software and log on to the LIMS by entering your username and password.

14.2 Under the **Sample Control** option of the main menu, select the choice **Work Order**. A window will appear on the screen with information on the Work Orders already in the LIMS.

14.3 Click the **Add** button to create a new Work Order with a number generated by the LIMS. The scheme for the Work Order number is: YMMDDXX. Work Orders are generated on a project-by-project basis, i.e. only one project may be entered for every Work Order.

14.4 The following fields on the Project and Receipt tabs must be completed before the LIMS will allow the Work Order to be saved. The Project and Receipt tabs of the Work Order window are presented in Table 24.1 and 24.2. Fields that must be manually updated are denoted with a solid bullet, while fields that auto-complete are denoted with an open bullet. It should be noted that it is sometimes necessary to change fields that are automatically populated (e.g. "Received by Person"), so care must be taken to make sure this information is correct.

Project Tab:

- Client
- Project
    - Client Project Manager
    - Lab Project Manager
    - Project Number
    - Date Received

Receipt Tab:

    - Date Logged In
    - Date Due
    - Received By Person
    - Logged In By Person
    - Turnaround Time (TAT)
- Shipper Container Temperature (°C)
- Shipped By

Once the Work Order has been completed with the correct information, click the green **Save** button to save the information.

14.5 To modify information in a Work Order already created, click the **Edit** button, make the necessary corrections, and then click the green **Save** button to save the changes.

Note: Only the last Work Order created can be deleted by clicking the **Delete** button in the Work Order window. All others may only be modified.

14.6 The Work Order window may be closed by clicking the **Done** button. If individual sample information for a Work Order is going to be created or modified, the **Samples>>** button can be clicked to access this information.

14.7 Input individual sample information by selecting the **Samples** option in the **Sample Control** menu or by clicking the **Samples>>** button in the Work Order window.

14.8 Select the appropriate Work Order number to the left of the window if the correct number does not appear.

14.9 Enter the sample information from the COC form into the fields on the Sample Information and Containers tabs listed below:

Sample Information Tab

- Sample Name
- Lab Matrix
  - Report Matrix (Automatically populates based on Lab Matrix)
- Sample Type
- Analysis
- Sample Begin Date/Time/Zone
- Sample End Date/Time/Zone
- Sample Comments
- Applicable User Fields for canister number and pressure

Containers Tab

- Sample Container
- Sample Location

The Sample Information and Container tabs of the Samples window are presented in Table 24.3 and 24.4. Keep in mind that available analyses will not appear in the window until a Matrix is chosen. Also, information entered into certain fields

such as Sample Name and Comments may be specific to a particular client and/or project.

Note: Recurrent sampling events can be logged in using archived sample information by selecting the pull down arrow from the "Name" field and selecting the appropriate sample name. LIMS will import the information from the previous sample logged in under the same name. Edit the imported sample information appropriately and select "Save."

14.10 Each time a sample is added, Element generates a LIMS ID number with the code YMMDDXX-YY. Record this number in the upper right corner on the respective COC form.

Note: For multiple samples collected at the same site on the same day, new samples can be added to the work order by selecting "Copy" at the bottom of the screen and editing the appropriate sample information.

14.11 Once the Work Orders and Sample Information have been entered for the day, print the Work Orders using the **Work Order** option under the **Print** menu (or by clicking the print icon from the Sample window). Multiple Work Orders may be printed simultaneously by clicking the **Multi** button and selecting multiple Work Order numbers to print. The print template most used is the wko_withstorage template, but other templates may also be used. The Print Work Order window is presented in Table 24.5.

14.12 Print sample labels using the **Sample Labels** option under the **Print** menu (or, if using the print icon from the Sample window, the Sample Labels Print window will automatically come up upon closing the Work Order Print window). Multiple sample labels may be printed simultaneously using the **Multi** button and choosing samples from the present day or other time periods. Canister sample labels use the lsx_m@5163ERG.rpt template and all others (carbonyl and metals samples) use the lsx_m@5160.rpt template. Labels are printed using the Avery 5163 and 5160 varieties, respectively. The Print Sample Labels window is presented in Table 24.6.

14.13 After the Work Orders and Sample Labels have been printed, separate the white and yellow copies of the COC forms and photocopy any white COC forms missing the yellow copy. Give the sample labels and white COC forms to the sample receipt person so they can be placed with the samples. Scan the yellow CoC forms and pass them along to the appropriate project manager with the printed work orders so that sample login can be reviewed.

14.14 Save the scanned copies of the CoCs to a designated location and insert into their respective work order in LIMS. This is achieved by returning to the **Work Order**

option and selecting the **PDF icon** next to "Chain Of Custody". A new window will open, select **Add** and choose the appropriate location and COC scan, then select **Done**. The COC PDF window is presented in Table 24.7.

14.15 The Project Manager or person designated by the Project Manager will compare the Work Orders against the COC forms and indicate the errors to be corrected by the Sample Login person.

14.16 The Project Manager will update the status of the newly logged samples in the Update Status window of the Laboratory menu. Samples may be queried in a variety of ways and displayed by Analysis or by Work Order. The samples or Work Orders to be updated are selected on the screen and updated to a status of Available, Invalid, or Cancelled. Invalid samples should have a comment in the Samples window including the reason for invalidation.

14.17 After the status updates and the necessary corrections have been made, the yellow COC forms and Work Orders can be filed in the appropriate places.

15.0 CALCULATIONS

N/A

16.0 QUALITY CONTROL

16.1 After completing the login of samples for the day, the Work Orders generated should be checked against the COC forms to find any discrepancies. Errors are to be corrected in a timely fashion.

16.2 Work Orders are checked by the respective Project Manager or designee to provide another level of QC.

17.0 PREVENTION

N/A

18.0 CORRECTIVE ACTION

LIMS entries are checked by the Project Manager or designee. Corrections to entries are indicated on the Work Order printouts, and the sheets are returned to the sample logger so that the logger can make the necessary corrections.

19.0 WASTE MANAGEMENT

N/A

20.0 MAINTENANCE

Should any issues with the LIMS software arise, contact the ERG LIMS administrator. An annual service agreement is maintained for the Promium Element.

21.0 SHORT-HAND PROCEDURE

21.1 Create a Work Order for each project/site for which samples are received. Add individual samples to each Work Order using information from the COC forms.

21.2 Record LIMS ID numbers on the COC forms.

21.3 When all Work Orders and samples have been added to the LIMS, print the Work Orders and sample labels.

21.4 Separate the white and yellow copies of the COC forms. The yellow copies are scanned and given to the Project Manager responsible for the samples along with the Work Orders.The white copies are returned to samples.

21.5 PDF scans of the COC forms are inserted into the respective LIMS work order.

21.6 The Project Manager checks the Work Orders against the COC forms.

21.7 The yellow CoC copies are then filed in a designated storage area.

22.0 DOCUMENTATION AND DOCUMENT CONTROL

22.1 White copies of COC forms are filed with the sample data packages and stored according to each project's requirements. Yellow copies of COC forms are filed according to LIMS ID number in the laboratory's central COC file cabinet. The yellow copies are transferred to long-term storage periodically.

22.2 Work Order printouts are mainly used to check the accuracy of data entry into the LIMS. Work Order printouts are stored and/or disposed of according to the applicable Project Manager's instructions.

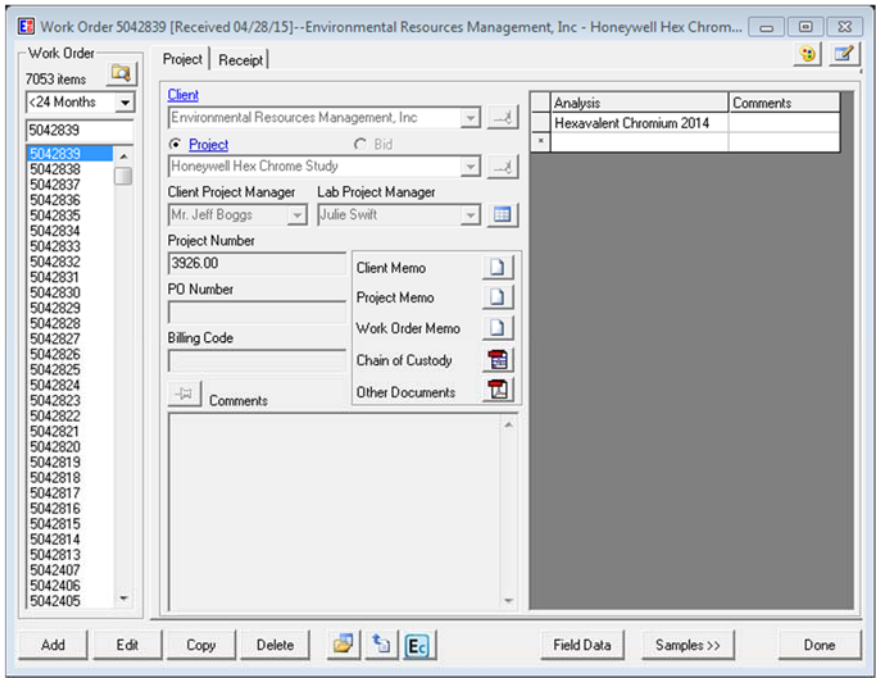
23.0 REFERENCES

Element Datasystem User=s Manual, Promium LLC.

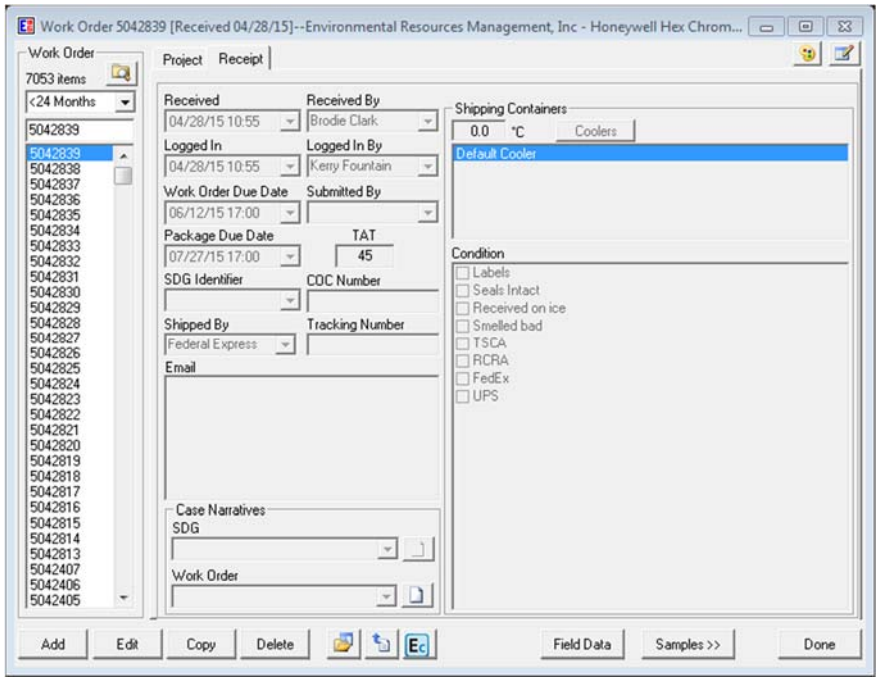
Promium website, www.promium.com

24.0 TABLES, DIAGRAM, FLOWCHARTS, VALIDATION DATA

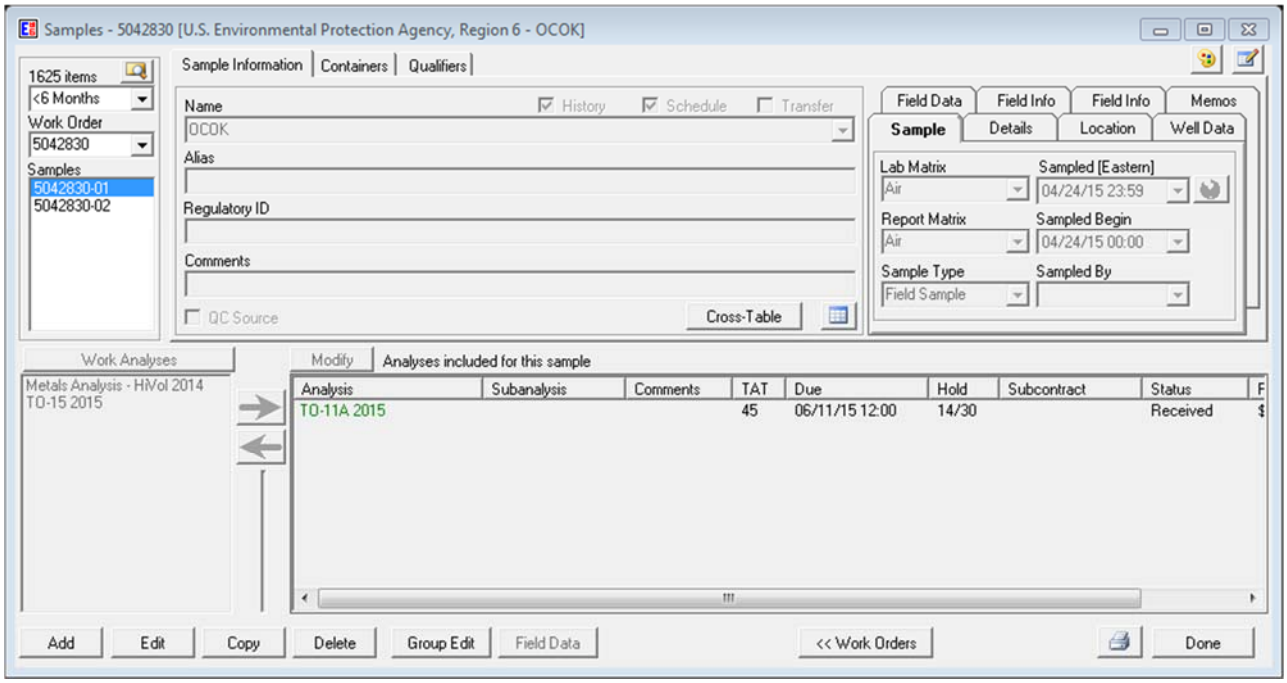
24.1 Work Order window- Project tab:



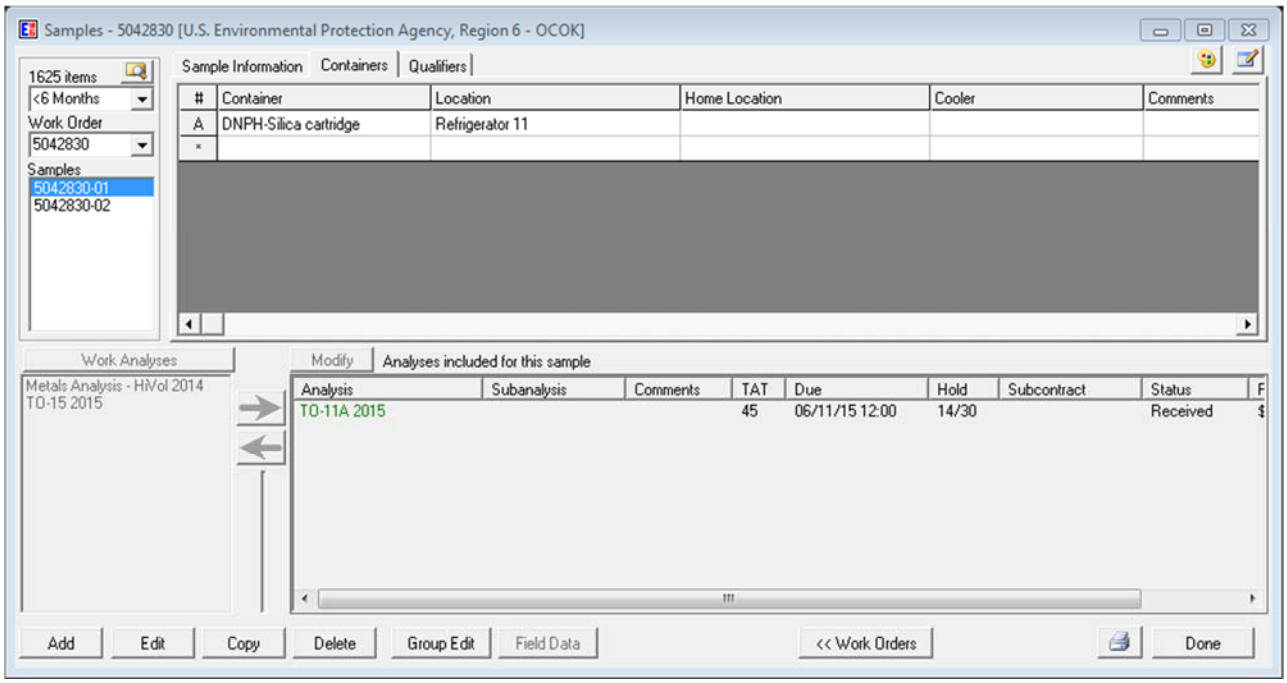
24.2 Work Order window – Receipt tab:



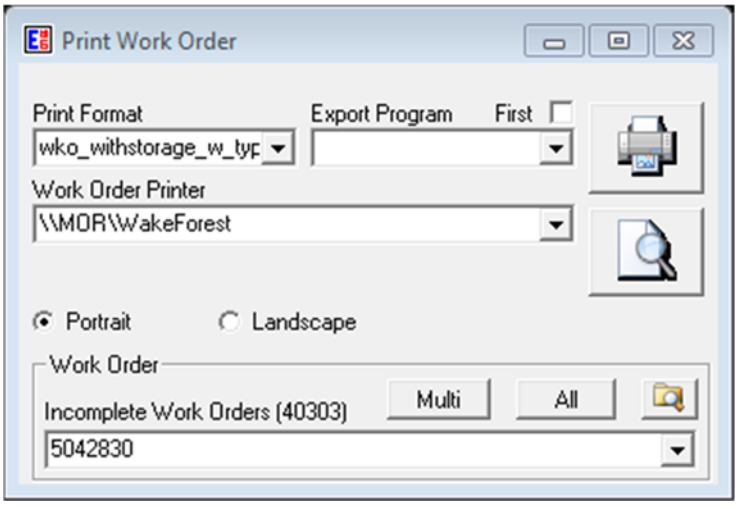
24.3 Sample window – Sample Information tab:



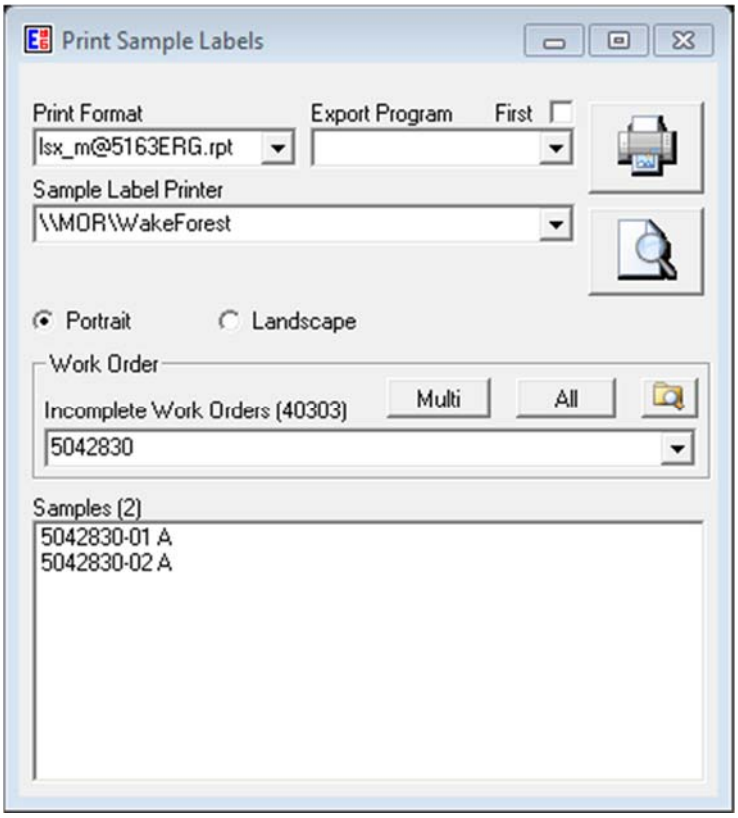
24.4 Sample window – Containers tab:



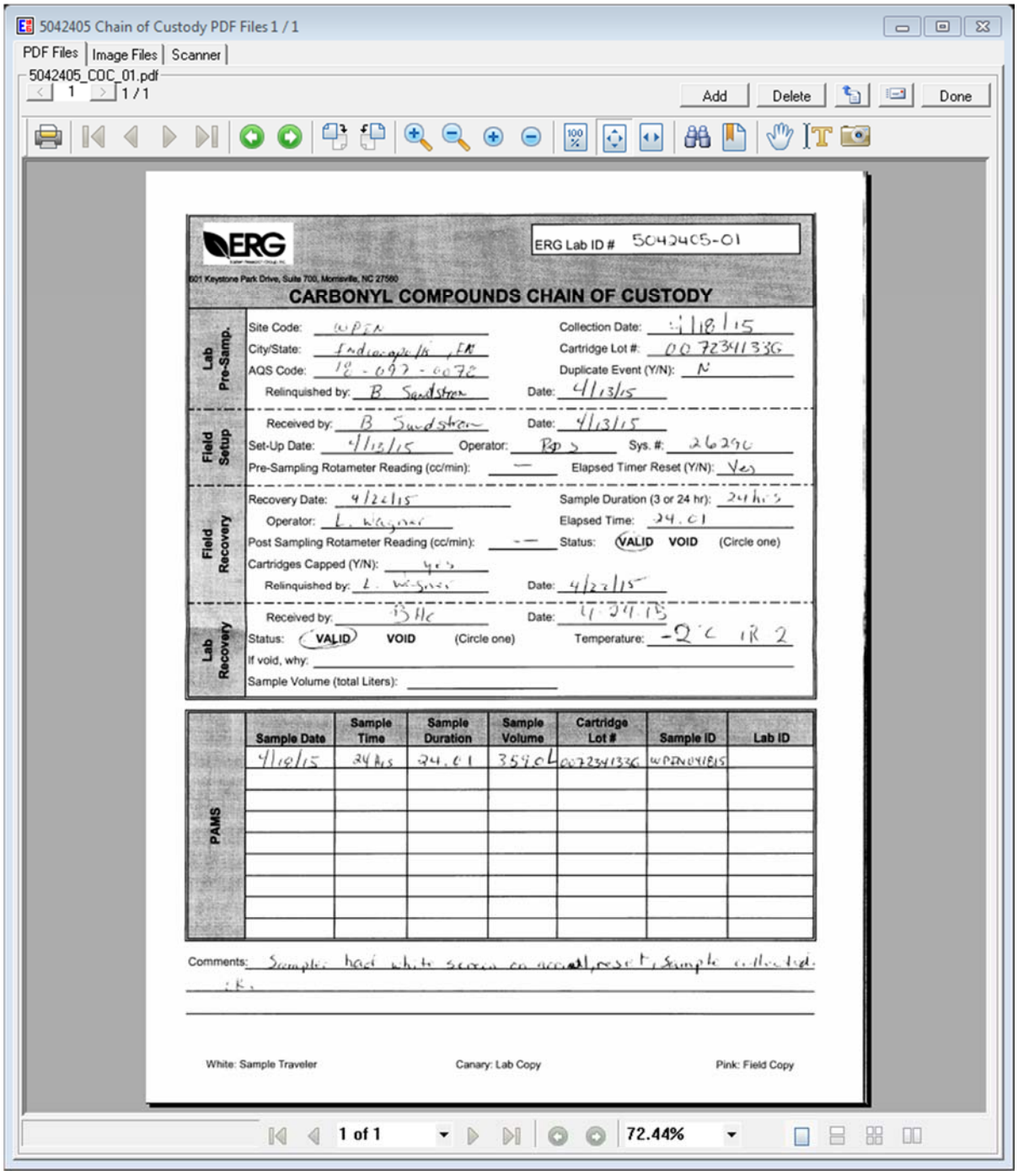
24.5 Print Work Order window:



24.6 Print Sample Label window:



24.7 Chain of Custody PDF window:



ENGINEERING AND SCIENCE DIVISION

TITLE: Standard Operating Procedure for the Preparation and Analysis of High Volume Quartz Filters for Metals by ICP-MS using Method IO 3.5 and FEM Method EQL-0512-201	EFFECTIVE DATE: APR - 3 2015
REFERENCES: ERG-MOR-031, ERG-MOR-033, ERG-MOR-045, Corporate Quality Management Plan, ERG Health and Safety Manual, Laboratory Quality Systems Manual, 40 CFR, Part 136, Appendix B, EPA Compendium Method IO-3.5, FEM Method "Standard Operating Procedure for the Determination of Lead in TSP by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with Hot Block Dilute Acid and Hydrogen Peroxide Filter Extraction" (EQL-0512-201)	
SATELLITE FILES: ICP-MS Laboratory	
REVISIONS: Updated MDLs, Added procedure for extraction record, Removed word duplicate from Collocate/Duplicate listed in Table 24-3 and review checklist	
WRITER/EDITOR: NAME/DATE Jennifer Nash 4/3/15	PROJECT MANAGER/TECHNICAL DIRECTOR: NAME/DATE Janet L. Swift 4/1/15
QUALITY ASSURANCE COORDINATOR: NAME/DATE Donna Tedder 4/1/15	NEXT SCHEDULED REVIEW: 1/31/2016

1.0 IDENTIFICATION AND PURPOSE

This standard operating procedure (SOP) provides the sample preparation and analysis procedures for suspended particulate matter collected on quartz filters (PM10 or TSP) for total metals determination by Inductively Coupled Plasma - Mass Spectrometer (ICP-MS).

2.0 MATRIX OR MATRICES

This procedure applies to the preparation and analysis of ambient particulate matter samples collected with quartz filters (PM10 or TSP) for total metals.

3.0 METHOD DETECTION LIMIT

3.1 Method Detection Limits (MDL)

3.1.1 The method detection limit (MDL) for each isotope is calculated according to Appendix D: DQ FAC Single Laboratory Procedure v2.4, 8/30/2007. MDL values are determined from historic method blank (BLK2) data following the procedures outlined in the document above.

3.1.2 The y-intercept for each linear calibration must be set to zero.

3.1.3 Use the same internal standards, calibration standards, instrument method and settings (sweeps and dwell) for the MDL study and field sample analysis.

3.1.4 The MDL determination should be reported in ng/L, ng/filter and ng/m^3 (assuming 2000 m^3 per sample). Refer to Table 24-1.

3.1.5 The MDL study should be repeated once per year and whenever a significant change in background or instrument response is expected (e.g., detector change).

4.0 SCOPE AND APPLICATION

4.1 Scope

This procedure details the acid extraction and trace elemental analysis of ambient air samples using an inductively coupled plasma-mass spectrometer (ICP-MS). The extraction procedures are suitable for high-volume ambient air samples collected on quartz membrane filters, sized 8 x 10". The procedure is applicable, but not limited to the metals listed in Table 24-1.

4.2 Applicability

This SOP is applicable to the analysis of suspended particulate matter collected with quartz filters. Acid digestion and filtration is required prior to analysis of quartz filter extracts. Analytes for which ERG has demonstrated the acceptability of this method are listed below. See Table 24-7 for a list of isotopes used for quantitation and monitoring.

Element	Symbol	CASRN
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
Mercury	Hg	7439-97-6
Molybdenum*	Mo	7439-98-7
Nickel	Ni	7440-02-0
Rubidium*	Rb	7440-17-7
Selenium	Se	7782-49-2
Strontium*	Sr	7440-24-6
Thallium*	Tl	7440-28-0
Thorium*	Th	7440-29-1
Uranium*	U	7440-61-1
Zinc*	Zn	7440-66-6

* Elements not on our standard EPA UATMP/NATTS analysis list of elements.

5.0 METHOD SUMMARY

This SOP describes the multi-elemental determination of total metals by ICP-MS in ambient air samples collected on quartz filters following guidelines in EPA method IO-3.5 and EPA FEM Method "Standard Operating Procedure for the Determination of Lead in TSP by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with Hot Block Dilute Acid and Hydrogen Peroxide Filter Extraction" (EQL-0512-201). An 8"x 1" portion is cut from the exposed filter. The filter is digested in a HotBlock™ for 2.5 hours using an extraction fluid containing 1.5% hydrochloric acid (HCl), 5.55% nitric acid (HNO_3) and 25 mg/L Au for mercury stabilization. Two aliquots of hydrogen peroxide (H_2O_2) are added after 1.5 hours and 2.0 hours of extraction and are allowed to effervesce. The extract is filtered and analyzed by ICP-MS. Data are collected using the manufacturer's software.

6.0 DEFINITIONS AND ABBREVIATIONS

6.1 Definitions

6.1.1 **Analytical Duplicate (DUP).** A second aliquot of a sample extract that is analyzed from the original sample in order to determine the precision of the method. This sample is also referred to as a replicate. See Section 16.4 for further elaboration on duplicates.

6.1.2 **Blank (BLK).** An analytical sample designed to assess specific sources of contamination. In this method there are two BLKs, the Laboratory Reagent Blank (LRB), which is always reported as BLK1 and the Method Blank (MB), which is always reported as BLK2.

6.1.3 **Blank Spike (BS).** A quality control sample (QCS) that contains a quartz filter strip spiked with a known quantity of analytes that is carried through the entire extraction process. This sample is synonymous with the Laboratory Control Sample (LCS).

6.1.4 **Calibration Blank.** A blank solution containing all of the reagents in the same concentration as those used in the analytical sample preparation when brought to final volume. This blank is not subject to the preparation method but contain the same matrix (i.e., the same amount of reagents and/or preservatives) as the sample preparations to be analyzed.

6.1.5 **Calibration Standards.** A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). The solutions are not subject to the preparation method but contain the same matrix (i.e., the same amount of reagents and/or preservatives) as the sample preparations to be analyzed.

6.1.6 **Continuing Calibration Blank (CCB).** A volume of ASTM Type I water acidified with the same acid matrix as is present in the calibration standards used to verify after every CCV that the instrument blank checks are reading ≤ MDL.

6.1.7 **Continuing Calibration Verification (CCV).** A multi-element standard solution prepared by the analyst and used to verify the stability of the instrument calibration with time, and the instrument performance during the analysis of samples. The CCV is the original calibration standard, whose concentration is at the midpoint of the calibration curve that is re-analyzed as a quality control (QC) sample.

6.1.8 **Field Blank (FB).** This is any sample that is submitted from the field and is identified as a blank. This also includes trip blanks.

6.1.9 **High Standard Verification (HSV).** The HSV is the highest calibration standard that is reanalyzed after the ICB and before the analysis of samples to verify the accuracy of the calibration curve at that concentration.

6.1.10 **Initial Calibration Blank (ICB).** The ICB is a re-analysis of the calibration blank, which is analyzed after the Initial Calibration Verification (ICV) and used to verify that the instrument blank checks read ≤ MDL.

6.1.11 **Initial Calibration Verification (ICV).** A solution prepared from a stock standard solution obtained from a source separate from that utilized to prepare the calibration standards. The ICV is used to verify the concentration of the calibration standards and the adequacy of the instrument calibration.

6.1.12 **Interference Check Standard (ICS).** A solution that may contain only interfering elements (ICSA) or both interfering elements and analytes of interest (ICSAB) in known concentrations that can be used to verify background and interference correction equations.

6.1.13 **Interferents.** Substances (atoms, ions, polyatomic ions, etc.) which may affect the analytical result for the element of interest.

6.1.14 **Internal Standard (ISTD).** A non-target element added to a sample at a known concentration after preparation but prior to analysis. Instrument responses to internal standards are monitored as a means of assessing overall instrument performance.

6.1.15 **Laboratory Control Sample (LCS).** A spiked aliquot of LRB with a blank quartz filter used as a QCS that is prepared and brought through the entire digestion/extraction and analytical process to demonstrate spike recoveries. This sample is synonymous with the BS.

6.1.16 **Laboratory Reagent Blank (LRB).** An aliquot of ASTM Type I water that is treated exactly as a sample including exposure to all labware, equipment, solvents, reagents and internal standards that are used with other samples that is always reported as BLK1. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or apparatus.

6.1.17 **Limit of Quantitation (LOQ).** The lowest concentration of an analyte that produces a signal/response that is sufficiently greater than the signal/response of lab reagent blanks to enable reliable detection and quantification during routine lab operating conditions. Statistically defined, this is the concentration of analyte in sample matrix that produces an instrument signal/response that is 10 times the standard deviation above the LRB (at 99% confidence, n-1 degree freedom; see Table 24-2).

6.1.18 **Linear Dynamic Range (LDR).** The concentration range over which the analytical working curve generated from the calibration standards is proven to remain linear. See Section 13.8 for more information on the LDR.

6.1.19 **Lower Limit of Quantitation Check (LLQC).** A check sample that is used to both establish and confirm the lower limit of quantitation and is prepared by spiking a low concentration of analyte into reagent water and carrying the solution through the entire preparation and analytical procedure.

6.1.20 **Lower Limit of Quantitation Limit (LLQL).** The lower limit of quantitation is considered the lowest reliable laboratory reporting concentrations and should be established from the lower limit of quantitation check sample and then confirmed using the lowest calibration point and/or from a low level calibration check standard.

6.1.21 **Low Level Calibration Verification (LCV).** A stock standard solution prepared using the same source as the calibration standards that is analyzed to verify the LLQL. The standard is prepared at the same concentration as the LLQL. An LCV is analyzed at the beginning, typically just before or after CCV1, and at the end of every analysis just before or after the final CCV.

6.1.22 **Matrix Interference/Effect.** In general, the interference and/or effect that particular matrix constituents may cause during sample processing and/or analysis. Matrix effects may be determined to exist from the careful interpretation of QC samples and criteria. Examples of observed effects include but are not limited to poor recoveries of spikes/ISTD and poor percent differences.

6.1.23 **Matrix Spike and Matrix Spike Duplicate (MS/MSD).** A sample chosen in a batch where additional filter strips are spiked prior to digestion/extraction with known quantities of specific analytes and carried through the entire analytical process to demonstrate their spike recoveries and precision.

6.1.24 **Method Blank (MB).** An aliquot of LRB with a blank quartz filter strip that is carried through the entire preparation and extraction process to demonstrate background contamination contribution from the filter and process and is always reported as BLK2.

6.1.25 **Method Detection Limit (MDL).** The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

6.1.26 **Performance Evaluation (PE) Sample.** A sample of known composition provided by a source outside the laboratory for analysis that evaluates the laboratory's analytical performance.

6.1.27 **Post Digestion Spike (PDS).** A spiked aliquot of an already digested sample used to demonstrate spike recoveries in the sample matrix when MS/MSD samples cannot be made. The analytical results of this spike may also be used to verify matrix interference in conjunction with the SRD results when the MS/MSD fail to meet criteria.

6.1.28 **Quality Control Sample (QCS).** A solution containing known concentrations of method analytes that is used to fortify an aliquot of LRB matrix. The QCS is prepared from a source(s) external to the laboratory and is used to verify the laboratory's analytical performance.

6.1.29 **Serial Dilution (SRD).** The dilution of a sample by a factor of five. If the undiluted parent sample concentration is minimally a factor of 50 above the MDL, the diluted sample should agree with the parent sample concentration within ± 10% when corrected by the dilution factor. The SRD may indicate the influence of interferents.

6.1.30 **Standard Reference Material (SRM).** A prepared standard material that has certified metals concentrations, for example the NIST SRM 1648a (Urban particulate matter with certified concentrations of lead at 0.655 ± 0.033 mass fraction (in %)). The SRM is used to verify the extraction procedure.

6.1.31 **Stock Standard Solution.** A commercially prepared standard solution (traceable to NIST or other certified standard sources), which can be diluted to derive other standards.

6.1.32 **Tuning Solution.** A solution used to determine acceptable instrument performance prior to calibration and sample analyses. This solution is used for mass calibration, nebulizer optimization, auto lens optimization, and daily performance reports.

6.2 Abbreviations

amu	Atomic Mass Units
ASTM	American Society for Testing and Materials
CASRN	Chemical Abstract Services Registry Number
COC	Chain of Custody
cps	Counts Per Second
DI	Deionized
DQO	Data Quality Objective
HNO_3	Nitric Acid
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
kW	Kilowatts
L	Liter(s)
LDPE	Low Density Polyethelyene
LIMS	Laboratory Information Management System
MΩ	Megohm
MCA	Multichannel Analyzer
MQO	Method Quality Objectives
m	Meter(s)
m^3	Cubic Meter(s)
mg	Milligram(s)
mg/L	Milligram(s) per liter(s)
min	Minute(s)
mL	Milliliter(s)
mm	Millimeter(s)
ms	Millisecond(s)
ng	Nanogram(s)
ng/L	Nanogram(s) per liter(s)
ng/mL	Nanogram(s) per milliliter(s)
NIST	National Institute of Standards and Technology
QC	Quality Control
RSD	Relative Standard Deviation
RPD	Relative Percent Difference
SD	Standard Deviation
SOP	Standard Operating Procedure
Std.	Standard
µg/L	Microgram(s) per liter
$\mu g/m^3$	Microgram(s) per cubic meter(s)
µg/mL	Microgram(s) per milliliter(s)
µL	Microliter (s)
µm	Micrometer
v/v	Volume per volume ratio

7.0 INTERFERENCES

Note: The background level of metals on a given lot of quartz filters can vary. Any background levels found on blanks should be documented for all the filters from the corresponding lot when available. It is recommended to consult 40 CFR Part 50, Section 6.1 Appendix G for guidance.

7.1 Laboratory Interferences

7.1.1 Wear powder-free nitrile or neoprene gloves when handling unexposed or exposed filters.

7.1.2 Clean all equipment used in the sample preparation and analysis in a manner consistent with good laboratory practices for metals analysis (See Section 20.3 in this SOP and Section 14.3.1 in SOP ERG-MOR-031).

7.1.3 Use ASTM Type I DI water or equivalent, with a resistivity greater than 17.3 MΩ, for sample extraction and standard preparation. Record the water resistivity prior to use.

7.2 Chemical Interferences

Pay close attention to the nature of solutions introduced to the ICP-MS.

7.2.1 Nitric acid must be less than 2% (v/v) for ICP-MS analysis to minimize the damage to the interface and to minimize isobaric molecular interferences. The use of platinum cones and other acid-resistant sample introduction components can be used for more aggressive acid matrices.

7.2.2 If higher acid extractions are required, dilute final digestate to 2% HNO_3.

7.2.3 The final dilutions of sample extracts must match the acid content of the calibration standards in order to match potential interferences.

7.2.4 The concentrations of dissolved solids in analysis solutions should be less than 2% to protect the sample interface on the instrument and prevent signal suppression. Higher concentrations may plug the sample and/or skimmer cone orifices.

Note: Protect the channel electron multiplier from high chemical concentrations (high ion currents). The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this period, response factors are constantly changing, which causes

instrument instability that invalidates the calibration curve, and thereby, invalidates all associated sample results. A sodium bicarbonate ($NaHCO_3$) sample matrix is known to cause this problem.

7.3 Instrument Interferences

7.3.1 Isobaric molecular and doubly charged ion interferences are caused by polyatomic ions (e.g., the contribution of ArCl on the 75As signal) or more than one charge (example, MoO+ ions on Cd isotopes).

7.3.2 Spectral interferences result from the presence of other isotopes or ions that have the same atomic weight or mass number as the analyte.

7.3.3 Transport interferences are a specific physical interference associated with the sample nebulization and transport process through the instrument. These usually result from sample matrix components that influence the aerosol formation or cause a change in the surface tension or viscosity. Changes in the matrix composition can cause observed signal suppression or enhancement.

7.3.4 Matrix interferences may be caused by elemental chemical and physical properties in the samples. For matrices of known composition, match the composition of the calibration and QC standards to that of the samples. For matrices of unknown composition, use an ISTD that has been matched to the analytes' chemical and physical properties (i.e., ionization potential, ±50 amu) so that the ISTD and element of interest behave similarly during the analytical process.

7.3.5 Memory interferences can occur when there are large concentration differences between samples or standards that are analyzed sequentially. Sample deposition on the sample and skimmer cones, spray chamber, peristaltic pump tubing and the type of nebulizer all affect the extent of the memory interferences that are observed. The rinse period between samples must be long enough to eliminate significant memory interferences.

7.3.6 Lead values are reported from isotope 208; however, all three isotopes must be used to quantitate lead to allow for the variability of lead isotopes in nature. The following correction equation must be applied to isotope 208:

$$(1.000)\ (^{206}Pb) + (1.000)\ (^{207}Pb) + (1.000)\ (^{208}Pb)$$

8.0 SAFETY

8.1 Personal protection should be used for all work performed in the inorganic laboratory, (e.g., gloves, safety glasses, laboratory coats, etc.).

8.2 The compressed gas cylinders must be stored and handled according to relevant safety codes outlined in the corporate health and safety manual. In use, the cylinders must be secured to an immovable structure and moved using a gas cylinder cart.

8.3 Make sure that sample vials are kept capped and in racks to prevent spills.

8.4 All personnel should be trained in the handling, extraction and analysis of acid samples for inorganic analysis.

8.5 Strong acids must not be stored with organic solvents or samples.

8.6 Follow normal laboratory safety procedures as outlined in the ERG Health and Safety Manual and the site-specific laboratory SOP.

9.0 EQUIPMENT

9.1 ICP-MS

The PerkinElmer SCIEX™ ELAN® 9000 ICP-MS consists of an inductively coupled plasma source, ion optics, a quadrupole mass spectrometer, a computer that controls the instrument, data acquisition and data handling software (ELAN® Software SCIEX™, Version 3.4), a printer, an autosampler (AS-93plus) and a recirculator. The quadrupole mass spectrometer has a mass range of 2 to 270 amu. Typical operating conditions are listed below.

Typical Operating Conditions

Plasma forward power	1.3 kW
Plasma/Coolant argon flow rate	13.8 L/min
Auxiliary argon flow rate	1.2 L/min
Nebulizer flow rate	0.9 L/min
Solution uptake rate	1.0 mL/min
Spray chamber temperature	Room Temperature
Detector mode	Dual (Pulse counting/Analog)
Replicate integrations	3
Mass range	6 - 240 amu
Dwell time	50 ms
Number of MCA channels	1

Number of scan sweeps	20
Total acquisition time	4.2 min/sample

9.2 Digestion System

Environmental Express HotBlock™ Digestion System or equivalent system capable of maintaining a temperature of 95°C within ± 2˚C. This temperature will heat the samples to a temperature of ~85°C (±5°C).

10.0 MATERIALS

10.1 Graduated polypropylene sample vials with screw caps, 50 mL volume (certified to be within ± 0.2mL).

10.2 Branson 8510, sonication bath with heating capability.

10.3 Pipetters with adjustable volumes ranging from 0.5 µL to 10 mL and disposable tips. Mechanical pipettes must be verified for accuracy quarterly (or every three months). Repeatable, mechanical pipettes, such as Eppendorf Research®, may be used and their accuracy should be verified on a quarterly basis to be within the manufacturer's specifications. If a pipette's accuracy exceeds the manufacturer's specifications its use should be discontinued and it should be replaced or sent in for repair.

10.4 Reflux caps and FilterMate™ 2 µm Teflon® filters with plungers.

10.5 Miscellaneous: powder-free nitrile or neoprene gloves; disposable laboratory wipes; self adhesive labels.

10.6 Volumetric flasks. Teflon®, Class A: 50, 100, 250 and 500 mL capacities.

10.7 Storage bottles. Wide and narrow mouth, Teflon® FEP (fluorinated ethylene propylene) with Tefzel ETFE (ethylene tetraflourethylene) screw closure: 50, 100, 250, 500, 1,000 and 2,000 mL capacities.

10.8 Wash bottles made of LDPE and Teflon® having 500 mL and 1 L capacities.

10.9 Plastic or Teflon® coated tweezers and Teflon stirring rods.

10.10 Filter cutting apparatus with 2 part Plexiglas board and plastic rotary cutter.

11.0 CHEMICALS, REAGENTS, STANDARDS AND THEIR PREPARATION

Note: In general, chemicals, reagents and commercial stock standards expire when specified by the manufacturer. If the manufacturer does not provide an expiration date then they shall expire one year from the opened date. Standards and other solutions prepared in-house expire as specified throughout the SOP. Proper disposal of hazardous wastes are discussed in detail in the Solid and Hazardous Wastes SOP (ERG-MOR-033).

11.1 High Purity Acids - ultrapure and concentrated stored in Teflon® Bottles. These reagents are used for the preparation of sample extraction fluid and all standards.

Note: Concentrated high purity reagents are not 100% of the specified reagent. It should be understood that all percentages in this SOP are expressed in terms of volume per volume (v/v) rather than true percentages of reagent in solution.

11.1.1 Nitric Acid (HNO_3), 60-70%

11.1.2 Hydrochloric Acid (HCl), 32-35%

11.1.3 Extraction fluid (1.5% (v/v) HCl, 5.55% (v/v) HNO_3, and 25 mg/L Au).

11.1.4 Standard solvent (0.3% (v/v) HCl, 1.11% (v/v) HNO_3 with 5 mg/L Au)

11.2 Hydrogen Peroxide (H_2O_2) - ultrapure and concentrated (30-32%) stored in Teflon® bottles. This reagent is used in the extraction procedure.

11.3 Nitric Acid-Trace Metal Grade in 2.5 L glass for rinse blank and labware cleaning.

11.3.1 Rinse blank (2% (v/v) HNO_3, 0.5% (v/v) HCl with 5 mg/L Au)

11.3.2 10% (v/v) HNO_3 acid bath for labware cleaning

Preparation: The acid bath solution is prepared by adding 2.5L of concentrated trace metal grade HNO_3 to 22.5 L of ASTM Type I DI water in a clean 42 L polypropylene acid bath tank. The acid bath should be stored in a fume hood.

11.4 ASTM Type I deionized water - with a resistivity greater than 17.3 MΩ.

11.5 Argon gas - purity > 99.996%, Oxygen < 5 mg/L, Hydrogen < 1 mg/L, Nitrogen < 20 mg/L and Water < 4 mg/L.

11.6 Secondary Source Control Standards - A commercially prepared single- or multi-element standard from a secondary source (different manufacturer from the multi-element calibration standard). These NIST traceable calibration standards are used to produce the ICV, which is run as a verification of the instrument's calibration for accuracy and precision.

11.7 Single-Element Stock Standard Solutions - Commercially prepared NIST traceable standards from ultra high-purity grade chemicals or metals (99.99 – 99.999% pure) designed for use with ICP-MS instruments (e.g., Mercury Std.).

11.8 Multi-Element Stock Standard Solutions - Commercially prepared NIST traceable standards from ultra high-purity grade chemicals or metals (99.99 – 99.999% pure) designed for use with ICP-MS instruments (e.g., ISTD solution).

11.9 Interference Check Standard - Commercially prepared standard that is diluted to prepare ICSA and ICSAB interferent checks.

11.10 Smart Tune Solution - Although custom tuning solutions may be used, the tuning solution for this SOP may be purchased through the manufacturer (Perkin Elmer #N8125040) or is prepared in-house using single-element standards to contain 10 µg/L of Be, Mg, Co, Rh, In, Ba, Ce, Pb, and U in 1% (v/v) HNO_3.

To prepare 1 L of this solution, add 10 mL of Ultrex Nitric Acid to ~ 900 mL of ASTM Type I deionized water and add 10 µL of each 1,000 µg/mL single-element standard, then bring to volume. This solution may be stored in LDPE bottles but ideally in Teflon®. The expiration date is either that specified by the manufacturer or if prepared in-house, no later than the earliest expiration date of any standard used for preparation.

11.11 Dual Detector Cross Calibration Solution - Refer to Section 13.3 for the purpose and final concentration of this solution. Although custom cross calibration solutions can be used, it may be purchased through the manufacturer (Perkin Elmer #8125032) or prepared in-house using single-element standards.

11.12 Multi-element ISTD stock standard – Commercially prepared standard that is used in conjunction with the single-element standards for Sc, Ga, and Li to prepare the internal standard.

11.13 Internal Standard Spike Solution - Prepared standard used to manually spike all calibration and QC standards as well as all samples that are analyzed by the ICP-MS.

11.14 Matrix Spike (MS) Standard - The MS standard is used to spike the BS/LCS and MS/MSD (See Section 16.3.2). Prepare the MS standard according to Table 24-6 with a final volume of 50 mL.

11.15 Post Digestion Spike (PDS) Standard - The PDS standard is used to spike the PDS source sample. This post digestion spike is used to help determine if poor matrix spike recoveries are due to interferents. Spike 1 µL per 1 mL of sample analyzed.

11.16 Second Source Working Standard - The second source working standard is used to create the ICV.

11.17 Citranox® Acid Cleaner and Detergent - Prepare a 5% solution by adding 500 mL of Citranox® to 9.5 L of warm – hot tap water for labware cleaning and decontamination. This detergent bath should be changed about once every month, depending on use.

11.18 Standard Reference Material (SRM) - The standard reference material used to prepare the SRM samples. NIST SRM 1648a (Urban particulate matter with certified concentrations of lead at 0.655 ± 0.033 mass fraction (in %) is used to verify the extraction procedure.

11.19 Lower Limit of Quantitation Check (LLQC) - This quality control sample is used to determine the LLQL, and is prepared by creating a spike solution that will create a final concentration of analyte in the sample matrix that produces and instrument signal/response that is 10x the standard deviation above the lab reagent blank (at 99% confidence; n-1 degrees of freedom). Lower limits of quantitation are verified when all analytes in the LLQC sample are detected within ± 30% of their true value.

12.0 COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

12.1 Collection and Handling of Filters

Whenever the filter is handled use clean disposable nitrile or neoprene gloves and if necessary clean Teflon® coated (no exposed metal surfaces) or plastic tweezers. Never touch the particulate laden surface of the filter and take care not to puncture or damage the filter with the tweezers. The filter should be folded in half lengthwise to prevent loss of particulate. See Section 16.1 for more information about filter condition.

12.2 Preservation and Storage of Filters

Samples do not have a preservative and can be stored for up to 180 days in ambient conditions. Upon retrieval from field sampling during humid or rainy

conditions be certain the filter is not moisture-laden. Damp filters may stick to the sample transport container causing damage and thereby invalidating the sample. If the sample is found to be moisture-laden allow the membrane to dry before enclosing in the transport container. Once the filter arrives at the laboratory, a unique LIMS identification number is assigned and placed on the outside of the COC, sample envelope and/or container for tracking and storage purposes. Extraction hold time is 180 days from the sample date.

12.3 Shipment of Filters

When filters are shipped to or from the laboratory follow proper handling instructions in Section 12.1 and take proper precautions when packing such that filters are not exposed to contaminants or damage during shipment.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Daily Optimization Procedures

Daily optimization is performed through the software's Smart Tune Wizard. Refer to Tables 24-4 and 24-5 for Optimization Procedures and Performance Specifications respectively. For more detailed information, the PerkinElmer Elan Version 3.4 Software Reference Guide is also available for reference as a PDF file on the desktop of the instrument computer.

13.2 Mass Calibration and Resolution

Before performing any kind of calibration or optimization, allow a period of not less than 30 minutes (preferably 1 hour) for instrument warm-up. After the warm-up, the mass calibration and resolution may be optimized using the tuning solution (see Section 11.11) by running a mass calibration and resolution optimization through the Smart Tune Wizard. Resolution at low mass is indicated by magnesium isotopes 24, 25, and 26. Resolution at high mass is indicated by lead isotopes 206, 207, and 208. These peaks may be viewed in the Interactive graphics window. For optimal performance, adjust spectrometer mass calibration to ± 0.05 amu and the resolution to produce a peak width of 0.70 ± 0.1 amu at 5% peak height. Repeat mass calibration and resolution optimization if it has shifted by more than ± 0.05 or ±0.1 amu respectively.

13.3 Dual Detector Cross Calibration

The dual detector cross calibration is used to provide a smooth transition from the pulse counting mode to the analog mode, which extends the linear dynamic range of the detector. Typically a 2% (v/v) nitric acid solution containing 200 µg/L of Mg, Cu, Rh, Cd, and Pb as well as 2000 µg/L of Be is used for this calibration

although custom solutions may be used. This calibration must be performed daily before each analysis to report values above the HCV.

13.4 Daily Performance

13.4.1 The daily performance report must be generated daily or before each analysis, whichever is more frequent.

13.4.2 Instrument stability must be demonstrated by running a daily performance check using the tuning solution. A minimum of five replicates with resulting relative standard deviations of absolute signals for all analytes of less than 3% is required prior to calibration. Performance specifications for the daily performance are listed in Table 24-5.

13.5 Calibration

13.5.1 Prior to initial calibration, set up proper instrument software routines for quantitative analysis (i.e., autosampler table, QC sample names etc.). The instrument must be calibrated using a minimum of a calibration blank and four non-zero calibration standards. Consideration should be give to adding more standards, particularly lower concentrations, in order to better define the LDR and quantitation limit (QL). A minimum of three replicate integrations with an RSD < 10.0% are required for data acquisition. RSDs > 10.0% are allowed for the first non-zero calibration standard (CAL2). Use the average of the integrations for instrument calibration and data reporting. To be considered acceptable, the calibration curve should have a correlation coefficient ≥ 0.998.

For a linear calibration to be considered acceptable, the calibration curve should have a correlation coefficient ≥ 0.998. The resulting curve should then be verified with mid-level and low-level calibration standards as described in Section 16.6.

Preparation: Non-blank calibration standards are prepared by diluting the calibration working standard to appropriate levels using the standard solvent.

13.5.2 For matrices of known composition, match the composition of the calibration and QC standards to that of the samples. For matrices of unknown composition, use an ISTD that has been matched to the analytes chemical and physical properties (i.e., ionization potential, ±50 amu) so that the ISTD and element of interest behave similarly during the analytical process.

13.5.3 The rinse blank should flush the system between solution changes for blanks, standards, and samples. Allow sufficient rinse time (≥ 1 min) to remove traces of the previous sample. Solutions should aspirate for at least 30 seconds prior to the acquisition of data to establish equilibrium.

13.5.4 Refer to Section 11.1.4 for the preparation of standard solvent. Once prepared, all calibration standards must be stored in Teflon® bottles/flasks.

Note: Commercial stock standards used to prepare calibration standards and other quality control standards must be used within their expiration date. Calibration blanks/standards and other QC standards made from the stock standards may be set to expire no later than the earliest expiration date of any standard used for preparation.

13.5.5 Refer to the quality control requirements presented in Table 24-3 for calibration acceptance criteria.

13.6 Internal Standardization

13.6.1 Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. ISTD quality control requirements as described in Section 16.7 must be followed.

13.6.2 Internal standards (ISTD) for this method are ^{45}Sc, ^{69}Ga, ^{89}Y, ^{115}In, and ^{209}Bi for analytes beginning with mass 6 and ending with mass 238. The ISTDs ^{6}Li, ^{72}Ge, ^{103}Rh, ^{159}Tb & ^{165}Ho may also be used if necessary. Internal standards must be manually added to each calibration standard **after** they are brought to volume in the proportion of 2.0 µL for every 1 mL. For example, add 200 µL of ISTD solution to a 100 mL standard.

13.6.3 Concentrations of the internal standards for this method are determined by the concentration of each element that will produce an intensity that is sufficiently stable. Typical intensities are between 200,000 and 500,000 cps; however, ideal intensities may be as high as 1,000,000 cps.

13.6.4 The concentration of the internal standard must be added equally and in the same manner to the calibration blank/standards, QC standards and samples.

13.6.5 Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. However, be aware that internal standards themselves may be responsible for polyatomic and/or doubly charged interferences.

13.7 Instrument Performance

13.7.1 After instrument calibration, an ICV and ICB must be analyzed for initial verification of the calibration curve. Refer to Sections 16.6.1, 16.2.2, and Table 24-3 for specific QC criteria.

13.7.2 To verify that the instrument is properly calibrated on a continuing basis, analyze a CCV and CCB before the analysis of samples and after every 10 samples.

13.8 Linear Dynamic Range (LDR)

The LDR study is performed every 6 months to determine the maximum concentration level at which the initial calibration is linear. The recovery criteria for the LDR are 90-110%. Dilutions must be performed for elements with concentrations over 90% of the established LDR. If an LDR study has not been performed within 6 months, any analytes with concentrations over the highest calibration concentration must be diluted.

13.9 Lower Limit of Quantitation Limit (LLQL)

The LLQL study is performed every 6 months to determine the lowest concentration level at which data may be reported. This is done by extracting and analyzing a lower limit quantitation check (LLQC). The recovery criterion for the LLQC is 70-130%. Any results reported below the LLQL must be qualified as an estimated value.

14.0 PROCEDURE

14.1 LIMS Batch Procedure

Note: Please perform the following procedure the same day that you plan to begin the extraction. If something happens and the extraction cannot be performed, edit the bench sheet with the correct extraction date, both in LIMS and on the hardcopy bench sheets.

14.1.1 Log into Element.

14.1.2 From the “Laboratory” menu, select “Batch.”

14.1.3 With the Inorganics department selected from the drop-down menu at the left of the screen, click “Add” at the bottom, left-hand corner. A blank bench sheet will appear. The following information should be input into

the bench sheet using the drop-down menus: 1) Preparation Method: ICP-MS Extraction and 2) Batch Matrix: Air

14.1.4 Select the appropriate inorganic analysis ("Metals Analysis – HiVol 20xx") from the "Available" analysis box and press the right-facing arrow button.

Note: Options: 1.) Additional information may be added in the "comments" box for batches that are different from standard samples, for example samples that are for the Midlothian or Schools projects. Reagent lot numbers used in the extraction are also added in the comments section. 2.) You may choose to press "Copy" instead of "Add" from Step3. Use caution here, as both the analysis and comments from the copied batch will be included in the new batch and this information may need to be changed.

14.1.5 Press the save button. The new LIMS-created batch number will be visible in the box to the left of the screen.

14.1.6 Select the "Bench Sheet" button at the bottom of the screen. This is where you will include sample information and appropriate batch QC.

14.1.7 Click "Edit" at the bottom of the new screen.

14.1.8 At the top of the screen, press "Add" and select "Sample by Container." Select the samples from the list that you would like to include in the batch. For each sample, the following information needs to be included: 1) Initial (m^3): This is the total flow through the filter as it was being sampled in the field. This information can be found or calculated from the information provided on the sample chain of custodies. Field blank samples are assigned the same volume as the primary sample collected on the same day. A field blank volume may also be an average of all the filter volumes for a given month. 2) Comments: Include two spaces followed by the sample ID for each sample in the list. This includes any additional designations such as C1, C2, FB, etc.

Note: A maximum of twenty samples may be selected for any given batch. If more than 20 samples are selected, additional batch QC must also be added to the bench sheet and extracted to meet the requirements described in Table 24-3.

14.1.9 Each batch requires QC to be prepared/extracted with each batch of twenty samples. This QC is included in the bottom box on the screen. Required QC includes:

i. Duplicate Samples: One duplicate QC sample is added per batch. Click the "Add" button at the top of the screen and select "Duplicate." Right click on a duplicate sample to assign its source sample and initial volume. This volume will be the same as the source sample. Duplicate samples must also be added for each collocated (C1/C2) or duplicate (D1/D2) spam type to be extracted.

ii. Blank Samples: Each batch must include one reagent blank and one method blank per twenty samples.

a.) One blank (BLK) sample is already included. To add another, click the "Add" button at the top of the screen and select "Blank."

b.) Change the sample name by right-clicking on each blank and selecting "Name." BLK1 should be changed to "Reagent Blank" and BLK2 should be changed to "Method Blank."

c.) Include the blank filter number in the comments section of the Method Blank.

iii. Spiked Samples: Each batch must include two spiked samples per twenty samples.

a.) One matrix spike (MS) and one matrix spike dup (MSD) are included for Hi-Vol extractions. Click on "Add" and select "Matrix Spike" and "Matrix Spike Dup" to include these QC. For each of these QC samples, assign the same source sample. The volume will be the same as that source sample.

b.) Identifying spikes: For both matrix spikes and laboratory control samples, the appropriate spike ID, type, and volume will need to be assigned in the same manner. Right click on the sample QC and select "Spike 1 ID." Select the appropriate standard from the list. Edit the "Spike 1 Type" to read "Pre-prep" and the "Spike 1 Volume" to read 500uL (or whatever volume is being used.)

iv. Post Spike (PS): Each batch must include one post spike (PS) sample per twenty samples.

a.) One post spike is automatically included for Hi-Vol extractions. Assign the appropriate spike ID, type, and volume using the instructions provided above. The correct spike amount is 50 µL and the spike type is "Post-prep."

v. Standard Reference Material: Each batch must include one SRM per twenty samples.

a.) Click on "Add" and select "Reference" to add the SRM to the bench sheet. Add the SRM identification number as assigned during weighing in the comments section. Identify the reference standard used by right-clicking on "Spike 1 ID" and selecting the appropriate standard. Indicate the weight of SRM digested (in mg) in the Spike 1 Volume. "Spike 1 Type" should be listed as "Pre-prep."

14.1.10 Print two copies of the bench sheet in landscape format. Both will need to be signed on the "Extraction Reviewed by" line and dated once the extraction is complete. One copy is to be three-hole punched and placed in the Extraction Notebook, while the other is to be kept bound to the corresponding samples in the cabinet in the lab.

14.2 Filter Extraction Procedure

14.2.1 Prior to sample processing, be sure to turn on the HotBlock ™ and select the appropriate program and initiate to allow it to warm to extraction temperature. Be sure to allow the HotBlock™ interface establish connection with the block itself (shown on the screen as "Please Wait") prior to beginning any extraction method. Failure to do this will cause the HotBlock™ to heat to higher than intended temperatures.

14.2.2 Wipe the filter-cutting apparatus and Teflon® rotary-cutter with a Kimwipe® prior to use.

14.2.3 If the filter is not already folded in half, carefully fold the filter in half along the 10" length with the side containing the particulates facing on the inside of the fold. Using the filter-cutting apparatus, align the 10" folded edge of the filter along the dashed line. Cut a 4" by 1" section of the folded filter using the Teflon® rotary-cutter.

14.2.4 Carefully fold the 4" by 1" section end over end into a size just larger than the mouth of the extraction vial. Place the folded filter into the labeled extraction vial and push to the bottom using a pre-cleaned Teflon® stirring rod for each sample to be sure the filter is below the 10 mL line.

Note: Do not place the filter flush with the bottom of the sample tube, as this will prevent proper acid flow through the tube during extraction. It is only necessary to make sure the filter is below the 10 mL line.

14.2.5 Add 0.5 mL of Matrix Spike Solution to the LCS, MS/MSD samples. Add 10 mL of extraction fluid (1.5% HCl (v/v), 5.55% HNO_3 (v/v) and 25 mg/L Au) to each extraction tube with a mechanical pipette.

14.2.6 The SRM sample is prepared for extraction by adding a blank 8x1" filter strip to a clean sample vial as described in Section 14.2.4. The loaded vial is then weighed, zeroed, and then re-weighed after an aliquot of SRM standard of approximately 2-3 mg is added to the vial. Add 10 mL extraction fluid to the extraction tube.

Note: It may be more efficient to weigh several SRM standard vials for extraction at one time. The weight information should be recorded in the balance room notebook. Individual standards should be numbered with the date the vial was created (i.e. "01012013-SRM01"). The vial number should be recorded in the LIMS in the SRM sample comments in the bench sheet.

14.2.7 Print out a copy of the Quartz Extraction Record from L:\Metals Lab (an example is shown in Table 24-10). Record the batch ID and extraction date. Record the temperature of the HotBlock™ as indicated by the calibrated thermometer, as well as the temperature indicated on the HotBlock UI.

14.2.8 Place all samples in a plastic HotBlock™ rack and place in HotBlock™. Add a reflux cap to each sample tube. Record the time samples were placed in the HotBlock on the table printed above. Samples will be extracted for a total time of 2.5 hours at a HotBlock™ temperature of 95ºC and an approximate sample temperature of 85ºC.

Note: Monitor sample temperature with a thermometer in an extraction tube with a reflux cap and 10 mL of extraction fluid.

14.2.9 After 1.5 hours of extraction, add 1.8 mL of hydrogen peroxide (H_2O_2) and allow to effervesce for 0.5 hours. Add an additional 1.8 mL of H_2O_2 after 2 hours of extraction and allow to effervesce again for 0.5 hours. This completes the extraction process. Record the time both aliquots of H2O2 were added on the Quartz Extraction Record.

14.2.10 After extraction is complete, remove the rack of samples and allow them to cool to room temperature. Record the time samples were removed, as well as the temperatures indicated by both the certified thermometer and HotBlock™ UI on the Quartz Extraction Record. Add 30 mL of DI water, cap, shake vigorously and allow to stand for 0.5 hours. This critical step must not be omitted; it allows the acid to diffuse from the filter into the

rinse. Record the time the DI water was added to the samples on the Quartz Extraction Record.

14.2.11 After this time period bring the sample volume to the 50 mL line on the vial with a wash bottle filled with ASTM Type I DI water prior to filtering. Record the time the samples were brought to final volume on the Quartz Extraction Record.

Note: If the final volume exceeds 50 mL measure the amount exceeded using an appropriate pipette and (usually the 1 or 5 mL) and record the final sample volume. Using the pipettor, pull sample from the vial in varying increments until enough liquid is removed so that the sample line is level with the 50 mL line on the vial. Add the amount of liquid removed to 50 mL and record that as the final volume. This information must be entered into the LIMS so that the final sample concentration is calculated and reported correctly. This overfilling may be avoided by using fine streamed wash bottles while adding the D.I. water.

14.2.12 Carefully filter the sample extract with a 2 µm FilterMate™ filter.

Note: When using a FilterMate™, slowly plunge the filter through the sample and be sure to get the filter all the way to the bottom. Do not force the filter or you will rupture the FilterMate™ filter. Ruptured filters that caused a loss of sample extract result in the re-extraction of that sample.

14.2.13 Homogenize the sample by inverting three times and then the extract is ready to be analyzed. The extracted filter and FilterMate™ remain in the sample vial with the extract to be analyzed. This does not interfere with sample recoveries or analysis.

14.2.14 Record the sample slot the certified thermometer was placed in during the sample extraction on the Quartz Extraction Record. After initialing the sheet, attach the Quartz Extraction Record to the batch paperwork.

14.3 LIMS Sequence Procedure

14.3.1 Log into LIMS Element Software.

14.3.2 From the “Laboratory” menu, select “Sequence.”

14.3.3 Click “Add” in the top right corner and select “Randy” as the Template ID then click done. This will automatically add all of the calibration standards and QC samples for a typical analysis sequence.

14.3.4 Click the pull-down menu for "Source Batch" at the upper middle part of the screen and select the batch you are going to analyze. Then click the "Add" button and select "Batch QC Sample." When the list of QC samples appears click the first sample and holding the shift button double-click the last sample and it will insert them into the sequence. Then click "Add" again and select "Batch Sample." Add all of the samples listed as you did for the Batch QC Samples.

14.3.5 Arrange all of the samples according to the example below, being sure to follow the requirements summarized in Table 24-3:

Autosampler Position	**Sample Name**
1	BTB0001-CAL1
2	BTB0001-CAL2
3	BTB0001-CAL3
4	BTB0001-CAL4
5	BTB0001-CAL5
6	BTB0001-ICV1
1	BTB0001-ICB1
5	BTB0001-HCV1
7	BTB0001-IFA1
8	BTB0001-IFB1
4	BTB0001-CCV1
2	BTB0001-LCV1
1	BTB0001-CCB1
9	B0B1707-BLK1
10	B0B1707-BLK2
11	B0B1707-SRM1
12	B0B1707-BS1
13	0020993-01
14	B0B1707-DUP1
15	B0B1707-MS1
16	B0B1707-MSD1
17	B0B1707-SRD1
18	B0B1707-PS1
4	BTB0001-CCV2
1	BTB0001-CCB2
7	BTB0001-IFA2
8	BTB0001-IFB2
4	BTB0001-CCV3
2	BTB0001-LCV2
1	BTB0001-CCB3

14.3.6 Right-click the SRD sample and choose the appropriate source sample from your batch.

Note: Make sure that the source sample for the SRD is updated to the current batch SRD sample or your data will not be saved.

14.3.7 Using the shift key select all of the samples in the sequence and right-click to choose "Internal Standard ID" then select the ISTD you are using for this sequence.

14.3.8 Right-click each calibration standard and QC sample and select "Standard ID" to set the current standard being used for each solution.

14.3.9 Click "Save" and print a double-sided copy in landscape format to use as the cover of the data package and to help enter the sequence in the Elan software.

14.4 Filter Analysis Procedure

14.4.1 Prior to analyzing samples, check the instrument performance by analyzing the tuning solution using the Daily Performance Check in the Smart Tune Wizard. The performance specifications that must be met are in Table 24-5. Also refer to Section 13.1 for other criteria. If the performance check fails, follow the optimization procedures in Table 24-4.

14.4.2 Before starting the calibration, be sure to flush the sample introduction system with sufficient rinse blank and be certain the rinse blank bottle has enough solution for the analysis. Enter all sequence information (sample and QC sample names) into the autosampler and QC tables in the Elan software. The autosampler table should be named as the month, day and year (e.g., 01012010.sam) and saved. Create the file name for the collected data with the numeric month, day and year (e.g., 01012010.rep) in the Method window under the "Report" tab (upper right) in the "Report Filename" field. Any changes made to the method (i.e., QC tables) must be saved before you exit that screen or they will be lost.

14.4.3 Pour off the calibration blank/standards (Blank (CAL1), LOQ (CAL2), CAL3, CAL4 and CAL5) and initial/continuing QC standards (ICV, ICB, ICSA, ICSAB, HSV, CCV, CCB) spiked with ISTD in the appropriate autosampler positions.

14.4.4 To start the analysis, highlight all samples in the autosampler table and click "Build Run." Then click "Run" in the following screen. Once the calibration has been completed and reviewed, save the calibration file with the same month, day and year as the .sam and .rep files in Section 14.4.2

and print the Quantitative Analysis Report to PDF to be included with the sequence files..

14.4.5 Label autosampler tubes with a black marker. Batch samples may be prepared by adding 20 µL of ISTD into the autosampler tube and then adding 10 mL of sample. Mix the sample well and place in appropriate autosampler location for analysis.

14.4.6 The PDS sample is prepared by adding 1.0 uL of spike solution to 1.0 mL of sample to be analyzed (i.e., 12 uL of PDS to 12 mL of sample).

14.4.7 Samples with analyte concentrations greater than 90% of the current LDR must be diluted and re-analyzed.

14.5 Unexpected Instrument Shutdown

In the event that the ICP-MS shuts down during an analysis the proper procedure to be followed by the analyst is:

14.5.1 Restart the instrument and allow it to warm-up for a minimum of 30 minutes but preferably one hour, especially if the instrument has been inoperable overnight and is at room temperature. If the analyst was present during the loss of the plasma and the instrument has not significantly cooled then a shorter time period for warm-up may be sufficient.

14.5.2 After the instrument has been thermally stabilized a new daily performance report (DPR) should be analyzed with the operating conditions being used for the analysis.

14.5.3 If the DPR passes the analysts must check the calibration by analyzing a continuing calibration verification (CCV) and a continuing calibration blank (CCB) to be sure the calibration is still valid. If the CCV & CCB passes the analyst may proceed with where the analysis left off. Any samples that didn't complete their analysis should be repeated.

14.5.4 If the DPR, CCV or CCB do not pass the analysis must be terminated and any samples not bracketed by valid CCV & CCB checks must be reanalyzed with a new analysis/calibration.

14.5.5 The DPR, CCV and CCB checks should be kept for documentation. The DPR may be placed in the DPR binder and the CCV & CCB checks must be included with the data package. The analyst should document the event briefly in the sequence narrative so the reviewer is aware of the instrument shutdown.

14.6 LIMS Data Upload Procedure

14.6.1 When a data package is complete, the analyst will transfer the data from the instrument computer to network server BART.

14.6.2 To begin LIMS upload, open Element. Go to the laboratory menu and click on "Data Entry/Review" In this window, select "Sequence" in the top left corner, making sure that "Inorganics" is selected from the drop-down menu. Highlight the correct sequence and click on "Create" in the Data Entry box in the top right corner. Once the spreadsheet is created in LIMS, select "DataTool" in the Data Entry box and save the file as the sequence name in the UserFiles folder of your harddrive (C:\ELMNT\UserFiles).

14.6.3 The DataTool interface should open to the "Select Data System Files" window. In this window, check to make sure the correct file information is selected:

1) File Type: PE ELAN_REP(*.rep)
2) Drives: y:\Bart

14.6.4 In the box below Drives: select the folder the data is stored in for the sequence. In the Bart drive, select the ICP-MS DATA folder, then the corresponding year, and finally the folder for the data the sequence was run.

14.6.5 All of the data files for that sequence will appear in the lower right-hand box. Double-click on the appropriate data file and click "Auto Select" for each file that needs to be included in the sequence. (*Note: Only undiluted samples and sequence QC should be included here.)

14.6.6 Click "Done" when all sample and QC files have been selected to return to the main window. Click "Merge Files" at the bottom of the window. DataTool will merge the files and show the data in the Data Transfer window.

Note: Review the content of the top windows in the Data Transfer window for red text. If there is any, the DataTool cross table requires editing. Seek the advice of the LIMS administrator to correct this.

14.6.7 Click "Save" and save the spreadsheet in the UserFiles folder of your hard drive. Close DataTool.

14.6.9 In Element, go back to the Data Entry/Review window. The newly merged data should appear in the window. Click "Save" to save the files to Element and then "Query" in the Data Review box. Element will perform all necessary calculations at this point.

14.6.10 In the Data Entry/Review window, samples and QC can be reviewed for pass/fails. Any data that does not pass its assigned criteria will have red text. Use appropriate data qualifiers to flag data that does not meet criteria.

14.7 LIMS Dilution Data Upload Procedure

Note: Dilution data is not uploaded with sequence QC, as this data is typically only required for one or two analytes in a given sample. Therefore, the data is hand-entered into Element.

14.7.1 Open Element and go to the Data Entry/Review window. Select the sequence that the diluted sample was originally run with. Click on "Query."

14.7.2 Scroll down to the needed sample information. Click "Edit" in the Data Review box. Right click on the sample & analyte that has dilution information and select "Qualifiers" -> "Quick Analyte Qualifiers." Select qualifier flag D-01 for dilutions.

14.7.3 In the IResult column, type the new dilution data. Make sure the new data has been corrected for the dilution factor (i.e. results for a 5x dilution should be multiplied by 5 if the instrument software did not make the correction). In the Diln column, type the dilution factor for the sample.

14.7.4 Repeat steps 2 & 3 for any additional dilution data that needs to be input for the sequence. If any QC data was altered (for example, Dups) then you will click on "Re-calc" and "Save." If only sample information was altered, click "Save."

14.7.5 Re-run the query to verify all dilution data was saved to the sequence.

Note: In LIMS, the dilution factor is applied to the associated MDL as well as to the sample concentration.

14.8 Data Review

All instrument data should be first reviewed by the analyst and then a secondary reviewer, usually the project task lead for metals analysis. Both the analyst and secondary review must use the "Quality Control Requirements for Metals

Analysis" checklist to complete data review (see Figure 24-8). Reviewers must initial and date each parameter check on the review form to verify that each meets the established acceptance criteria.

14.8.1 Initial Calibration

In addition to the requirements outlined in Figure 24-8, the analyst and secondary reviewer must also verify that the intensities measured for reportable analytes in the calibration blank are acceptable and will not interfere with the sensitivity. A review of previously analyzed calibration blanks can demonstrate acceptable intensity values. The intensities of the internal standards in the calibration standard should be monitored relative to the intensities seen in the calibration blank.

14.8.2 Internal Standards

Internal standards must be monitored for each sample throughout a sequence; the measured intensities must stay between 60 and 125% of the measured intensity of internal standard in the calibration blank. See Section 16.7 for corrective actions to remedy internal standard intensities that are measured outside of this range.

14.8.3 Relative Standard Deviation's RSD's

Follow the prescribed acceptance criteria for RSD's of calibration standards as listed in Table 24-3. Sample RSD's should also be monitored throughout analysis. High RSD's (greater than 20%) for concentrations above the MDL can indicate memory interference from previous samples, as well as other instrumentation issues that may need to be corrected before analysis can be continued.

14.8.4 Element/LIMS Data

The analyst and second reviewer must verify quantities imported into the LIMS reflect the raw data. This can be accomplished by checking a few analytes for random client samples and QC samples. Hand entered data (i.e., dilution) should be verified by the second reviewer to be certain the values, dilution factors and flags are properly inserted. The LIMS calculated final value should also be checked to ensure the system is correctly using the method's custom equation.

14.8.5 Multiple Isotopes

If an element has more than 1 monitored isotope, examine the concentration calculated for each isotope, or isotope ratios, to detect a possible spectral interference. Consider both primary and secondary isotopes when evaluating the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences that the primary recommended isotopes; therefore, differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

14.8.6 Reprocessing Data

Reprocessed data must include reprocessing of all calibration standards and QC samples associated with the reprocessed sample results. Original data shall be kept with the reprocessed data and annotated with the reason for reprocessing. It is imperative that the calibration file be saved as a separate file from the original calibration file. The reprocessed calibration file shall be renamed with the added distinction of "_reprocessed" (i.e. 03052010_reprocessed). All other samples including QC are automatically saved to the dataset file.

15.0 CALCULATIONS

15.1 Analyte Concentration

Metal concentration in the air sample should be calculated as follows:

$$C = \frac{[C_i \times V_f \times 9]}{V_{std}}$$

Where:

C = concentration, ng metal/m3

C_i = metal concentration determined from Section 14.4, ng metal/L.

V_f = total sample extraction volume from extraction procedure (i.e., 0.05 L).

9 = [Usable filter area (8"×9")] / [Exposed area of one strip ((4"×1") × 2 (representing a strip that has been folded)]

V_{std} = standard air volume pulled through the filter, m3

15.2 Method Detection Limits

The MDL is calculated as follows for the CFR MDL calculation method:

$$MDL = (K) \times (SD)$$

Where:

K = K Value as prescribed in Appendix D: DQ FAC Single Laboratory Procedure v2.4, 08/30/2007
SD = standard deviation of the historical BLK2 analysis.

15.3 Relative Percent Difference (RPD)

The RPD is calculated as follows:

$$RPD = \frac{R_1 - R_2}{(R_1 + R_2)/2} \times 100$$

Where:

R_1, R_2 = values that are being compared (i.e., duplicate and replicate analysis data)

15.4 Percent Recovery

Percent Recovery is calculated as follows:

$$Percent\ Recovery = \frac{Analytical\ Result}{Theoretical\ Result} \times 100$$

15.5 Relative Standard Deviation (RSD)

RSD is calculated as follows:

$$RSD = \frac{Standard\ Deviation}{Average} \times 100$$

16.0 QUALITY CONTROL

The analyst must perform the quality control checks listed in Table 24-3 and meet the requirements in this section. Data Quality Objectives (DQO) and data assessment criteria are determined from the results of the quality control samples. The DQO criteria are summarized in Table 24-3.

16.1 Sample Collection Quality Control

16.1.1 Filters which are dropped or become contaminated with any foreign matter (i.e., dirt, finger marks, ink, liquids, etc.) are invalid.

16.1.2 Filters with tears or pinholes that occurred before or during sampling are invalid.

16.1.3 A power failure during a field sample collection event invalidates the sample collected during that event. See SOP ERG-MOR-045 for more information about the sample acceptance criteria.

16.2 Blanks

16.2.1 The Rinse Blank must be used to flush the system between standards and samples. Refer to Section 11.3.1 for preparation details.

16.2.2 Initial Calibration Blank (ICB) is analyzed immediately following the initial calibration verification. The absolute value of the instrument response should be less than the method detection limit. If the ICB fails it may be re-analyzed twice. If the ICB still does not pass, the analysis should be terminated, the problem corrected and the ICV and ICB must be verified again before the analysis can continue. If the ICV or ICB still fail, recalibrate the instrument and verify the ICV and ICB again before continuing. If recalibration fails to correct the problem, all QC and samples included in the sequence must be flagged.

16.2.3 Continuing Calibration Blanks (CCB) are analyzed following each continuing calibration verification sample. The acceptance criteria are the same as the ICB. If the first CCB analyzed fails it may be reanalyzed twice. If it fails again the analysis should be terminated, the instrument recalibrated and the initial QC repeated. If the CCB fails later in the analysis it may also be reanalyzed twice. If it continues to fail the affected analyte must be flagged. If multiple elements fail any samples analyzed before or after the failing CCB must be reanalyzed.

16.2.4 Laboratory Reagent Blank (LRB/BLK1) consists of all reagents (extraction fluid) used to process samples and is carried through the entire preparation and extraction process to determine the background levels, if any, from the extraction fluid and process. If the absolute value of the analyte concentration of the LRB is less than or equal to the MDL (See Table 24-1), no further action is required. If the BLK1 fails it may be reanalyzed once. If it fails again and the concentration is greater than the MDL, but less than 5 times the MDL, the BLK1 and all associated

samples are flagged. If the concentration of a reported analyte is greater than 5 times the MDL all associated samples must have that analyte result blank subtracted and flagged as such.

16.2.5 The Method Blank (MB/BLK2) is prepared as an LRB but with the addition of a blank quartz filter strip and analyzed as a sample to determine the background levels, if any, from the blank filter and extraction process. Resulting data is recorded and used to determine FAC MDL values. While the absolute value of resulting values should be less than the established MDL, there is no corrective action procedure should the BLK2 fail.

16.3 Spikes

16.3.1 Laboratory Control Sample (LCS/BS): An LCS is prepared and carried through the entire sample digestion process. At least one LCS is analyzed with each sample batch. The LCS is essentially a MB with a spike added and is referred to as a BS. The results of the spike recovery must be within 80 -120% of actual values, with the exception of Al and Sb. Mercury may recover within 75-125% of actual value. In cases where background contamination is present from the filter media, these criteria may fail; however, it is appropriate to subtract the known background concentration found in the method blank but if it still fails the LCS must be flagged appropriately.

16.3.2 Standard Reference Material (SRM) is prepared and carried through the entire sample digestion process. At least one SRM is analyzed with each batch. The SRM is a NIST Urban dust that is prepared with a blank filter and can be referred to as a SRM in the LIMS. The results of the SRM Pb recovery must be within 80 – 120% of the certified value. If not, the sample may be reanalyzed once. If the SRM still fails to meet criteria, all associated samples must be flagged.

16.3.3 Matrix Spike and Matrix Spike Duplicate (MS/MSD): A sample from an extraction is chosen to be the source sample for the MS/MSD sample. Two extra filter strips are cut from the source sample filter for this purpose. They are prepared and carried through the entire preparation and extraction procedure as described in Section 14.2. These samples should recover within 75% to 125% of the true value. If not, the MS and/or MSD may be reanalyzed once each. If they still do not pass, examine the result of the PDS and SRD for possible matrix interference. If matrix interference is confirmed, the MS and/or MSD sample must be flagged as such. If the PDS and SRD are within their acceptance criteria and a matrix interference is not suspected, re-extraction of the samples should be

considered. Otherwise, all related samples may be flagged to indicate MS DQO failure.

Note: If the parent sample concentration is greater than 4 times the spike concentration, the recovery criteria does not apply and the sample should be flagged appropriately.

16.3.4 Post Digestion Spike (PDS, also known as PS): The PDS is an analyzed aliquot of an extracted sample that is spiked with the PDS standard (See Section 11.16). Preferably, the same sample that is used for the MS/MSD is also spiked for the PDS. The PDS spike addition should produce a minimum level of 10 times and a maximum of 100 times the QL. The spike recovery should be within ± 25%, or 75% to 125%, of the true spike value. If the PDS fails, the analyst should assess the SRD. If both the PDS and SRD fail for the same element it is an indication that matrix interference has occurred and any analytes that have failed should be flagged as possible matrix interference. In the event that the parent sample used for the PDS requires a dilution, the PDS should be prepared by diluting the sample and then spike with the PDS standard.

16.4 Duplicates

There are three types of duplicates found in this procedure:

16.4.1 Matrix spike duplicate (MSD): A true spiked laboratory duplicate of a separate strip of the parent (also called source) sample filter used to prepare the matrix spike. The RPD for this duplicate is ± 20%.

16.4.2 Laboratory duplicate: This duplicate is also prepared with an additional strip of the parent (or source) sample filter. An RPD of ± 20% from the parent sample values is required for values greater than or equal to 10 times the MDL.

16.4.3 Analytical duplicate (or replicate): A second aliquot of an extracted sample analyzed using the same analytical method as the first, or primary aliquot. These are performed on duplicate and collocated samples collected in the field. The RPD for analytical duplicates (replicates) shall be less than or equal to ± 10% for values greater than or equal to 10 times the MDL. If a duplicate/collocated sample fails to meet the established criteria, the duplicate or collocated sample must be reanalyzed. If initial sample results are confirmed then the replicate or collocated sample must be flagged.

16.5 Performance Evaluation (PE) Samples

Performance evaluation samples should be obtained as available from independent sources and analyzed as a routine sample. PE samples are prepared and analyzed in the same way as field samples and should be analyzed in replicate to verify results.

16.6 Standard Checks

16.6.1 Immediately after the initial calibration, the ICV is analyzed. The measured concentrations should be within ±10%, or 90-110%, of the actual concentration. If the criteria are not met, reanalyze the standard. If the criteria are still not met, a fresh standard may be prepared and analyzed or repeat the initial calibration and ICV.

16.6.2 The HSV must be analyzed after the ICB and prior to analysis of samples. The measured concentration should be within 95% to 105% of the actual concentration. If the HSV fails it may be reanalyzed twice. If the HSV still fails, a fresh standard may be prepared and analyzed. If it continues to fail, the instrument must be recalibrated and all initial QC must also be reanalyzed.

16.6.3 Before the analysis of samples and after every 10 samples during a batch analysis, the calibration must be verified using a CCV. Results must be within ±10%, or 90% - 110%, of the target value for each analyte to verify that the calibration is valid. If a standard check exceeds the limit, the analysis must be stopped and the check standard must be reanalyzed. If the target value exceeds the limit again, a fresh standard may be prepared and analyzed or the instrument must be recalibrated. Any samples analyzed before or after an invalid CCV must be reanalyzed, minimally for the failing element.

16.6.4 Following the first and last CCV of each analysis, an LCV must be analyzed. The measured Pb concentration should be within ± 30% of the true concentration. If the criteria are not met for the first LCV, reanalyze the standard once. If criteria still are not met, a fresh standard may be prepared and analyzed or terminate the analysis, correct any issues, and repeat the initial calibration, and reanalyze all initial QC. Should the second LCV fail for Pb, the analysis should be reanalyzed for Pb only.

16.6.5 Document each standard check value as a percent ratio of the actual value over the target value.

16.7 Internal Standards

The intensities of all ISTDs must be monitored for every analysis (see Table 24-7 for isotopes). When the intensity of any ISTD fails to register between 60 to 125% of the intensity of that ISTD in the calibration blank, the following procedure is implemented:

16.7.1 If the intensities are too high as a result of the internal standard being present in the sample, the sample must be diluted and reanalyzed with the addition of appropriate amounts of ISTD.

16.7.2 Repeat and increase the dilution until the internal standard intensities fall within the prescribed window.

16.7.3 If the intensities are determined to be a result of instrument drift, stop the analysis, find and correct the problem, recalibrate if needed and reanalyze the affected samples since the last acceptable ISTD recoveries.

16.8 Interferences

16.8.1 The interference check standards (ICS) are analyzed at the beginning and end of the run and for every 8 hours of continuous operation. They consist of two different standards, the ICSA and ICSAB. The interference check standards obtained from suppliers are never contaminant free. The certificate of analysis documents the levels found in each lot obtained. Therefore, the presence of target elements in the ICSA and ICSAB are expected and may vary from lot to lot of ICS solution used to make these standards. In some cases these contaminants may cause the ICSA or ICSAB to fail the QC requirements. It is acceptable to use the concentrations from the certificate of analysis to correct for these observed contaminants. The known concentrations of contaminants in the ICSA or ICSAB solutions may be subtracted from the experimental values and the established QC criteria must be met or the associated samples are flagged. Samples containing levels of the interferents above the levels in the ICS should be considered for dilution.

16.8.2 The first interference check standard (ICSA) contains only the interference analytes of interest. Any components of the ICS that are calibrated by the instrument must recover within 20% of the expected value. Values obtained for reported analytes not present in the standard should be within ±3 times the QL values (See Table 24-3). If the ICSA fails, it may be reanalyzed. If it fails again, a fresh standard may be prepared and analyzed. If it continues to fail, terminate the analysis and correct the

problem. .Any samples analyzed before or after a failing ICSA sample must be reanalyzed.

16.8.3 The second interference check standard (ICSAB) contains the same concentration of interference analytes in the ICSA as well as a known concentration of reported analytes. The concentration of known analytes should be near the middle of the calibration curve. The values obtained for reported analytes should be within 80% to 120% of the known concentration. If the ICSAB fails it may be reanalyzed. If it fails again a fresh standard may be prepared and analyzed. If it continues to fail terminate the analysis and correct the problem. Any samples analyzed before or after a failing ICSAB sample must be reanalyzed.

16.8.4 Failing ICS are commonly the result of correction equations that need to be adjusted for new instrument conditions. If this is suspected, calculate the new interference equations and reprocess the analytical sequences as described in Section 14.8.6.

16.9 Dilutions

16.9.1 Serial Dilution

The SRD analysis must be performed on one sample per batch, preferably on the parent sample chosen for the MS/MSD as guidance for poor recoveries in the spiked samples that may be due to matrix interference. The same sample matrix used to extract the parent sample must be used as the diluent. After the dilution is applied to the SRD results, the analyte concentration should be within 90% and 110% of the undiluted sample results if the parent sample analyte concentration is minimally a factor of 50 above the MDL in the original sample. If the SRD, MS/MSD, and PDS all fail for the same analyte, a matrix interference must be suspected and the QC data must be flagged for all affected elements. If matrix interference is not suspected, the SRD should be reprepared and analyzed a second time.

16.9.2 Sample Dilution

Any samples needing dilution due to concentrations exceeding the LDR or the presence of ISTD in the sample shall be diluted in an appropriate manner to bring the diluted concentration within the calibration curve and preferably near the mid-point. See Section 16.7 for dilutions required due to high ISTD recoveries. If the parent sample of a DUP/MS/MSD/PDS sample needs to be diluted, the dilution should be performed on each of these QC samples (See also Section 16.3.3). If the SRD was performed on

the parent sample of a DUP or PDS the results from the SRD may be used to report values of that parent sample if the 5 times dilution was appropriate.

Note: Dilution also increases the associated MDL by the dilution factor, so care must be taken not to dilute a sample so that the corrected concentration value is less than increased MDL.

16.10 Initial Demonstration of Capability

Each analyst must demonstrate initial proficiency for sample preparation and analysis by generating data of acceptable accuracy and precision for four LCSs. For demonstration of proficiency, acceptable accuracy and precision is defined as having both RSD ≤20% and percent recovery of 75-125%. This demonstration is repeated whenever new staff receives training or significant changes in extraction procedure or instrumentation are made. The applicable LCS recoveries are collected and maintained in the staff training files.

16.11 Decontaminating/Cleaning Labware

Procedures for proper cleaning and removal of trace metals from labware are found in Section 14.3.1 in SOP ERG-MOR-031. Detergent bath preparation instructions can be found in Section 11.19. Transport/dip baths of DI water ("To" and "From" acid baths) should be labeled with the date they are filled with fresh DI and changed about once every month to minimize contaminants being brought to the acid bath and from being reintroduced to clean labware. This will not only extend the life of the acid bath but it will help reduce hazardous waste production. To be certain that the acid bath will effectively clean and not contaminate labware a 5x dilution should be analyzed to determine the background about once a month.

17.0 PREVENTION

When possible, minimize the amount of chemicals used in the preparation and analysis of the metals filters to reduce waste.

18.0 DATA REVIEW AND CORRECTIVE ACTION

18.1 Data Review Documentation

Project files including at a minimum the information required in Section 22 are assembled and maintained by the performing analyst. Documentation for metals analysis by ICP/Mass Spectrometry will be reviewed for completeness and

meeting acceptance criteria by the Task Lead or secondary reviewer associated with the project or program requiring the analysis as described in this section.

A second review of the data is performed by the Task leader or designated secondary reviewer using the QC review checklist (checklist) shown in Figure 24-8 to confirm that quality requirements have been met. Corrections and flags are added to the data consistent with the corrective action required for each review finding. Second level reviewers must complete, initial and date the checklist.

The completed check list is included as part of the data package. Data not meeting SOP requirements are flagged and brought to the attention of the Project Manager for resolution.

18.2 Quality Staff Review

A minimum of 10% of the data is reviewed by ERG Quality Staff. Quality staff review checks that all SOP required quality parameters have been met and that data reviewers have completed their review checklists. Additional items may also be reviewed at the discretion of the data reviewer. Quality staff reviews are documented on the review form initiated in Section 18.1 by the primary data reviewer. Comments or issues with data identified by the Quality Staff reviewer are brought to the attention of the Project Manager for resolution. Quality Staff will use the review process as an indication of episodic or systematic quality program issues that may require improvements to the ERG laboratory quality system and or additional training for ERG staff.

As an option, Quality Staff may request an additional review of 1% of the data from this method for a project. The one percent (1%) review will follow the guidance in Section18.2.

Corrective action for metals by ICP/Mass Spectrometry analysis data quality issues are presented in Table 24-3.

If required, a corrective action form is filled out as described in the ERG Laboratory Quality Systems Manual.

19.0 WASTE MANAGEMENT

Hazardous waste disposal is discussed in detail in SOP ERG-MOR-033. Sample digestate, including the extracted filter and FilterMate™ filter, is retained in its original tube for a period of at least 6 months from the sample date. After this time, sample digestate is disposed of by pouring it off in the satellite waste containers located in the laboratory. Used sample vials are disposed of in the laboratory waste bin.

20.0 MAINTENANCE

The ICP-MS system is not maintained under a service contract. The preventative and routine maintenance are performed by the analyst(s). In the event a maintenance issue cannot be addressed by the analyst a service call is placed with the manufacturer and when appropriate a service engineer will perform any necessary maintenance. All maintenance activities are documented in the instrument maintenance logs.

20.1 The following maintenance procedures need to be addressed daily.

20.1.1 Check sample waste container level.

20.1.2 Inspect liquid argon cylinder supply and its pressure to the instrument.

20.1.3 Inspect chiller coolant level and connections for possible leaks.

20.1.4 Inspect torch and aerosol injector tubes.

20.1.5 Inspect nebulizer for clogs.

20.1.6 Inspect sample capillary tubing to be sure it is clean and in good condition.

20.1.7 Check peristaltic pump tubing before operation.

20.1.8 At the end of each analysis, flush system for 5 minutes with the plasma on with a maximum of 2% nitric acid, followed by deionized water.

20.1.9 Inspect vacuum pump oil level and replace as needed.

20.1.10 Inspect sample and skimmer cones for excessive salt build-up.

20.2 The following maintenance procedures need to be addressed quarterly (or more frequently if instrument performance indicates maintenance is needed).

20.2.1 Clean torch components and replace any worn O-rings on the torch assembly.

20.2.2 Inspect and clean the RF coil.

20.2.3 Inspect nebulizer spray pattern. Clean and replace gem tips and O-rings as necessary.

20.2.4 Check nebulizer components and replace worn O-ring on the transducer face.

20.2.5 Check spray chamber drain fitting for leaks.

20.2.6 Check that pump rollers are clean and remove and clean pump head as necessary.

20.2.7 Clean skimmer and sampling cones (See Section 20.3) and inspect orifices for damage or corrosion. Replace cones and/or O-rings as needed.

20.2.8 Replace interface roughing and turbo backing vacuum pump oil.

20.2.9 Inspect autosampler rinse pump rollers and clean or replace as necessary.

20.3 Cleaning Sample Introduction Components

20.3.1 Fill small plastic tank for sonicating components with warm to hot 2% Citranox® solution. Place torch, injector, spray chamber, gem tips, and transfer tube (remove all o-rings) into the tank. Sonicate all components for 15 minutes.

20.3.2 After removing the o-rings from the cones, **gently** insert each cone into a separate beaker with enough detergent solution to cover completely and allow to soak for ~ 1.75 hours. Care must be taken to only handle cones by the base – any contact with either cone orifice can easily cause irreparable damage.

20.3.3 Rinse all components thoroughly with tap water followed by a thorough rinse with DI water.

20.3.4 Place all components back in the cleaned tank/beakers with DI water and sonicate for another 15 minutes. Cones should be contained in a separate container from the other sample introduction components.

20.3.5 Carefully remove sample introduction components and rinse thoroughly with DI water.

20.3.6 Inspect cones under dissecting microscope to be sure that the edges of the orifices are not damaged and that the surfaces inside and out of the cone orifice area have been cleaned well. If the cones still appear to be dirty, place in 2% HNO_3 and sonicate for **no more than** 2 minutes (more than 2 minutes of acid exposure will damage the cones) then rinse thoroughly with DI water and reinspect. If cones are needed immediately they may be dried by spraying Dust Off® over the entire surface, taking care not to make physical contact with the cones.

All other sample components that need further cleaning should be sonicated for 2 or more minutes in 2% HNO_3. Place in Class 100 hood or leave to air dry on a dust free cloth (e.g., Technicloth®) or Kimwipes® may be used.

20.3.7 For cones that are still dirty after the procedure described in 20.3.6 and believed to be usable, refer to the Spectron Cone Cleaning Guide for additional procedures. Cones that are no longer usable may be returned to the manufacturer for recycling and platinum cones can be sent in for refurbishing.

21.0 SHORTHAND PROCEDURE

The flow chart shown in Figure 24-9 shows the procedural steps and sequence for analysis of inorganic samples.

22.0 DOCUMENTATION AND DOCUMENT CONTROL

22.1 All information concerning sample preparation, standard preparation, instrument conditions, etc., must be documented in the appropriate binders (i.e., Extraction Log, Daily Performance Reports, Standards Log etc.) and/or electronically in either the LIMS or the local instrument computer.

22.2 All calculations and the type of method for determining concentration must be recorded in the analyst's notebook. Any unusual problems or conditions must also be noted.

22.3 Record all maintenance performed on the instrument in the maintenance logbook for this particular instrument.

22.4 Record all sample analyses, including quality control samples, performed by the instrument in the ICP-MS run logbook for this particular instrument.

22.5 Reviewer must sign laboratory notebook weekly.

22.6 Any hard copies of instrument data should be filed chronologically. Electronic copies of instrument data are maintained on the L: drive in the “Metals Lab” folder.

22.7 It is imperative the project documentation be updated following each analysis. Analysts will copy raw instrument and QC files to a designated corporate network shared drive at the completion of each analysis sequence or batch. Primary data reviewers will use the data on the shared network drive for their data review

process. The completed data packages ready for upload into the ERG LIMS system will be retained on the network drive as the backup for this data.

22.8 All processed data are archived in the LIMS on the shared network drive. Data is archived monthly to compact disc (CD) or digital versatile disc (DVD), verified on the system where the data originated and stored for at least five years in the laboratory. An archive copy of a data package is retained for at least five years in the laboratory data storage. The data backup should include enough information to manually generate the numbers used for reporting.

22.9 Reporting

22.9.1 Sample results are uploaded into the LIMS in ng/L as analyzed. Any dilutions performed must be accounted for in the instrument software. The internal standard recoveries must be included with the result calculation. Final results should be reported in ng/m^3 to three significant figures as shown in Section 12.1. If required by the sampling organization, results can also be reported in $\mu g/m^3$ by multiplying the ng/m^3 results by 1,000.

22.9.2 Sample results should not be corrected based on analyte results from the laboratory blanks, field, trip, or filter lot blanks provided by sampling agencies, unless specifically requested. However, samples are blank-subtracted if any analyte is detected in the LRB at greater than 5 times the MDL as described in Section 16.2.4.

22.9.3 As stated in Section 11.2.6, samples with metal concentrations greater than 90% of the current LDR must be diluted and re-analyzed. The diluted value will be reported to the sampling agency.

22.9.4 Data should meet all specifications as presented in Table 24-3. If data does not meet specifications, corrective reporting actions listed must be followed (flag or invalidate data).

23.0 REFERENCES

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24.0 TABLES, DIAGRAMS, FLOWCHARTS, VALIDATION DATA

Table 24-1. 2015 Method Detection Limits (MDLs) for Metals Hi-Vol Filters

Element	2015 MDL by FAC[1] (ng/L)	2015 MDL by FAC[2] (ng/filter)	2015 MDL by FAC[2,3] (ng/m^3)
Aluminum *	88512	39830	19.9
Antimony	55.1	24.8	0.012
Arsenic	252.8	114	0.057
Barium *	17901	8055	4.03
Beryllium	9.468	4.26	0.002
Cadmium	25	11.24	0.006
Calcium *	873889	393250	197
Chromium	11376	5119	2.56
Cobalt	189.6	85.3	0.043
Copper *	2302	1036	0.518
Iron *	112437	50596	25.3
Lead	503	226	0.113
Magnesium *	202561	91152	45.6
Manganese	966.8	435	0.218
Mercury	28.5	12.82	0.006
Molybdenum *	628.3	283	0.141
Nickel	2542	1144	0.572
Rubidium *	69.2	31.1	0.016
Selenium	137.2	61.8	0.031
Strontium *	1721	774	0.387
Thallium *	1.57	0.705	0.0004
Thorium *	15.3	6.86	0.003
Uranium *	25.6	11.5	0.006
Zinc *	34975	15739	7.87

* Elements not on our standard analysis list of elements.
† Total Chromium.

Table 24-2. 2015 Limit of Quantitation (LOQ) for Metals

Element	ng/L
Aluminum*	78015
Antimony	100
Arsenic	742
Barium*	32676
Beryllium	25.6
Cadmium	58.2
Calcium*	817139
Chromium†	11396
Cobalt	467
Copper*	3672
Iron*	205994
Lead	982
Magnesium*	264057
Manganese	1460
Mercury	59.2
Molybdenum*	553
Nickel	3935
Rubidium*	129
Selenium	428
Strontium*	2839
Thallium*	2.95
Thorium*	33.0
Uranium*	20.6
Zinc*	56292

* Elements not on our standard analysis list of elements
† Total Chromium.

Note: This calculation assumes a total volume of 2000 m^3.

Table 24-3. Summary of Quality Control Procedures for Metals Analysis

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Daily Performance Check (DPR)	Daily, prior to samples	Mg-24 > 40,000 cps, < 3% RSD In > 300,000 cps, < 3% RSD Pb-208 >100,000, <3% RSD Ba/Ba++ and Ce/CeO < 0.03 Bkgd < 30 cps at Mass 220	1)Repeat analysis of DPR 2)Re-optimize instrument tuning parameters 3) Reprepare DPR standard 4) Perform instrument maintenance
Initial Calibration Standards (IC)	Daily, at least 5 calibration points	Correlation coefficient ≥ 0.998 & %RSD ≤ 10. RSDs >10 are acceptable for the CAL2 standard.	1) Repeat analysis of calibration standards 2) Reprepare calibration standards and reanalyze
Initial Calibration Verification (ICV)	Immediately after calibration	Recovery 90-110%, with the exception of Al	1) Repeat analysis of ICV 2)) Reprepare ICV standard 3Recalibrate and reanalyze
Initial Calibration Blank (ICB)	Immediately after ICV	Absolute value must be ≤ MDL	1) Locate and resolve contamination problems before continuing 2) Reanalyze, recalibrate or flag failing elements for the entire analysis when appropriate
High standard verification (HSV)	After ICB and before ICS	Recovery from 95-105% with the exception of Al	1) Repeat analysis of HSV 2) Reprepare HSV
Interference Check Standard (ICSA/IFA)	Following the HSV, every 8 hours and at the end of each run	Within ±3 times LOQ from zero or from the standard background contamination when present	1) Repeat analysis of ICSA 2) Reprepare ICSA and analyze 3) Adjust correction equation(s) and reprocess entire analysis
Interference Check Standard (ICSAB/IFB)	Following each ICSA	Recovery 80-120% of true value plus standard background contamination when present	1) Repeat analysis of ICSAB 2) Reprepare ICSAB and analyze 3) Adjust correction equation(s) and reprocess entire analysis
Continuing Calibration Verification (CCV)	Analyze before samples, after every 10 samples, and at the end of each run	Recovery 90-110%, with the exception of Al	1) Reanalyze CCV 2) Reprepare CCV 3) Recalibrate and reanalyze samples since last acceptable CCV
Low Calibration Verification (LCV)	At the beginning and end of each analysis, between the CCV and CCB	Recovery 70-130% for Pb only	1) Reanalyze LCV 2) Reprepare LCV 3) Recalibrate and reanalyze samples since last acceptable LCV
Continuing Calibration Blanks (CCB)	Analyzed after each CCV	Absolute value must be ≤ MDL	1) Reanalyze CCB 2) Reanalyze samples since last acceptable CCB
Laboratory Reagent Blank (LRB/BLK1)	1 per 20 samples, a minimum of 1 per batch	Absolute value must be ≤ MDL	1) Reanalyze 2) If > MDL, but < 5x MDL, sample results for that element must be flagged for the entire analysis 3) If > 5x the MDL then sample results for that element must be blank subtracted
Method Blank (MB/BLK2)	1 per 20 samples, a minimum of 1 per batch	Absolute value must be ≤ MDL. Note: The MB is used only for the purpose of MDL generation	This standard is not required by the method and there is no corrective action

Table 24-3 (Cont'd) Summary of Quality Control Procedures for Metals Analysis

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Standard Reference Material (SRM)	1 per 20 samples, a minimum of 1 per batch	Recovery 80-120% for Pb only	1) Reanalyze 2) Flag sample data 3) Re-extract batch
Laboratory Control Sample (LCS/BS)	1 per 20 samples, a minimum of 1 per batch	Recovery 80-120%, with the exception of Al and Sb	1) Reanalyze 2) Flag data if recovery for only one or two elements fail criteria 3) Re-prepare sample batch if recovery for most elements fail criteria
Replicates (DUP) (Replicate Analysis)	1 per 20 samples, a minimum of 1 per batch	≤ ±20% RPD for sample and duplicate values ≥ 10 times the MDL	1) Check for matrix interference in the cased of DUP1. 2) Repeat replicate analysis 3) Flag data
Collocated Samples (C1/C2)	10% of samples annually	≤ ±20% RPD for sample and collocate values ≥ 10 times the MDL	1) Flag C2 data if associated replicate analysis are within criteria 2) Repeat analysis if replicate analysis fail.
Matrix Spike (MS) and Matrix Spike Duplicate (MSD) for 8x10" Quart filters only	1 per 20 samples per sample batch	Recovery 75-125%, with the exception of Al and Sb, when the parent sample concentration is less than 4 times the spike concentration	1) Flag data if recovery for only one or two elements fail criteria, or when a matrix interference is confirmed by SRD and/or PDS results 2) Reanalyze 3) Reprepare sample batch if recovery for most elements fail criteria or contamination is evident.
Post Digestion Spike (PDS)	1 per 20 samples, minimum of 1 per batch	Recovery 75%-125%	1) Flag failed elements for parent sample and PDS 2) Reprepare PDS if preparation issue is suspected reason for failure.
Serial Dilution (SRD)	1 per batch	Recovery 90-110% of undiluted sample if the element concentration is minimally a factor of 50 above the MDL in the original sample	1) Re-prepare dilution if preparation issue is suspected reason for failure. 2) Flag failed analytes
Internal Standards (ISTD)	Every Calibration, QC and Field Sample	Recovery 60-125% of the measured intensity of the calibration blank	1) If drift suspected, stop analysis and determine cause, recalibrate if necessary 2) Reprepare sample 3) If recovery > 125% due to inherent ISTD, dilute sample and reanalyze

Table 24-4. Optimization Procedures

Procedure	When to Perform
Nebulizer Gas Optimization	Daily.
Ion Lens Voltage Optimization	Daily.
Auto Lens Optimization	Daily, when Auto Lens is used in the acquisition method.
Dual Detector Cross Calibration	Cross calibration is necessary if you have selected Dual Mode as your Processing Method. This would only be done when you require extended dynamic range (above 2 million cps). **Note:** This must be performed before each analysis for this method.
Instrument Performance Check	Daily.
X-Y Adjustment	Whenever the cones have been cleaned or replaced, or after any torch maintenance procedure.
Detector Optimization: Pulse Stage Voltage Analog Stage Voltage	When sensitivity cannot be recovered through other cleaning or optimization methods or when the detector is replaced.
Deadtime Correction	This procedure should only be performed if a detector has been replaced, and after the new detector has been optimized.

Table 24-5. Instrument Performance Specifications

24Mg Sensitivity	> 40,000 cps	< 3% RSD
In Sensitivity	> 300,000 cps	< 3% RSD
208Pb Sensitivity	> 100,000 cps	< 3% RSD
CeO/Ce	<0.03	N/A
Ba++/Ba+	<0.03	N/A
Background	< 30 cps @ Mass 220	N/A

Table 24-6 Matrix Spike Standard Preparation

Element	Stock Std. Concentration (µg/mL)	Added Volume (mL)
Al	1000	1.5
Sb	100	0.25
As	100	1.0
Ba	1000	0.5
Be	100	0.25
Cd	100	0.25
Ca	1000	1.25
Cr	100	2.5
Co	100	0.25
Cu	1000	0.5
Fe	1000	0.5
Pb	100	0.25
Mg	1000	0.5
Mn	100	0.5
Hg	10	0.5
Mo	100	0.25
Ni	100	0.5
Rb	1000	0.025
Se	100	1.0
Sr	100	0.25
Tl	10	0.5
Th	10	0.5
U	10	0.5
Zn	1000	0.5

Table 24-7. Analytical Isotopes for Quantitation and Monitoring of Reported Elements

Element	Quantitation Isotope(s)	Monitored/Confirmation Isotope(s)
Aluminum	27	NA
Antimony	121	123
Arsenic	75	NA
Beryllium	9	NA
Barium	137	135
Bismuth (ISTD)	209	NA
Cadmium	111	106, 108, 114
Calcium	43	NA
Chromium	52	53
Cobalt	59	NA
Copper	63	65
Iron	57	54
Gallium (ISTD)	71	NA
Indium (ISTD)	115	NA
Lead	208	206, 207
Lithium (ISTD)	6	NA
Magnesium	25	24
Manganese	55	NA
Mercury	201	200, 202
Molybdenum	98	92, 94, 95, 97
Nickel	60	62
Rubidium	85	NA
Scandium (ISTD)	45	NA
Selenium	82	77, 78
Strontium	88	NA
Thallium	205	203
Thorium	232	NA
Uranium	238	NA
Yttrium (ISTD)	89	NA
Zinc	66	67, 68

NA = Not applicable/none.

Figure 24-8. Quality Control Review Form (Page 1)

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Quality Control Review Form Metals Analysis -- 8x10" Quartz Filters 2015-1

Sequence ID: _____ **Instrument:** _____ **Batch:** _____
Cal Curve (Method): _____ **Analyst:** _____ **Date:** _____
10% Review Sample IDs: _____ **Reviewer:** _____ **Date:** _____
Optional 1% Review Sample IDs: _____ **Reviewer:** _____ **Date:** _____

Parameter	Acceptance Criteria	Analyst Check (Initials and Date)	Task Lead/Data (Initials and Date)	10% QA Review (Initials and Date)	1% Optional QA Review (Initials and Date)	Comments
Instrument QC						
Daily Performance Report	Mg-24 > 40,000 cps, < 3% RSD In > 300,000 cps, < 3% RSD Pb-208 >100,000, < 3% RSD Ba/Ba++ and Ce/CeO < 0.03 Bkgd < 30 cps at Mass 220					
Initial Calibration Standards (IC)	≥0.998□ correlation coefficient & RSD ≤10. RSDs >10 are acceptable for the CAL2 standard.					
Initial Calibration Verification (ICV)	Recovery 90-110%.					
Initial Calibration Blank (ICB)	Absolute value must be ≤ MDL.					
High Calibration Verification (HCV)	Recovery 95-105%.					
Interference Check Standard (ISCA/IFA)	ICSA: ±3 times QL from zero or from the standard background contamination when present					
Interference Check Standard (ICSAB/IFB)	ICSAB: Recovery 80-120% of true value plus standard background contamination when present					
Continuing Calibration Verification (CCV)	Recovery 90-110%.					
Low Calibration Verification (LCV)	Recovery 70-130% for Pb; must be analyzed at the beginning and end of each analysis.					

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Figure 24-8. Quality Control Review Form (Page 2)

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Quality Control Review Form Metals Analysis -- 8x10" Quartz Filters 2015-1 (Continued)

Parameter	Acceptance Criteria	Analyst Check (Initials and Date)	Task Lead/Data (Initials and Date)	10% QA Review (Initials and Date)	1% Optional QA Review (Initials and Date)	Comments
Continuing Calibration Blanks (CCB)	Absolute value must be ≤ MDL.					
Internal Standard Response	Recovery must be between 60 and 125% of the measured intensity of the calibration blank					
Linear Dynamic Range Check	All sample values must less than 90% of the established linear dynamic range.					
Extraction QC						
Check Sample Volume	Check COC or filter envelope against Bench Sheet to make sure sample volumes are correct.					
Laboratory Reagent Blank (LRB/BLK1)	Absolute value must be ≤ MDL.					
Method Blank (MB/BLK2)	Absolute value must be ≤ MDL.					
Standard Reference Material (SRM)	Recovery 80-120% for Pb.					
Laboratory Control Sample (LCS/BS)	Recovery 80-120%, with the exception of Sb (and Al).					
Collocated Samples (C1/C2)	±20% RPD when concentration of either sample is ≥ 10x the MDL					
Replicate Analyses (DUP)	For DUP1: ±20% RPD when concentration of the parent sample is ≥ 10x the MDL, all other DUPs ±10% RPD when concentration of the parent sample is ≥10x the MDL					
Matrix Spike (MS) and Matrix Spike Duplicate (MSD)	Recovery 75-125%, with the exception of Sb (and Al).					

Figure 24-8. Quality Control Review Form (Page 3)

SOP ERG-MOR-084
Quality Control Review Form Metals Analysis -- 8x10" Quartz Filters 2015-1 (Continued)

Parameter	Acceptance Criteria	Analyst Check (Initials and Date)	Task Lead/Data (Initials and Date)	10% QA Review (Initials and Date)	1% Optional QA Review (Initials and Date)	Comments
Serial Dilution (SRD)	Recovery 90-110% of undiluted sample if the parent sample concentration is > than 50x the MDL.					
Post Digestion Spike (PDS)	Recovery 75-125%					
Reporting Requirements						
Manual Check of Calculations	Hand calculate an equation - a unit conversion equation, a sample concentration equation, a dilution equation, etc. – to verify equation					
Check LIMS Qualifiers	Check to make sure the LIMS data flags are correct					
Negative Sample Values	Negative sample values must be less than the absolute value of the MDL.					

This review check sheet must be completed by primary data reviewer/TL/QA.

Figure 24-9. Flow Diagram for ICP-MS Preparation and Analysis for PM10 or TSP Filters

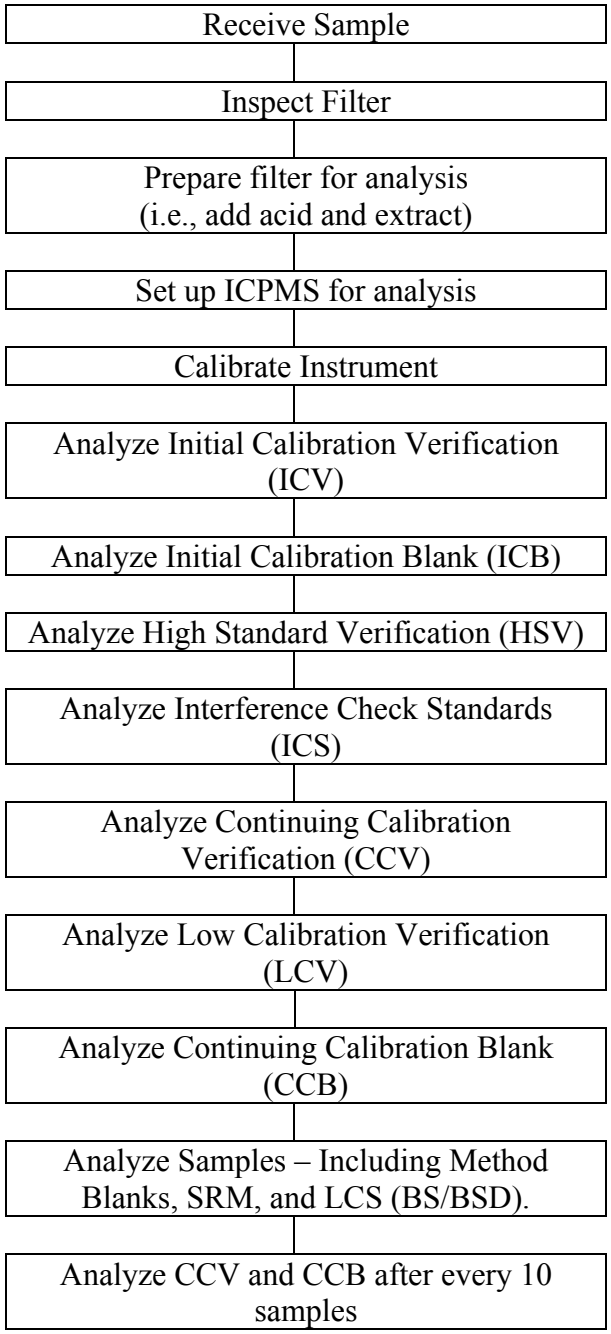

Table 24-10. Quartz Extraction Record

Record for Quartz Extraction Times, Temperatures & H_2O_2 additions 2014-1

Batch: **Date:** **Initials:**_____

Start Time	
Start Block Temperature (°C)*	
Sample Temperature (°C)†/Time	
Time 1st aliquot of H_2O_2 was added	
Time 2nd aliquot of H_2O_2 was added	
Stop Time (Removed from Block)	
Stop Block Temperature (°C)*	
Sample Temperature (°C)†/Time	
Time D.I. H_20 added & shaken/Sample Temp. (°C)	
Time brought to final volume	

*Block temperature is read from the HotBlock™ controller using an internal thermocouple.
†Sample thermometer serial #: 19583, actual thermometer temperature not the corrected temp.;

Thermometer block position # _____

ENGINEERING AND SCIENCE DIVISION

TITLE: Standard Operating Procedure for the Preparation and Analysis of 47mm Filters for Metals by ICP-MS using Method IO 3.5 and FEM Method EQL-0512-202	EFFECTIVE DATE: APR - 3 2015
REFERENCES: ERG-MOR-031, ERG-MOR-033, ERG-MOR-045, EPA Compendium Method IO-3.5, Corporate Quality Management Plan, ERG Health and Safety Manual, ERG Laboratory Quality Systems Manual, 40 CFR, Part 136, Appendix B, FEM Method "Standard Operating Procedure for the Determination of Lead in PM_{10} by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with Hot Block Dilute Acid and Hydrogen Peroxide Filter Extraction" (EQL-0512-202)	
SATELLITE FILES: ICP-MS Laboratory	
REVISIONS: Updated MDLs, Added procedure for extraction record, Removed word duplicate from Collocate/Duplicate listed in Table 24-3 and review checklist, Corrected standard solvent recipe. DST 4/1/15	
WRITER/EDITOR: NAME/DATE Jennifer Nash 4/3/15	PROJECT MANAGER/TECHNICAL DIRECTOR: NAME/DATE Julie C. Swit 4/1/15
QUALITY ASSURANCE COORDINATOR: NAME/DATE Donna Tedder 4/1/15	NEXT SCHEDULED REVIEW: 1/31/2016

1.0 IDENTIFICATION AND PURPOSE

This standard operating procedure (SOP) provides the sample preparation and analysis procedures for suspended particulate matter collected on Teflon® 47mm filters for total metals determination by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS).

2.0 MATRIX OR MATRICES

This procedure applies to the preparation and analysis of ambient particulate matter samples obtained by low-volume sampling on 47mm Teflon® filters for total metals.

3.0 METHOD DETECTION LIMIT

3.1 Method Detection Limits (MDL)

3.1.1 The method detection limit (MDL) for each isotope is calculated according to Appendix D: DQ FAC Single Laboratory Procedure v2.4, 8/30/2007, with the exception of arsenic. MDL values are determined from historic method blank (BLK2) data following the procedure in the document above.

In the case of arsenic, where the FAC MDL calculation method does not provide MDLs lower than an analyte's minimum risk level (MRL), the MDL method described in the CFR is employed instead. This involves spiking ten filters with a known concentration between 3 and 5 times the estimated MDL. The filters are then extracted and analyzed following the entire analytical method.

3.1.2 The y-intercept for each linear calibration must be set to zero.

3.1.3 Use the same internal standards, calibration standards, instrument method and settings (sweeps and dwell) for the MDL study and field sample analysis.

3.1.4 The MDL determination should be reported in ng/L, ng/filter and ng/m3 (assuming 24.04 m^3 per sample). Refer to Table 24-1.

3.1.5 The MDL study should be repeated once per year and whenever a significant change in background or instrument response is expected (e.g., detector change).

4.0 SCOPE AND APPLICATION

4.1 Scope

This procedure details the acid extraction and trace elemental analysis of ambient air samples using an inductively coupled plasma-mass spectrometer (ICP-MS). The extraction procedures are suitable for low-volume ambient air samples collected on Teflon® membrane filters, sized up to 47 millimeters in diameter. The procedure is applicable, but not limited to the metals listed in Table 24-1.

4.2 Applicability

This SOP is applicable to the analysis of suspended particulate matter collected with Teflon® filters. Acid digestion of samples and filtration (if necessary) is

required prior to analysis of Teflon® filter extracts. Analytes for which ERG has demonstrated the acceptability of this method are listed below. See Table 24-7 for a list of isotopes used for quantitation and monitoring.

Element	Symbol	CASRN
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
Mercury	Hg	7439-97-6
Molybdenum*	Mo	7439-98-7
Nickel	Ni	7440-02-0
Rubidium*	Rb	7440-17-7
Selenium	Se	7782-49-2
Strontium*	Sr	7440-24-6
Thallium*	Tl	7440-28-0
Thorium*	Th	7440-29-1
Uranium*	U	7440-61-1
Zinc*	Zn	7440-66-6

* Elements not on our standard EPA UATMP/NATTS analysis list of elements.

5.0 METHOD SUMMARY

This SOP describes the multi-elemental determination of total metals by ICP-MS in ambient air samples collected on 47mm Teflon® filters following guidelines in EPA method IO-3.5 and EPA FEM Method "Standard Operating Procedure for the Determination of Lead in PM_{10} by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with Hot Block Dilute Acid and Hydrogen Peroxide Filter Extraction" (EQL-0512-202). The filters are digested in a HotBlock™ for 2.5 hours using an extraction fluid containing 1.85% nitric acid (HNO_3), 0.5% hydrochloric acid (HCl), and 0.17% hydrofluoric acid (HF) with 8.33 mg/L of gold added for mercury stabilization. One aliquot of hydrogen peroxide (H_2O_2) is added after 1.5 hours of extraction and is allowed

to effervesce. The extract is analyzed by ICP-MS and the data are collected using the manufacturer's software.

6.0 DEFINITIONS AND ABBREVIATIONS

6.1 Definitions

6.1.1 **Analytical Duplicate (DUP).** A second aliquot of a sample extract that is treated the same as the original sample in order to determine the precision of the method. This sample is also referred to as a replicate. Due to the fact that Teflon® filters are not collected as duplicates, the DUP in this method is performed by analyzing a second aliquot of the parent sample digestate as an analytical duplicate. See Section 16.4 for further elaboration on duplicates.

6.1.2 **Blank (BLK).** An analytical sample designed to assess specific sources of contamination. In this method there are two BLKs, the Laboratory Reagent Blank (LRB), which is always reported as BLK1 and the Method Blank (MB), which is always reported as BLK2.

6.1.3 **Blank Spike/Blank Spike Duplicate (BS/BSD).** A spiked aliquot of LRB with a blank Teflon® filter used as a quality control sample (QCS) to demonstrate spike recoveries and precision.

6.1.4 **Calibration Blank.** A volume of ASTM Type I water acidified with the same acid matrix as is present in the calibration standards and sample extracts ready for analysis. This blank is not subject to the extraction procedure but contains the same matrix (i.e., the same amount of reagents and/or preservatives) as the sample preparations to be analyzed.

6.1.5 **Calibration Standards.** A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). The solutions are not subject to the extraction procedure but contain the same matrix (i.e., the same amount of reagents and/or preservatives) as the sample extracts to be analyzed.

6.1.6 **Continuing Calibration Blank (CCB).** The CCB is a re-analysis of the calibration blank after every CCV to verify that the instrument blank checks are reading ≤ MDL.

6.1.7 **Continuing Calibration Verification (CCV).** A multi-element standard solution prepared by the analyst and used to verify the stability of the instrument calibration with time, and the instrument performance during the analysis of samples. The CCV is the original calibration standard

whose concentration is at the midpoint of the calibration curve that is re-analyzed as a quality control (QC) sample.

6.1.8 **Field Blank.** This is any sample that is submitted from the field and is identified as a blank. This also includes trip blanks.

6.1.9 **High Standard Verification (HSV).** The HSV is the highest calibration standard that is reanalyzed to verify the accuracy of the calibration curve at that concentration before the analysis of samples.

6.1.10 **Initial Calibration Blank (ICB).**The ICB is a re-analysis of the calibration blank, which is analyzed after the ICV and used to verify that the instrument blank checks are ≤ MDL.

6.1.11 **Initial Calibration Verification (ICV).** A solution prepared from a stock standard solution obtained from a source separate from that utilized to prepare the calibration standards. The ICV is used to verify the concentration of the calibration standards and the adequacy of the instrument calibration.

6.1.12 **Interference Check Standard (ICS).** A solution that may contain only interfering elements (ICSA) or both interfering elements and analytes of interest (ICSAB) in known concentrations that can be used to verify background and interference correction equations.

6.1.13 **Interferents.** Substances (atoms, ions, polyatomic ions, etc.) which may affect the analytical result for the element of interest.

6.1.14 **Internal Standard (ISTD).** A non-target element added to a sample at a known concentration after preparation but prior to analysis. Instrument responses to internal standards are monitored as a means of assessing overall instrument performance.

6.1.15 **Laboratory Control Sample (LCS).** A spiked aliquot of LRB with a blank Teflon® filter used as a QCS that is prepared and brought through the entire digestion/extraction and analytical process to demonstrate spike recoveries. This sample is synonymous with the BS/BSD.

6.1.16 **Laboratory Reagent Blank (LRB).** An aliquot of ASTM Type I water that is treated exactly as a sample including exposure to all labware, equipment, solvents, reagents and internal standards that are used with other samples that is always reported as BLK1. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or apparatus.

6.1.17 **Limit of Quantitation (LOQ)** – The lowest concentration of an analyte that produces a signal/response that is sufficiently greater than the signal/response of lab reagent blanks to enable reliable detection and quantification during routine lab operating conditions. Statistically defined, this is the concentration of analyte in sample matrix that produces an instrument signal/response that is 10 times the standard deviation above the LRB (at 99% confidence, n-1 degree freedom; see Table 24-2).

6.1.18 **Linear Dynamic Range (LDR).** The concentration range over which the analytical working curve generated from the calibration standards is proven to remain linear. See Section 13.8 for more information on the LDR.

6.1.19 **Lower Limit of Quantitation Check (LLQC)** – A check sample that is used to both establish and confirm the lower limit of quantitation and is prepared by spiking a low concentration of analyte into reagent water and carrying the solution through the entire preparation and analytical procedure.

6.1.20 **Lower Limit of Quantitation Limit (LLQL)** – The lower limit of quantitation is considered the lowest reliable laboratory reporting concentrations and should be established from the lower limit of quantitation check sample and then confirmed using the lowest calibration point and/or from a low level calibration check standard.

6.1.21 **Low Level Calibration Verification (LCV)** – A stock standard solution prepared using the same source as the calibration standards that is analyzed to verify the LLQL. The standard is prepared at the same concentration as the LLQL. An LCV is analyzed at the beginning, typically just before or after CCV1, and at the end of every analysis just before or after the final CCV.

6.1.22 **Matrix Interference/Effect.** In general, the interference and/or effect that particular matrix constituents may cause during sample processing and/or analysis. Matrix effects may be determined to exist from the careful interpretation of QC samples and criteria. Examples of observed effects include but are not limited to poor recoveries of spikes/ISTD and poor percent differences.

6.1.23 **Method Blank (MB).** An aliquot of LRB with a blank Teflon® filter that is carried through the entire preparation and extraction process to demonstrate background contamination contribution from the filter and process and is always reported as BLK2.

6.1.24 **Method Detection Limit (MDL).** The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

6.1.25 **Performance Evaluation (PE) Sample.** A sample of known composition provided by a source outside the laboratory for analysis that evaluates the laboratory's analytical performance.

6.1.26 **Post Digestion Spike (PDS).** A spiked aliquot of an already digested sample used to demonstrate spike recoveries in the sample matrix. The analytical results of this spike may be used to verify matrix interference in conjunction with the SRD results.

6.1.27 **Quality Control Sample (QCS).** A solution containing known concentrations of method analytes that is used to fortify an aliquot of LRB matrix. The QCS is prepared from a source(s) external to the laboratory and is used to verify the laboratory's analytical performance.

6.1.28 **Serial Dilution (SRD).** The dilution of a sample by a factor of five. If the undiluted parent sample concentration is minimally a factor of 50 above the MDL, the diluted sample should agree with the parent sample concentration within ± 10% when corrected by the dilution factor. The SRD may indicate the influence of interferents.

6.1.29 **Standard Reference Material (SRM)** – A prepared standard material that has certified metals concentrations, for example the NIST SRM 1648a (Urban particulate matter with certified concentrations of lead at 0.655 ± 0.033 mass fraction (in %)). The SRM is used to verify the extraction procedure.

6.1.30 **Stock Standard Solution.** A commercially prepared standard solution (traceable to NIST or other certified standard sources), which can be diluted to derive other standards.

6.1.31 **Tuning Solution.** A solution used to determine acceptable instrument performance prior to calibration and sample analyses. This solution is used for mass calibration, nebulizer optimization, auto lens optimization, and daily performance reports.

6.2 Abbreviations

amu	Atomic Mass Units
ASTM	American Society for Testing and Materials
CASRN	Chemical Abstract Services Registry Number

COC	Chain of Custody
cps	Counts Per Second
DI	Deionized
DQO	Data Quality Objective
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
kW	Kilowatt(s)
L	Liter(s)
LDPE	Low Density Polyethelyene
LIMS	Laboratory Information Management System
MΩ	Megohm
MCA	Multichannel Analyzer
MQO	Method Quality Objectives
m	Meter(s)
m^3	Cubic Meter(s)
mg	Milligram(s)
mg/L	Milligram(s) per liter(s)
min	Minute(s)
mL	Milliliter(s)
mm	Millimeter(s)
ms	Millisecond(s)
ng	Nanogram(s)
ng/L	Nanogram(s) per liter(s)
ng/mL	Nanogram(s) per milliliter(s)
NIST	National Institute of Standards and Technology
QC	Quality Control
RSD	Relative Standard Deviation
RPD	Relative Percent Difference
SD	Standard Deviation
SOP	Standard Operating Procedures
Std.	Standard
µg/L	Microgram(s) per liter(s)
$\mu g/m^3$	Microgram(s) per cubic meter(s)
µg/mL	Microgram(s) per milliliter(s)
µL	Microliter
µm	Micrometer
v/v	Volume per volume ratio

7.0 INTERFERENCES

Note: The background level of metals on a given lot of Teflon® filters can vary. Any background levels found on blanks should be documented for all the filters from the corresponding lot when available. It is recommended to consult 40 CFR Part 50, Section 6.1 Appendix G for guidance.

7.1 Laboratory Interferences

7.1.1 Wear powder-free nitrile or neoprene gloves when handling unexposed or exposed filters.

7.1.2 Clean all equipment used in the sample preparation and analysis in a manner consistent with good laboratory practices for metals analysis (See Section 20.3 in this SOP and Section 14.3.1 in SOP ERG-MOR-031).

7.1.3 Use ASTM Type I DI water or equivalent, with a resistivity greater than 17.3 MΩ, for sample extraction and standard preparation. Record the water resistivity prior to use.

7.2 Chemical Interferences

Pay close attention to the nature of solutions introduced to the ICP-MS.

7.2.1 Nitric acid must be less than 2% (v/v) for ICP-MS analysis to minimize the damage to the interface and to minimize isobaric molecular interferences. The use of platinum cones and other acid-resistant sample introduction components can be used for more aggressive acid matrices.

7.2.2 If higher acid extractions are required, dilute final digestate to 2% HNO_3.

7.2.3 The final dilutions of sample extracts must match the acid content of the calibration standards in order to match potential interferences.

7.2.4 The concentrations of dissolved solids in analysis solutions should be less than 2% to protect the sample interface on the instrument and prevent signal suppression. Higher concentrations may plug the sample and/or skimmer cone orifices.

Note: Protect the channel electron multiplier from high chemical concentrations (high ion currents). The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this period, response factors are constantly changing, which causes instrument instability that invalidates the calibration curve, and thereby, invalidates all associated sample results. A sodium bicarbonate ($NaHCO_3$) sample matrix is known to cause this problem.

7.3 Instrument Interferences

7.3.1 Isobaric molecular and doubly charged ion interferences are caused by more than one atom (example, the contribution of ArCl on the 75As signal) or more than one charge (example, MoO+ ions on Cd isotopes).

7.3.2 Spectral interferences result from the presence of other isotopes or ions that have the same atomic weight or mass number as the analyte.

7.3.3 Transport interferences are a specific physical interference associated with the sample nebulization and transport process through the instrument. These usually result from sample matrix components that influence the aerosol formation or cause a change in the surface tension or viscosity. Changes in the matrix composition can cause observed signal suppression or enhancement.

7.3.4 Matrix interferences may be caused by elemental chemical and physical properties in the samples. For matrices of known composition, match the composition of the calibration and QC standards to that of the samples. For matrices of unknown composition, use an ISTD that has been matched to the analytes' chemical and physical properties (i.e., ionization potential, ±50 amu) so that the ISTD and element of interest behave similarly during the analytical process.

7.3.5 Memory interferences can occur when there are large concentration differences between samples or standards that are analyzed sequentially. Sample deposition on the sample and skimmer cones, spray chamber, peristaltic pump tubing and the type of nebulizer all affect the extent of the memory interferences that are observed. The rinse period between samples must be long enough to eliminate significant memory interferences.

7.3.6 Lead values are reported from isotope 208; however, all three isotopes must be used to quantitate lead to allow for the variability of lead isotopes in nature. The following correction equation must be applied to isotope 208:

$$(1.000)\ (^{206}Pb) + (1.000)\ (^{207}Pb) + (1.000)\ (^{208}Pb)$$

8.0 SAFETY

8.1 Personal protection should be used for all work performed in the inorganic laboratory, (e.g., gloves, safety glasses, laboratory coats, etc.).

8.2 The compressed gas cylinders must be stored and handled according to relevant safety codes outlined in the corporate health and safety manual. In use, the cylinders must be secured to an immovable structure and moved using a gas cylinder cart.

8.3 Make sure that sample vials are kept capped and in racks to prevent spills.

8.4 All personnel should be trained in the handling, extraction and analysis of acid samples for inorganic analysis.

8.5 Strong acids must not be stored with organic solvents or samples.

8.6 Follow normal laboratory safety procedures as outlined in the ERG Health and Safety Manual and the site-specific laboratory SOP.

9.0 EQUIPMENT

9.1 ICP-MS

The PerkinElmer SCIEX™ ELAN® 9000 ICP-MS consists of an inductively coupled plasma source, ion optics, a quadrupole mass spectrometer, a computer that controls the instrument, data acquisition and data handling software (ELAN® Software SCIEX™, Version 3.4), a printer, an autosampler (AS-93plus) and a recirculator. The quadrupole mass spectrometer has a mass range of 2 to 270 amu. Typical operating conditions are listed below.

Typical Operating Conditions

Plasma forward power	1.3 kW
Plasma/Coolant argon flow rate	13.8 L/min
Auxiliary argon flow rate	1.2 L/min
Nebulizer flow rate	0.9 L/min
Solution uptake rate	1.0 mL/min
Spray chamber temperature	Room Temperature
Detector mode(s)	Pulse counting/Analog
Replicate integrations	3
Mass range	6 - 240 amu
Dwell time	50 ms
Number of MCA channels	1
Number of scan sweeps	20
Total acquisition time	4.2 min/sample

9.2 Digestion System

Environmental Express HotBlock™ Digestion System or equivalent system capable of maintaining a temperature of 95°C within ± 2˚C. This temperature will heat the samples to a temperature of ~85°C (±5°C).

10.0 MATERIALS

10.1 Graduated polypropylene sample vials with screw caps, 50 mL volume (certified to be within ± 0.2mL).

10.2 Branson 8510 sonication bath with heating capability.

10.3 Pipetters with adjustable volumes ranging from 0.5 µL to 10 mL and disposable tips. Mechanical pipettes must be verified for accuracy quarterly (or every three months). Repeatable, mechanical pipettes, such as Eppendorf Research®, may be used and their accuracy should be verified on a quarterly basis to be within the manufacturer's specifications. If a pipette's accuracy exceeds the manufacturer's specifications its use should be discontinued and it should be replaced or sent in for repair.

10.4 Miscellaneous: powder-free nitrile or nitrile gloves; disposable laboratory wipes; self adhesive labels.

10.5 Volumetric flasks. Teflon®, Class A, 50, 100, 250 and 500 mL capacities.

10.6 Storage bottles. Wide and narrow mouth, Teflon® FEP (fluorinated ethylene propylene) with Tefzel® ETFE (ethylene tetraflourethylene) screw closure, 50, 100, 250, 500, 1,000 and 2,000 mL capacities.

10.7 Reflux caps and FilterMate™ 2 µm Teflon® filters.

10.8 Wash bottles made of LDPE and Teflon® having 500 mL and 1 L capacities.

10.9 Plastic or Teflon® coated tweezers.

11.0 CHEMICALS, REAGENTS, STANDARDS AND THEIR PREPARATION

Note: In general, chemicals, reagents and commercial stock standards expire when specified by the manufacturer. If the manufacturer does not provide an expiration date then they shall expire one year from the opened date. Standards and other solutions prepared in-house expire as specified throughout the SOP. Proper disposal of hazardous wastes are discussed in detail in the Solid and Hazardous Wastes SOP (ERG-MOR-033).

11.1 High Purity Acids - ultrapure and concentrated stored in Teflon® Bottles. These reagents are used for the preparation of sample extraction fluid and all standards.

Note: Concentrated high purity reagents are not 100% of the specified reagent. It should be understood that all percentages in this SOP are expressed in terms of volume per volume (v/v) rather than true percentages of reagents in solution.

11.1.1 Nitric Acid (HNO_3), 60-70%

11.1.2 Hydrochloric Acid (HCl), 32-35%

11.1.3 Hydrofluoric Acid (HF), 47-51%

11.1.4 Extraction fluid (0.5% (v/v) HCl, 1.85% (v/v) HNO_3, 0.17% (v/v) HF and 8.30 mg/L Au)

11.1.5 Standard solvent (0.30% (v/v) HCl, 1.11% (v/v) HNO_3, 0.10% (v/v) HF with 5 mg/L Au)

11.2 Hydrogen Peroxide (H_2O_2) - ultrapure and concentrated (30-32%) stored in Teflon® bottles. This reagent is used for the extraction procedure.

11.3 Nitric Acid - Trace Metal Grade in 2.5 L glass for rinse blank and labware cleaning.

11.3.1 Rinse blank (2% (v/v) HNO_3, 0.5% (v/v) HCl with 5 mg/L Au)

11.3.2 10% (v/v) HNO_3 acid bath for labware cleaning

Preparation: The acid bath solution is prepared by adding 2.5L of concentrated trace metal grade HNO_3 to 22.5 L of ASTM Type I DI water in a clean 42 L polypropylene acid bath tank. The acid bath should be stored in a fume hood.

11.4 ASTM Type I deionized water - with a resistivity greater than 17.3 MΩ.

11.5 Argon gas - purity > 99.996%, Oxygen < 5 mg/L, Hydrogen < 1 mg/L, Nitrogen < 20 mg/L and Water < 4 mg/L.

11.6 Secondary Source Control Standards - A commercially prepared single- or multi-element secondary source (different manufacturer from the multi-element calibration standard). These NIST traceable calibration standards are used to produce the ICV, which is run as a verification of the instrument's calibration for accuracy and precision.

11.7 Single-Element Stock Standard Solutions - Commercially prepared NIST traceable standards from ultra high-purity grade chemicals or metals (99.99 – 99.999% pure) designed for use with ICP-MS instruments (e.g., Mercury Std.).

11.8 Multi-Element Stock Standard Solutions - Commercially prepared NIST traceable standards from ultra high-purity grade chemicals or metals (99.99 – 99.999% pure) designed for use with ICP-MS instruments (e.g., ISTD solution).

11.9 Interference Check Standard - Commercially prepared standard that is diluted to prepare ICSA and ICSAB interferent checks.

11.10 Smart Tune Solution - Although custom tuning solutions may be used, the tuning solution for this SOP may be purchased through the manufacturer (Perkin Elmer #N8125040) or is prepared in-house using single-element standards to contain 10 µg/L of Be, Mg, Co, Rh, In, Ba, Ce, Pb, and U in 1% (v/v) HNO_3.

To prepare 1 L of this solution, add 10 mL of Ultrex Nitric Acid to ~ 900 mL of ASTM Type I deionized water and add 10 µL of each 1,000 µg/mL single-element standard, then bring to volume. This solution may be stored in LDPE bottles but ideally in Teflon®. The expiration date is either that specified by the manufacturer or if prepared in-house no later than the earliest expiration date of any standard or reagent used for preparation.

11.11 Dual Detector Cross Calibration Solution - Refer to Section 13.3 for the purpose and final concentration of this solution. Although custom cross calibration solutions can be used, it may be purchased through the manufacturer (Perkin Elmer #8125032) or it is prepared in-house using single-element standards.

11.12 Multi-element ISTD stock standard – Commercially prepared standard that is used in conjunction with the single-element standards for Sc, Ga, and Li to prepare the internal standard.

11.13 Internal Standard Spike Solution – Prepared standard used to manually spike all calibration and QC standards as well as all samples that are analyzed by the ICP-MS.

11.14 Blank Spike (BS) Standard – The BS standard is used to spike the BS/BSD (See Section 16.3). Prepare the BS standard according to Table 24-6 with a final volume of 50 mL.

11.15 Post Digestion Spike (PDS) Standard –The PDS standard is used to spike the PDS source sample. This post digestion spike is used to help determine if poor matrix spike recoveries are due to interferents. Spike 1 µL/mL of sample analyzed.

11.16 Second Source Working Standard – The second source working standard is used to create the ICV.

11.17 Citranox® Acid Cleaner and Detergent - Prepare a 5% solution by adding 500 mL of Citranox® to 9.5 L of warm – hot tap water for labware cleaning and decontamination. This detergent bath should be changed about once every month, depending on use.

11.18 Standard Reference Material (SRM) – The standard reference material used to prepare the SRM samples. NIST SRM 1648a (Urban particulate matter with certified concentrations of lead at 0.655 ± 0.033 mass fraction (in %) is used to verify the extraction procedure.

11.19 Lower Limit of Quantitation Check (LLQC) –This quality control sample is used to determine the LLQL, and is prepared by creating a spike solution that will create a final concentration of analyte in the sample matrix that produces and instrument signal/response that is 10x the standard deviation above the lab reagent blank (at 99% confidence; n-1 degrees of freedom). Lower limits of quantitation are verified when all analytes in the LLQC sample are detected within ± 30% of their true value.

12.0 COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

12.1 Collection and Handling of Filters

Whenever the filter is handled use clean disposable nitrile or neoprene gloves and if necessary clean Teflon® coated (no exposed metal surfaces) or plastic tweezers. Never touch the membrane of the filter and take care not to puncture or damage the filter with the tweezers. See Section 16.1 for more information about filter condition.

12.2 Preservation and Storage of Filters

Samples do not have a preservative and can be stored for up to 180 days in ambient conditions. Upon retrieval from field sampling during humid or rainy conditions be certain the filter is not moisture-laden. Damp filters may stick to the sample transport container causing damage and thereby invalidating the sample. If the sample is found to be moisture-laden allow the membrane to dry before enclosing in the transport container. Once the filter arrives at the laboratory, a unique LIMS identification number is assigned and placed on the outside of the COC, sample envelope and/or container for tracking and storage purposes. Extraction hold time is 180 days from the sample date.

12.3 Shipment of Filters

When filters are shipped to or from the laboratory follow proper handling instructions in Section 12.1 and take proper precautions when packing such that filters are not exposed to contaminants or damage during shipment.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Daily Optimization Procedures

Daily optimization is performed through the software's Smart Tune Wizard. Refer to Tables 24-4 and 24-5 for Optimization Procedures and Performance Specifications respectively. For more detailed information, the PerkinElmer Elan Version 3.4 Software Reference Guide is also available for reference as a PDF file on the desktop of the instrument computer.

13.2 Mass Calibration and Resolution

Before performing any kind of calibration or optimization, allow a period of not less than 30 minutes (preferably 1 hour) for instrument warm-up. After the warm-up, the mass calibration and resolution may be optimized using the tuning solution (see Section 11.11) by running a mass calibration and resolution optimization through the Smart Tune Wizard. Resolution at low mass is indicated by magnesium isotopes 24, 25, and 26. Resolution at high mass is indicated by lead isotopes 206, 207, and 208. These peaks may be viewed in the Interactive graphics window. For optimal performance, adjust spectrometer mass calibration to ± 0.05 amu and the resolution to produce a peak width of 0.70 ± 0.1 amu at 5% peak height. Repeat mass calibration and resolution optimization if it has shifted by more than ± 0.05 or ±0.1 amu respectively.

13.3 Dual Detector Cross Calibration

The dual detector cross calibration is used to provide a smooth transition from the pulse counting mode to the analog mode, which extends the linear dynamic range of the detector. Typically a 2% nitric acid solution containing 200 µg/L of Mg, Cu, Rh, Cd, and Pb as well as 2000 µg/L of Be is used for this calibration although custom solutions may be used. This calibration must be performed daily before each analysis to report values above the HCV.

13.4 Daily Performance

13.4.1 The daily performance report must be generated daily or before each analysis, whichever is more frequent.

13.4.2 Instrument stability must be demonstrated by running a daily performance check using the tuning solution. A minimum of five replicates with resulting relative standard deviations of absolute signals for all analytes of less than 3% is required prior to calibration.

13.5 Calibration

13.5.1 Prior to initial calibration, set up proper instrument software routines for quantitative analysis (i.e., autosampler table, QC sample names etc.). The instrument must be calibrated using a minimum of a calibration blank and four non-zero calibration standards. Consideration should be give to adding more standards, particularly lower concentrations, in order to better define the LDR and quantitation limit (QL). A minimum of three replicate integrations are required for data acquisition with an RSD < 10.0%. RSDs > 10.0% are allowed for the first non-zero calibration standard (CAL2). Use the average of the integrations for instrument calibration and data reporting.

For a linear calibration to be considered acceptable, the calibration curve should have a correlation coefficient ≥ 0.998. The resulting curve should then be verified with mid-level and low-level calibration standards as described in Section 16.6.

Preparation: Non-blank calibration standards are prepared by diluting the calibration working standard to appropriate levels using the standard solvent.

13.5.2 For matrices of known composition, match the composition of the calibration and QC standards to that of the samples. For matrices of unknown composition, use an ISTD that has been matched to the analytes chemical and physical properties (i.e., ionization potential, ±50 amu) so that the ISTD and element of interest behave similarly during the analytical process.

13.5.3 The rinse blank should flush the system between solution changes for blanks, standards, and samples. Allow sufficient rinse time (≥ 1 min) to remove traces of the previous sample. Solutions should aspirate for at least 30 seconds prior to the acquisition of data to establish equilibrium.

13.5.4 Refer to Section 11.1.4 for the preparation of standard solvent. Once prepared, all calibration standards must be stored in Teflon® bottles/flasks.

Note: Commercial stock standards used to prepare calibration standards and other quality control standards must be used within their expiration

date. Calibration blanks/standards and other QC standards made from the stock standards may be set to expire no later than the earliest expiration date of any standard used for preparation.

13.5.5 Refer to the quality control requirements presented in Table 24-3 for calibration acceptance criteria.

13.6 Internal Standardization

13.6.1 Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. ISTD quality control requirements as described in Section 16.7 must be followed.

13.6.2 Internal standards (ISTD) for this method are ^{45}Sc ^{69}Ga, ^{89}Y, ^{115}In, and ^{209}Bi for analytes beginning with mass 6 and ending with mass 238. The ISTDs^{6}Li,, ^{72}Ge ^{103}Rh, ^{159}Tb & ^{165}Ho may also be used if necessary. Internal standards must be manually added to each calibration standard **after** they are brought to volume in the proportion of 2.0 µL for every mL. For example, add 200 µL of ISTD solution to a 100 mL standard.

13.6.3 Concentrations of the internal standards for this method are determined by the concentration of each element that will produce an intensity that is sufficiently stable. Typical intensities are between 200,000 and 500,000 cps; however, ideal intensities may be as high as 1,000,000 cps.

13.6.4 The concentration of the internal standard must be added equally and in the same manner to the calibration blank/standards, QC standards and samples.

13.6.5 Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. However, be aware that internal standards themselves may be responsible for polyatomic and/or doubly charged interferences.

13.7 Instrument Performance

13.7.1 After instrument calibration an ICV and ICB must be analyzed for initial verification of the calibration curve. Refer to Sections 16.6.1, 16.2.2, and Table 24-3 for specific QC criteria.

13.7.2 To verify that the instrument is properly calibrated on a continuing basis, analyze a CCV and CCB before the analysis of samples and after every 10 samples.

13.8 Linear Dynamic Range (LDR)

The LDR study is performed every 6 months to determine the maximum concentration level at which the initial calibration is linear. The recovery criterion for the LDR are 90-110%. Dilutions must be performed for elements with concentrations over 90% of the established LDR. If the LDR study has not been performed within 6 months, any elements with concentrations over the highest calibration concentration must be diluted.

13.9 Lower Limit of Quantitation Limit (LLQL)

The LLQL study is performed every 6 months to determine the lowest concentration level at which data may be reported. This is done by extracting and analyzing a lower limit quantitation check (LLQC). The recovery criterion for the LLQC is 70-130%. Any results reported below the LLQL must be qualified as an estimated value.

14.0 PROCEDURE

14.1 LIMS Batch Procedure

Note: Please perform the following procedure the same day that you plan to begin the extraction. If something happens and the extraction cannot be performed, edit the bench sheet with the correct extraction date, both in LIMS and on the hardcopy bench sheets.

14.1.1 Log into Element.

14.1.2 From the "Laboratory" menu, select "Batch."

14.1.3 With the Inorganics department selected from the drop-down menu at the left of the screen, click "Add" at the bottom, left-hand corner. A blank bench sheet will appear. The following information should be input into the bench sheet using the drop-down menus: 1) Preparation Method: ICP-MS Extraction and 2) Batch Matrix: Air

14.1.4 Select the appropriate inorganic analysis ("Metals Analysis – 47mm 20xx") from the "Available" analysis box and press the right-facing arrow button. **Note:** Options: 1.) Additional information may be added in the "comments" box for batches that are different from standard samples, for example samples that are for the Midlothian or Schools projects. Reagent lot numbers used in the extraction are also added in the comment section. 2.) You may choose to press "Copy" instead of "Add" from Step3. Use

caution here as both the analysis and comments from the copied batch will be included in the new batch and this information may need to be changed.

14.1.5 Press the save button. The new LIMS-created batch number will be visible in the box to the left of the screen.

14.1.6 Select the "Bench Sheet" button at the bottom of the screen. This is where you will include sample information and appropriate batch QC.

14.1.7 Click "Edit" at the bottom of the new screen.

14.1.8 At the top of the screen, press "Add" and select "Sample by Container." Select the samples from the list that you would like to include in the batch. For each sample, the following information needs to be included: 1) Initial (m^3): This is the total flow through the filter as it was being sampled in the field. This information can be found or calculated from the information provided on the sample chain of custodies. Field blank samples are assigned the same volume as the primary sample collected on the same day. A field blank volume may also be an average of all the filter volumes for a given month. 2) Comments: Include two spaces followed by the sample ID for each sample in the list. This includes any additional designations such as C1, C2, FB, etc.

Note: A maximum of twenty samples may be selected for any given batch. If more than 20 samples are selected, additional batch QC must also be added to the bench sheet and extracted to meet the requirements described in Table 24-3.

14.1.9 Each batch requires QC to be prepared/extracted with each batch of twenty samples. This QC is included in the bottom box on the screen. Required QC includes:

i. Duplicate Samples: One duplicate QC sample is added per batch. Click the "Add" button at the top of the screen and select "Duplicate." Right click on a duplicate sample to assign its source sample and initial volume. This volume will be the same as the source sample. Duplicate samples must also be added for each collocated (C1/C2) or duplicate (D1/D2) sample type to be extracted.

ii. Blank Samples: Each batch must include one reagent blank and one method blank per twenty samples.

a.) One blank (BLK) sample is already included. To add another, click the "Add" button at the top of the screen and select "Blank."

b.) Change the sample name by right-clicking on each blank and selecting "Name." BLK1 should be changed to "Reagent Blank" and BLK2 should be changed to "Method Blank."

c.) Include the filter lot number in the comments section of the Method Blank.

iii. Spiked Samples: Each batch must include two spiked samples per twenty samples.

a.) One laboratory control sample (BS) and one laboratory control sample dup (BSD) are included for 47mm extractions. The BS should already be included, so click on "Add" and select "Laboratory Control Sample Dup" to add the second BS to the list. For each of these QC samples, include the Teflon filter lot blank in the comments section.

b.) Identifying spikes: For laboratory control samples, the appropriate spike ID, type, and volume will need to be assigned in the same manner. Right click on the sample QC and select "Spike 1 ID." Select the appropriate standard from the list. Edit the "Spike 1 Type" to read "Pre-prep" and the "Spike 1 Volume" to read 500uL (or whatever volume is being used.)

iv. Post Spike (PS): Each batch must include one post spike (PS) sample per twenty samples.

a.) One post spike is automatically included for 47mm extractions. Assign the appropriate spike ID, type, and volume using the instructions provided above. The correct spike amount is 50 µL and the spike type is "Post-prep."

v. Standard Reference Material: Each batch must include one SRM per twenty samples.

a.) Click on "Add" and select "Reference" to add the SRM to the bench sheet. Add the SRM identification number as assigned during weighing in the comments section. Identify the reference standard used by right-clicking on "Spike 1 ID" and selecting the appropriate standard. Indicate the weight of SRM digested (in mg) in the Spike 1 Volume. "Spike 1 Type" should be listed as "Pre-prep."

14.1.10 Print two copies of the bench sheet in landscape format. Both will need to be signed on the "Extraction Reviewed by" line and dated once the extraction is complete. One copy is to be three-hole punched and placed in the Extraction Notebook, while the other is to be kept bound to the corresponding samples in the cabinet in the lab.

14.2 Filter Extraction Procedure

14.2.1 Prior to sample processing, be sure to turn on the HotBlock ™ and select the appropriate program and initiate to allow it to warm to extraction temperature. Be sure to allow the HotBlock™ interface establish connection with the block itself (shown on the screen as "Please Wait") prior to beginning any extraction method. Failure to do this will cause the HotBlock™ to heat to higher than intended temperatures.

14.2.2 Place filter in a labeled extraction tube as far down as possible. This is done by gently gripping the Teflon® support ring with gloved fingers and bending the filter so that it fits in the tube. Use the tip of a gloved finger to slide the filter to the bottom of the tube.

14.2.3 Add 0.5 mL of Matrix Spike to BS/BSD samples. Add 30 mL of extraction fluid (0.5% (v/v) HCl, 1.85% (v/v) HNO_3, 0.17% (v/v) HF and 8.33 mg/L Au) to the extraction tube with the filter.

14.2.4 The SRM sample is prepared for extraction by adding a blank Teflon filter to a clean sample vial as described in Section 14.2.2. The loaded vial is then weighed, zeroed, and then re-weighed after an aliquot of SRM standard of approximately 2-3 mg is added to the vial. Add 30 mL extraction fluid to the extraction tube.

Note: It may be more efficient to weigh several SRM standard vials for extraction at one time. The weight information should be recorded in the balance room notebook. Individual standards should be numbered with the date the vial was created (i.e. "01012013-SRM01"). The vial number should be recorded in the LIMS in the SRM sample comments in the bench sheet.

14.2.5 Print out a copy of the Teflon Extraction Record from L:\Metals Lab (an example is shown in Table 24-10). Record the batch ID and extraction date. Record the temperature of the HotBlock™ as indicated by the calibrated thermometer, as well as the temperature indicated on the HotBlock UI.

14.2.6 Place all samples in plastic HotBlock™ rack and place in HotBlock™. Add a reflux cap to each sample tube. Record the time samples were placed in the HotBlock on the table printed above. Samples will be extracted for a total time of 2.5 hours at a HotBlock™ temperature of 95ºC and an approximate sample temperature of 85ºC.

Note: Monitor sample temperature with a thermometer in an extraction tube with a reflux cap and 30 mL of extraction fluid.

14.2.7 After 1.5 hours of extraction, add 1.8 mL of hydrogen peroxide (H_2O_2) and allow to effervesce for 0.5 hours. Record the time the aliquot of H2O2 was added on the Teflon Extraction Record.

14.2.8 Check the filters occasionally during extraction. If a filter floats out of the acid, use acid-cleaned teflon stirring rods to push the filter below the extraction fluid.

14.2.9 After extraction, samples must be removed from the HotBlock™ as soon as possible so they are not allowed to heat to dryness. Allow the samples to cool to room temperature. Record the time samples were removed, as well as the temperatures indicated by both the certified thermometer and HotBlock™ UI on the Teflon Extraction Record.

14.2.10 Leaving the Teflon filter in the sample vial, bring the sample volume to the 50 mL line on the vial with a wash bottle filled with DI water prior to filtering. Record the time the samples were brought to final volume on the Teflon Extraction Record.

Note: If the final volume exceeds 50 mL, measure the amount exceeded using an appropriate pipette (usually the 1 or 5 mL) and record the final sample volume. Using the pipettor, pull sample from the vial in varying increments until enough liquid is removed so that the sample line is level with the 50 mL line on the vial. Add the amount of liquid removed to 50 mL and record that as the final volume. This information must be entered into the LIMS so that the final sample concentration is calculated and reported correctly. This overfilling may be avoided by using fine streamed wash bottles while adding the D.I. water.

14.2.11 Homogenize the sample by inverting three times and then the extract is ready to be analyzed. Should the sample contain noticeable particulate material, an aliquot of sample may be poured off and filtered with the use of a FilterMate™, however; this is not typically necessary. Alternatively, the sample may be allowed to rest until all debris settle. Care should be taken to not disturb the sample when transferring sample extract to an

autosampler tube. For samples with no noticeable particulate matter, it is not necessary to allow the sample to settle prior to analysis.

14.2.12 Record the sample slot the certified thermometer was placed in during the sample extraction on the Teflon Extraction Record. After initialing the sheet, attach the Teflon Extraction Record to the batch paperwork.

14.3 LIMS Sequence Procedure

14.3.1 Log into LIMS Element Software.

14.3.2 From the "Laboratory" menu, select "Sequence."

14.3.3 Click "Add" in the top right corner and select "Randy" as the Template ID then click done. This will automatically add all of the calibration standards and QC samples for a typical analysis sequence.

14.3.4 Click the pull-down menu for "Source Batch" at the upper middle part of the screen and select the batch you are going to analyze. Then click the "Add" button and select "Batch QC Sample." When the list of QC samples appears click the first sample and holding the shift button double-click the last sample and it will insert them into the sequence. Then click "Add" again and select "Batch Sample." Add all of the samples listed as you did for the Batch QC Samples.

14.3.5 Arrange all of the samples according to the example below, being sure to follow the requirements summarized in Table 24-3:

Autosampler Position	Sample Name
1	BTB0001-CAL1
2	BTB0001-CAL2
3	BTB0001-CAL3
4	BTB0001-CAL4
5	BTB0001-CAL5
6	BTB0001-ICV1
1	BTB0001-ICB1
5	BTB0001-HCV1
7	BTB0001-IFA1
8	BTB0001-IFB1
4	BTB0001-CCV1
2	BTB0001-LCV1
1	BTB0001-CCB1
9	B0B1707-BLK1
10	B0B1707-BLK2

Autosampler Position	Sample Name
11	B0B1707-SRM1
12	B0B1707-BS1
13	B0B1707-BSD1
14	0020993-01
15	B0B1707-DUP1
16	B0B1707-SRD1
17	B0B1707-PS1
18	0020993-02
4	BTB0001-CCV2
1	BTB0001-CCB2
7	BTB0001-IFA2
8	BTB0001-IFB2
4	BTB0001-CCV3
2	BTB0001-LCV2
1	BTB0001-CCB3

14.3.6 Right-click the SRD sample and choose the appropriate source sample from your batch.

Note: Make sure that the source sample for the SRD is updated to the current batch sample SRD sample or your data will not be saved.

14.3.7 Using the shift key select all of the samples in the sequence and right-click to choose "Internal Standard ID" then select the ISTD you are using for this sequence.

14.3.8 Right-click each calibration standard and QC sample and select "Standard ID" to set the current standard being used for each solution.

14.3.9 Click "Save" and print a double-sided copy in landscape format to use as the cover of the data package and to help enter the sequence in the Elan software.

14.4 Filter Analysis Procedure

14.4.1 Prior to analyzing samples, check the instrument performance by analyzing the tuning solution using the Daily Performance Check in the Smart Tune Wizard. The performance specifications that must be met are in Table 24-5. Also refer to Section 13.1 for other criteria. If the performance check fails, follow the optimization procedures in Table 24-4.

14.4.2 Before starting the calibration be sure to flush the sample introduction system with enough rinse blank and be certain the rinse blank bottle has enough solution for the analysis. Enter all sequence information (sample and QC sample names) into the autosampler and QC tables (see Section 14.3.5). The autosampler table should be named as the month, day and year (e.g., 01012010.sam) and saved. Create the file name for the collected data with the numeric month, day and year (e.g., 01012010.rep) in the Method window under the "Report" tab (upper right) in the "Report Filename" field. Any changes made to the method (i.e., QC tables) must be saved before you exit that screen or they will be lost.

14.4.3 Pour off the calibration blank/standards (Blank (CAL1), LOQ (CAL2), CAL3, CAL4 and CAL5) and initial/continuing QC standards (ICV, ICB, ICSA, ICSAB, HSV, CCV, CCB) spiked with ISTD in the appropriate autosampler positions.

14.4.4 To start the analysis, highlight all samples in the autosampler table and click "Build Run." Then click "Run" in the following screen. Once the calibration has been completed and reviewed, save the calibration file with the same month, day and year as the .sam and .rep files in Section 14.4.2 and print the Quantitative Analysis Report to PDF to be included with the sequence files.

14.4.5 Label autosampler tubes with a black marker. Batch samples may be prepared by adding 20 µl of ISTD into the autosampler tube and then adding 10 mL of sample. Mix the sample well and place in appropriate autosampler location for analysis.

14.4.6 The PDS sample is prepared by adding 1.0 uL of spike solution to 1.0 mL of sample to be analyzed (i.e., 10 uL of PDS to 10 mL of sample).

14.4.7 Samples with analyte concentrations greater than 90% of the current LDR must be diluted and re-analyzed.

14.5 Unexpected Instrument Shutdown

In the event that the ICP-MS shuts down during an analysis the proper procedure to be followed by the analyst is:

14.5.1 Restart the instrument and allow it to warm-up for a minimum of 30 minutes but preferably one hour, especially if the instrument has been inoperable overnight and is at room temperature. If the analyst was present during the loss of the plasma and the instrument has not significantly cooled then a shorter time period for warm-up may be sufficient.

14.5.2 After the instrument has been thermally stabilized a new daily performance report (DPR) should be analyzed with the operating conditions being used for the analysis.

14.5.3 If the DPR passes the analyst must check the calibration by analyzing a continuing calibration verification (CCV) and a continuing calibration blank (CCB) to be sure the calibration is still valid. If the CCV & CCB passes the analyst may proceed with where the analysis left off. Any samples that didn't complete their analysis should be repeated.

14.5.4 If the DPR, CCV or CCB do not pass the analysis must be terminated and any samples not bracketed by valid CCV & CCB checks must be reanalyzed with a new analysis/calibration.

14.5.5 The DPR, CCV and CCB checks should be kept for documentation. The DPR may be place in the DPR binder and the CCV/CCB checks must be included with the data package. The analyst should document the event briefly in the sequence narrative so the reviewer is aware of the instrument shutdown.

14.6 LIMS Data Upload Procedure

14.6.1 When a data package is complete, the analyst will transfer the data from the instrument computer to BART.

14.6.2 To begin LIMS upload, open Element. Go to the laboratory menu and click on "Data Entry/Review" In this window, select "Sequence" in the top left corner, making sure that "Inorganics" is selected from the drop-down menu. Highlight the correct sequence and click on "Create" in the Data Entry box in the top right corner. Once the spreadsheet is created in LIMS, select "DataTool" in the Data Entry box and save the file as the sequence name in the UserFiles folder of your harddrive (C:\ELMNT\UserFiles).

14.6.3 The DataTool interface should open to the "Select Data System Files" window. In this window, check to make sure the correct file information is selected:

1) File Type: PE ELAN_REP(*.rep)
2) Drives: y:\Bart

14.6.4 In the box below Drives: select the folder the data is stored in for the sequence. In the Bart drive, select the ICP-MS DATA folder, then the

corresponding year, and finally the folder for the data the sequence was run.

14.6.5 All of the data files for that sequence will appear in the lower right-hand box. Double-click on the appropriate data file and click "Auto Select" for each file that needs to be included in the sequence. (*Note: Only undiluted samples and sequence QC should be included here.)

14.6.6 Click "Done" when all sample and QC files have been selected to return to the main window. Click "Merge Files" at the bottom of the window. DataTool will merge the files and show the data in the Data Transfer window.

Note: Review the content of the top windows in the Data Transfer window for red text. If there is any, the DataTool cross table requires editing. Seek the advice of the LIMS administrator to correct this.

14.6.7 Click "Save" and save the spreadsheet in the UserFiles folder of your hard drive. Close DataTool.

14.6.8 In Element, go back to the Data Entry/Review window. The newly merged data should appear in the window. Click "Save" to save the files to Element and then "Query" in the Data Review box. Element will perform all necessary calculations at this point.

14.6.9 In the Data Entry/Review window, samples and QC can be reviewed for pass/fails. Any data that does not pass its assigned criteria will have red text. Use appropriate data qualifiers to flag data that does not meet criteria.

14.7 LIMS Dilution Data Upload Procedure

Note: Dilution data is not uploaded with sequence QC, as this data is typically only required for one or two analytes in a given sample. Therefore, the data is hand-entered into Element.

14.7.1 Open Element and go to the Data Entry/Review window. Select the sequence that the diluted sample was originally run with. Click on "Query."

14.7.2 Scroll down to the needed sample information. Click "Edit" in the Data Review box. Right click on the sample & analyte that has dilution information and select "Qualifiers" -> "Quick Analyte Qualifiers." Select qualifier flag D-01 for dilutions.

14.7.3 In the IResult column, type the new dilution data. Make sure the new data has been corrected for the dilution factor (i.e. results for a 5x dilution should be multiplied by 5 if the instrument software did not make the correction). In the Diln column, type the dilution factor for the sample.

14.7.4 Repeat steps 2 & 3 for any additional dilution data that needs to be input for the sequence. If any QC data was altered (for example, Dups) then you will click on "Re-calc" and "Save." If only sample information was altered, click "Save."

14.7.5 Re-run the query to verify all dilution data was saved to the sequence.

Note: In LIMS, the dilution factor is applied to the associated MDL as well as to the sample concentration.

14.8 Data Review

All instrument data should be first reviewed by the analyst and then a secondary reviewer, usually the project task lead for metals analysis. Both the analyst and secondary review must use the "Quality Control Requirements for Metals Analysis" checklist to complete data review (see Figure 24-8). Reviewers must initial and date each parameter check on the review form to verify that each meets the established acceptance criteria.

14.8.1 Initial Calibration

In addition to the requirements outlined in Table 24-3, the analyst and secondary reviewer must also verify that the intensities measured for reportable analytes in the calibration blank are acceptable and will not interfere with the sensitivity. A review of previously analyzed calibration blanks can demonstrate acceptable intensity values. The intensities of the internal standards in the calibration standard should be monitored relative to the intensities seen in the calibration blank.

14.8.2 Internal Standards

Internal standards must be monitored for each sample throughout a sequence; the measured intensities must stay between 60 and 125% of the measured intensity of internal standards in the calibration blank. See Section 16.7 for corrective actions to remedy internal standard intensities that are measured outside of this range.

14.8.3 Relative Standard Deviation's

Follow the prescribed acceptance criteria for RSD's of calibration standards as listed in Table 24-3. Sample RSD's should also be monitored throughout analysis. High RSD's (greater than 20%) for concentrations above the MDL can indicate memory interference from previous samples, as well as other instrumentation issues that may need to be corrected before analysis can be continued.

14.8.4 Element/LIMS Data

The analyst and second reviewer must verify quantities imported into the LIMS reflect the raw data. This can be accomplished by checking a few analytes for random client samples and QC samples. Hand entered data (i.e., dilution) should be verified by the second reviewer to be certain the values, dilution factors and flags are properly inserted. The LIMS calculated final value should also be checked to ensure the system is using the correct equation.

14.8.5 Multiple Isotopes

If an element has more than 1 monitored isotope, examine the concentration calculated for each isotope, or isotope ratios, to detect a possible spectral interference. Consider both primary and secondary isotopes when evaluating the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences that the primary recommended isotopes; therefore, differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

14.8.6 Reprocessing Data

Reprocessed data must include reprocessing of all calibration standards and QC samples associated with the reprocessed sample results. Original data shall be kept with the reprocessed data and annotated with the reason for reprocessing. It is imperative that the calibration file be saved as a separate file from the original calibration file. The reprocessed calibration file shall be renamed with the added distinction of "_reprocessed" (i.e. 03052010_reprocessed). All other samples including QC are automatically saved to the dataset file.

15.0 CALCULATIONS

15.1 Analyte Concentration

Metal concentration in the air sample should be calculated as follows:

$$C = \frac{(C_i \times V_f)}{V_{std}}$$

Where:

C = concentration, ng metal/m^3
C_i = metal concentration determined from Section 14.4, ng metal/L.
V_f = total sample extraction volume from extraction procedure (i.e., 0.05 L).
V_{std} = standard air volume pulled through the filter, m^3

15.2 Method Detection Limits

The MDL is calculated as follows for the CFR MDL calculation method:

$$MDL = (t) \times (SD)$$

Where:
t = Student's t value for a 99% confidence level and a standard deviation estimate with n - 1 degrees of freedom [t = 3.14 for seven replicates]
SD= standard deviation of the replicate analysis.

The MDL is calculated as follows for the FAC MDL calculation method:

$$MDL = (K) \times (SD)$$

Where:

K = Value as prescribed in Appendix D: DQ FAC Single Laboratory Procedure v2.4, 08/30/2007
SD= standard deviation of the historical BLK2 analysis.

15.3 Relative Percent Difference (RPD)

The RPD is calculated as follows:

$$RPD = \frac{R_1 - R_2}{(R_1 + R_2)/2} \times 100$$

Where:

R_1, R_2 = values that are being compared (i.e., duplicate and replicate analysis data)

15.4 Percent Recovery

Percent Recovery is calculated as follows:

$$Percent\ Recovery = \frac{Analytical\ Result}{Theoretical\ Result} \times 100$$

15.5 Relative Standard Deviation (RSD)

RSD is calculated as follows:

$$RSD = \frac{Standard\ Deviation}{Average} \times 100$$

16.0 QUALITY CONTROL

The analyst must perform the quality control checks listed in Table 24-3 and meet the requirements in this section. Data Quality Objectives (DQO) and data assessment criteria are determined from the results of the quality control samples. The DQO criteria are summarized in Table 24-3.

16.1 Sample Collection Quality Control

16.1.1 Filters which are dropped or become contaminated with any foreign matter (i.e., dirt, finger marks, ink, liquids, etc.) are invalid.

16.1.2 Filters with tears or pinholes that occurred before or during sampling are invalid.

16.1.3 A power failure during a field sample collection event invalidates the sample collected during that event. See SOP ERG-MOR-045 for more information about the sample acceptance criteria.

16.2 Blanks

16.2.1 The Rinse Blank must be used to flush the system between standards and samples. Refer to Section 11.3.1 for preparation details.

16.2.2 Initial Calibration Blank (ICB) is analyzed immediately following the initial calibration verification. The absolute value of the instrument response should be less than the method detection limit. If the ICB fails it may be re-analyzed once. If the ICB still does not pass, the analysis should be terminated, the problem corrected and, the ICV and ICB must be verified again before the analysis can continue. If the ICV or ICB still fail, recalibrate the instrument and verify the ICV and ICB again before continuing. If recalibration fails to correct the problem, all QC and samples included in the sequence must be flagged.

16.2.3 Continuing Calibration Blanks (CCB) are analyzed following each continuing calibration verification sample. The acceptance criteria are the same as the ICB. If the first CCB analyzed fails it may be reanalyzed once. If it fails again the analysis should be terminated, the instrument recalibrated and the initial QC repeated. If the CCB fails later in the analysis it may also be reanalyzed twice. If it continues to fail again the affected analyte must be flagged. If multiple elements fail any samples analyzed before or after the failing CCB must be reanalyzed.

16.2.4 Laboratory Reagent Blank (LRB/BLK1) consists of all reagents (extraction fluid) used to process samples and is carried through the entire preparation and extraction process to determine the background levels, if any, from the extraction fluid and process. If the absolute value of the analyte concentration of the LRB is less than or equal to the MDL (See Table 24-1), no further action is required. If the BLK1 fails it may be reanalyzed once. If it fails again and the concentration is greater than the MDL, but less than 5 times the MDL, the BLK1 and all associated samples are flagged. If the concentration of a reported analyte is greater than 5 times the MDL all associated samples must have that analyte result blank subtracted and flagged as such.

16.2.5 The Method Blank (MB/BLK2) is prepared as an LRB but with the addition of a blank Teflon® filter and analyzed as a sample to determine the background levels, if any, from the blank filter and extraction process. Resulting data is recorded and used to determine FACA MDL values. While the absolute value of resulting values should be less than the established MDL, there is no corrective action procedure should the BLK2 fail.

16.3 Spikes

16.3.1 Laboratory Control Sample (LCS): An LCS is prepared and carried through the entire sample digestion process. At least two LCS are analyzed with each sample batch. The LCS is represented by the BS/BSD

samples. They are prepared by spiking blank Teflon® filters and carrying them through the entire preparation and extraction procedure. The results must be within 80 -120% of actual values, with the exception of Al. Mercury may recover within 75-125% of actual value. If not, the BS and/or BSD may be reanalyzed once each. If criteria are still not met the batch of samples associated with the BS/BSD must be flagged for any analytes that failed in either or both. A re-extraction of the samples in this case is not possible because the entire available sample has been used.

16.3.2 Standard Reference Material (SRM) is prepared and carried through the entire sample digestion process. At least one SRM is analyzed with each batch. The SRM is a NIST Urban dust that is prepared with a blank filter and can be referred to as a SRM in the LIMS. The results of the SRM Pb recovery must be within 80 – 120% of the certified value. If not, the sample may be reanalyzed once. If the SRM still fails to meet criteria, all associated samples must be flagged.

16.3.3 Matrix Spike and Matrix Spike Duplicate (MS/MSD): Due to the lack of actual sample duplicates for Teflon® filter sampling events, the traditional MS/MSD cannot be prepared. In place of the MS/MSD, a Blank Spike and Blank Spike Duplicate (BS/BSD) are prepared. See Section 16.3.1 for more detailed information.

16.3.4 Post Digestion Spike (PDS): In order to demonstrate spike recovery in an actual sample matrix at least one PDS sample is analyzed with every batch. The PDS is an analyzed aliquot of an extracted sample that is spiked with the PDS standard (See Section 11.16). The PDS spike addition should produce a minimum level of 10 times and a maximum of 100 times the QL. The spike recovery should be within ± 25% or 75% to 125% of the true spike value. If the PDS fails, the analyst should assess the SRD. If both the PDS and SRD fail for the same element it is an indication that matrix interference has occurred and any analytes that have failed should be flagged as possible matrix interference. In the event that the parent sample used for the PDS requires a dilution, the PDS should be prepared by diluting the sample and then spike with the PDS standard.

16.4 Duplicates

There are two types of duplicates found in this procedure:

16.4.1 Blank spike duplicate (BSD): A true laboratory duplicate of the blank spike prepared using a separate blank Teflon filter. The RPD for this duplicate is ± 20%.

16.4.2 Analytical duplicate (or a replicate): A second aliquot of an extracted sample analyzed using the same analytical method as the first, or primary aliquot. These are performed on duplicate and collocated samples collected in the field. The RPD for analytical duplicates (replicates) shall be less than or equal to ± 10% for values greater than or equal to 10 times the MDL. If a duplicate/collocated sample fails to meet the established criteria, the duplicate or collocated sample must be reanalyzed. If initial sample results are confirmed then the replicate or collocated sample must be flagged.

16.5 Performance Evaluation (PE) Samples

Performance evaluation samples should be obtained as available from independent sources and analyzed as a routine sample. PE samples are prepared and analyzed in the same way as field samples and should be analyzed in replicate to verify results.

16.6 Standard Checks

16.6.1 Immediately after the initial calibration, the ICV is analyzed. The measured concentrations should be within ±10%, or 90-110%, of the actual concentration. If the criteria are not met, reanalyze the standard. If the criteria are still not met, a fresh standard may be prepared and analyzed or repeat the initial calibration and ICV.

16.6.2 The HSV must be analyzed after the ICB and prior to analysis of samples. The measured concentration should be within 95% to 105% of the actual concentration. If the HSV fails it may be reanalyzed once. If the HSV still fails, a fresh standard may be prepared and analyzed. If it continues to fail, the instrument must be recalibrated and all initial QC must also be reanalyzed.

16.6.3 Before the analysis of samples and after every 10 samples during a batch analysis, the calibration must be verified using the CCV. Results must be within ±10% or 90% to 110% of the target value for each analyte to verify that the calibration is valid. If a standard check exceeds the limit, the analysis must be stopped and the check standard must be reanalyzed. If the target value exceeds the limit again, a fresh standard may be prepared and analyzed or the instrument must be recalibrated. Any samples analyzed before or after an invalid CCV must be reanalyzed, minimally for the failing element.

16.6.4 Following the first and last CCV of each analysis an LCV must be analyzed. The measured Pb concentration should be within ± 30% of the

true concentration. If the criteria are not met for the first LCV, reanalyze the standard once. If criteria still are not met, a fresh standard may be prepared and analyzed or terminate the analysis, correct any issues, and repeat the initial calibration, and reanalyze all initial QC. Should the second LCV fail for Pb, the analysis should be reanalyzed for Pb only.

16.6.5 Document each standard check value as a percent ratio of the actual value over the target value.

16.7 Internal Standards

The intensities of all ISTDs must be monitored for every analysis (see Table 24-7 for isotopes). When the intensity of any ISTD fails to register between 60 to 125% of the intensity of that ISTD in the calibration blank, the following procedure is implemented:

16.7.1 If the intensities are too high as a result of the ISTD being present in the sample, the sample must be diluted and reanalyzed with the addition of appropriate amounts of ISTD.

16.7.2 Repeat and increase the dilution until the internal standard intensities fall within the prescribed window.

16.7.3 If the intensities are determined to be a result of instrument drift, stop the analysis, find and correct the problem, recalibrate if needed and reanalyze the affected samples since the last acceptable ISTD recoveries.

16.8 Interferences

16.8.1 The interference check standards (ICS) are analyzed at the beginning and end of the run and for every 8 hours of continuous operation. They consist of two different standards the ICSA and ICSAB. The interference check standards obtained from suppliers are never contaminant free. The certificate of analysis documents the levels found in each lot obtained. Therefore, the presence of target elements in the ICSA and ICSAB are expected and may vary from lot to lot of ICS solution used to make these standards. In some cases these contaminants may cause the ICSA or ICSAB to fail the QC requirements. It is acceptable to use the concentrations from the certificate of analysis to correct for these observed contaminants. The known concentrations of contaminants in the ICSA or ICSAB solutions may be subtracted from the experimental values and the established QC criteria must be met or the associated samples are flagged. Samples containing levels of the interferents above the levels in the ICS should be considered for dilution.

16.8.2 The first interference check standard (ICSA) contains only the interference analytes of interest. Any components of the ICS that are calibrated by the instrument must recover within 20% of the expected value. Values obtained for reported analytes not present in the standard should be within ±3 times the LOQ values (See Table 24-2). If the ICSA fails it may be reanalyzed. If it fails again a fresh standard may be prepared and analyzed. If it continues to fail, terminate the analysis and correct the problem. Any samples analyzed before or after an invalid ICSA sample must be reanalyzed.

16.8.3 The second interference check standard (ICSAB) contains the same concentration of interference analytes in the ICSA as well as a known concentration of reported analytes. The concentration of known analytes should be near the middle of the calibration curve. The values obtained for reported analytes should be within 80% to 120% of the known concentration. If the ICSAB fails it may be reanalyzed. If it fails again a fresh standard may be prepared and analyzed. If it continues to fail terminate the analysis and correct the problem. Any samples analyzed before or after an invalid ICSAB sample must be reanalyzed.

16.8.4 Failing ICS are commonly the result of correction equations that need to be adjusted for new instrument conditions. If this is suspected, calculate the new interference equations and reprocess the analytical sequences as described in Section 14.8.6.

16.9 Dilutions

16.9.1 Serial Dilution

The SRD analysis must be performed on one sample per batch, preferably with the parent sample chosen for the analytical duplicate and PDS. The same sample matrix used to extract the parent sample must be used as the diluent. After the dilution is applied to the SRD results, the analyte concentration should be within 90% and 110% of the undiluted sample results if the parent sample analyte concentration is minimally a factor of 50 above the MDL in the original sample. If the SRD and PDS fail for the same analyte, a matrix interference must be suspected and the data flagged for all affected elements. If matrix interference is not suspected, the SRD should be reprepared and analyzed a second time.

16.9.2 Sample Dilution

Any samples needing dilution due to concentrations exceeding the LDR or the presence of ISTD in the sample shall be diluted in an appropriate manner to bring the diluted concentration within the calibration curve and preferably near the mid-point. (See Section 16.7 for dilutions required due to high ISTD recoveries. If the parent sample of a DUP/PDS sample needs to be diluted, the dilution should be performed on each of these QC samples (See also Section 16.3.3). If the SRD was performed on the parent sample of a DUP or PDS the results from the SRD may be used to report values of that parent sample if the 5 times dilution was appropriate.

Note: Dilution also increases the associated MDL by the dilution factor, so care must be taken not to dilute a sample so that the corrected concentration value is less than increased MDL.

16.10 Initial Demonstration of Capability

Each analyst must demonstrate initial proficiency for sample preparation and analysis by generating data of acceptable accuracy and precision for four LCSs. For demonstration of proficiency, acceptable accuracy and precision is defined as having both RSD $\leq$ 20% and percent recovery of 75%-125%. This demonstration is repeated whenever new staff receives training or significant changes in extraction procedure or instrumentation are made. The associated LCS recoveries are collected and maintained in the staff training files.

16.11 Decontaminating/Cleaning Labware

Procedures for proper cleaning and removal of trace metals from labware are found in Section 14.3.1 in SOP ERG-MOR-031. Detergent bath preparation instructions can be found in Section 11.19. Transport/dip baths of DI water ("To" and "From" acid baths) should be labeled with the date they are filled with fresh DI and changed about once every month to minimize contaminants being brought to the acid bath and from being reintroduced to clean labware. This will not only extend the life of the acid bath but it will help reduce hazardous waste production. To be certain that the acid bath will effectively clean and not contaminate labware a 5x dilution should be analyzed to determine the background about once a month.

17.0 PREVENTION

When possible, minimize the amount of chemicals used in the preparation and analysis of the metals filters to reduce waste.

18.0 DATA REVIEW AND CORRECTIVE ACTION

18.1 Data Review Documentation

Project files including at a minimum the information required in Section 22 are assembled and maintained by the performing analyst. Documentation for metals analysis by ICP/Mass Spectrometry will be reviewed for completeness and meeting acceptance criteria by the Task Lead or secondary reviewer associated with the project or program requiring the analysis as described in this section.

A second review of the data is performed by the Task leader or designated secondary reviewer using the QC review checklist (checklist) shown in Figure 24-8 to confirm that quality requirements have been met. Corrections and flags are added to the data consistent with the corrective action required for each review finding. Second level reviewers must complete, initial and date the checklist.

The completed check list is included as part of the data package. Data not meeting SOP requirements are flagged and brought to the attention of the Project Manager for resolution.

18.2 Quality Staff Review

A minimum of 10% of the data is reviewed by ERG Quality Staff. Quality staff review checks that all SOP required quality parameters have been met and that data reviewers have completed their review checklists. Additional items may also be reviewed at the discretion of the data reviewer. Quality staff reviews are documented on the review form initiated in Section 18.1 by the primary data reviewer. Comments or issues with data identified by the Quality Staff reviewer are brought to the attention of the Project Manager for resolution. Quality Staff will use the review process as an indication of episodic or systematic quality program issues that may require improvements to the ERG laboratory quality system and or additional training for ERG staff. As an option, Quality Staff may request a secondary review of 1% of the data from this method for a project. One percent (1%) review will follow the guidance in this section.

Corrective action for metals by ICP/Mass Spectrometry analysis data quality issues are presented in Table 24-3.

If required, a corrective action form is filled out as described in the ERG Laboratory Quality Systems Manual.

19.0 WASTE MANAGEMENT

Hazardous waste disposal is discussed in detail in SOP ERG-MOR-033. Sample digestate, including the extracted filter, is retained in its original tube for a period of at least 6 months from the sample date. After this time, sample digestate is disposed of by pouring it off in the satellite waste containers located in the laboratory. Used sample vials are disposed of in the laboratory waste bin.

20.0 MAINTENANCE

The ICP-MS system is not maintained under a service contract. The preventative and routine maintenance are performed by the analyst(s). In the event a maintenance issue cannot be addressed by the analyst a service call is placed with the manufacturer and when appropriate a service engineer will perform any necessary maintenance. All maintenance activities are documented in the instrument maintenance log.

20.1 The following maintenance procedures need to be addressed daily.

20.1.1 Check sample waste container level.

20.1.2 Inspect argon tank supply and its pressure to the instrument.

20.1.3 Inspect chiller coolant level and connections for possible leaks.

20.1.4 Inspect torch and aerosol injector tubes.

20.1.5 Inspect nebulizer for clogs.

20.1.6 Inspect sample capillary tubing to be sure it is clean and in good condition.

20.1.7 Check peristaltic pump tubing before operation.

20.1.8 At the end of each analysis, flush system for 5 minutes with the plasma on with a maximum of 2% nitric acid, followed by deionized water.

20.1.9 Inspect vacuum pump oil and replace as needed.

20.1.10 Inspect sample and skimmer cones for excessive salt build-up.

20.2 The following maintenance procedures need to be addressed quarterly (or more frequently if instrument performance indicates maintenance is needed).

20.2.1 Clean torch components and replace any worn O-rings on the torch assembly.

20.2.2 Inspect and clean the RF coil.

20.2.3 Inspect nebulizer spray pattern. Clean and replace gem tips and O-rings as necessary.

20.2.4 Check nebulizer components and replace worn O-ring on the transducer face.

20.2.5 Check spray chamber drain fitting for leaks.

20.2.6 Check that pump rollers are clean and remove and clean pump head as necessary.

20.2.7 Clean skimmer and sampling cones (See Section 20.3) and inspect orifices for damage or corrosion. Replace cones and/or O-rings as needed.

20.2.8 Replace interface roughing and turbo backing vacuum pump oil.

20.2.9 Inspect autosampler rinse pump rollers and clean or replace as necessary.

20.3 Cleaning Sample Introduction Components

20.3.1 Fill small plastic tank for sonicating components with warm to hot 2% Citranox® solution.Place torch, injector, spray chamber, gem tips, and transfer tube (remove all o-rings) into the tank. Sonicate all components for 15 minutes.

20.3.2 After removing the o-rings from the cones, **gently** insert each cone into a separate beaker with enough detergent solution to cover completely and allow to soak for ~ 1.75 hours. Care must be taken to only handle cones by the base – any contact with either cone orifice can easily cause irreparable damage.

20.3.3 Rinse all components thoroughly with tap water followed by a thorough rinse with DI water.

20.3.4 Place all components back in the cleaned tank/beakers with DI water and sonicate for another 15 minutes. Cones should be contained in a separate container from the other sample introduction components.

20.3.5 Carefully remove sample introduction components and rinse thoroughly with DI water.

20.3.6 Inspect cones under dissecting microscope to be sure that the edges of the orifices are not damaged and that the surfaces inside and out of the cone orifice area has been cleaned well. If the cones still appear to be dirty place in 2% HNO_3 and sonicate for **no more than** 2 minutes (more than 2 minutes of acid exposure will damage the cones) then rinse thoroughly with DI water and reinspect. If cones are needed immediately they may be dried by spraying Dust Off® over the entire surface, taking care not to make physical contact with the cones.

All other sample components that need further cleaning should be sonicated for 2 or more minutes in 2% HNO_3. Place in Class 100 hood or leave to air dry on a dust free cloth (e.g., Technicloth®) or Kimwipes® may be used. If cones are needed immediately they may be dried by spraying Dust Off® over the entire cone.

20.3.7 For cones that are still dirty after the procedure described in 20.3.6, and believed to be usable, refer to the Spectron Cone Cleaning Guide for additional procedures. Cones that are no longer usable may be returned to the manufacturer for recycling and platinum cones can be sent in for refurbishing.

21.0 SHORTHAND PROCEDURE

The flow chart shown in Figure 24-9 shows the procedural steps and sequence for analysis of inorganic samples.

22.0 DOCUMENTATION AND DOCUMENT CONTROL

22.1 All information concerning sample preparation, standard preparation, instrument conditions, etc., must be documented in the appropriate binders (i.e., Extraction Log, Daily Performance Reports, Standards Log etc.) and/or electronically in either the LIMS or the local instrument computer.

22.2 All calculations and the type of method for determining concentration must be recorded in the analyst's notebook. Any unusual problems or conditions must also be noted.

22.3 Record all maintenance performed on the instrument in the maintenance logbook for this particular instrument.

22.4 Record all sample analyses, including quality control samples, performed by the instrument in the ICP-MS run logbook for this particular instrument.

22.5 Reviewer must sign laboratory notebook weekly.

22.6 Any hard copies of instrument data should be filed chronologically. Electronic copies of instrument data are maintained on the L: drive in the "Metals Lab" folder.

22.7 It is imperative the project documentation be updated following each analysis. Analysts will copy raw instrument and QC files to a designated corporate network shared drive at the completion of each analysis sequence or batch. Primary data reviewers will use the data on the shared network drive for their data review process. The completed data packages ready for upload into the ERG LIMS system will be retained on the network drive as the backup for this data.

22.8 All processed data are archived in the LIMS on the shared network drive. Data is archived monthly to compact disc (CD) or digital versatile disc (DVD), verified on the system where the data originated and stored for at least five years in the laboratory. An archive copy of a data package is retained for at least five years in the laboratory data storage. The data backup should include enough information to manually generate the numbers used for reporting.

22.9 Reporting

22.9.1 Sample results are uploaded into the LIMS in ng/L as analyzed. Any dilutions performed must be accounted for in the instrument software. The internal standard recoveries must be included with the result calculation. Final results should be reported in ng/m^3 to three significant figures as shown in Section 12.1. If required by the sampling organization, results can also be reported in $\mu g/m^3$ by multiplying the ng/m^3 results by 1,000.

22.9.2 Sample results should not be corrected based on analyte results from the laboratory blanks, field, trip, or filter lot blanks provided by sampling agencies, unless specifically requested. However, samples are blank-subtracted if any analyte is detected in the LRB at greater than 5 times the MDL as described in Section 16.2.4.

22.9.3 As stated in Section 11.2.6, samples with metal concentrations greater than 90% of the current LDR must be diluted and re-analyzed. The diluted value will be reported to the sampling agency.

22.9.4 Data should meet all specifications as presented in Table 24-3. If data does not meet specifications, corrective reporting actions listed must be followed (flag or invalidate data).

23.0 REFERENCES

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24.0 TABLES, DIAGRAMS, FLOWCHARTS, VALIDATION DATA

Table 24-1. 2015 Method Detection Limits (MDLs) for Metals 47 mm Teflon Filters

Element	2015 MDL by FAC[1] (ng/L)	2015 MDL by FAC[2] (ng/filter)	2015 MDL by FAC[2,3] (ng/m^3)
Aluminum *	25779.74	1289	53.6
Antimony	19.647	0.98	0.041
Arsenic	73.69	3.68	0.153
Barium *	132.847	6.64	0.276
Beryllium	8.293	0.415	0.017
Cadmium	5.071	0.254	0.011
Calcium *	50738.52	2537	106
Chromium	5791.16	290	12.0
Cobalt	5.994	0.300	0.012
Copper *	250.362	12.52	0.521
Iron *	7579.5	379	15.8
Lead	18.638	0.932	0.039
Magnesium *	2615.008	131	5.44
Manganese	60.982	3.05	0.127
Mercury	17.111	0.856	0.036
Molybdenum *	42.075	2.10	0.088
Nickel	137.733	6.89	0.286
Rubidium *	3.269	0.163	0.007
Selenium	140.446	7.02	0.292
Strontium *	54.749	2.74	0.114
Thallium *	0.886	0.044	0.002
Thorium *	3.287	0.164	0.007
Uranium *	0.449	0.022	0.001
Zinc *	7055.234	353	14.7

* Elements not on our standard analysis list of elements.
† Total Chromium.
¥ MDL Calculated using the CFR Method.

Table 24-2. 2015 Limit of Quantitation (LOQ) for Metals

Element	ng/L
Aluminum*	23414
Antimony	70.6
Arsenic	261
Barium*	350
Beryllium	28.9
Cadmium	16.3
Calcium*	95407
Chromium†	5291
Cobalt	21.5
Copper*	709
Iron*	19063
Lead	53.4
Magnesium*	5443
Manganese	151
Mercury	38.0
Molybdenum*	151
Nickel	409
Rubidium*	10.7
Selenium	505
Strontium*	125
Thallium*	2.45
Thorium*	11.8
Uranium*	1.46
Zinc*	14896

* Elements not on our standard analysis list of elements.
† Total Chromium.

Note: This calculation assumes a total volume of 24.04 m^3.

Table 24-3. Summary of Quality Control Procedures for Metals Analysis

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Daily Performance Check (DPR)	Daily, prior to samples	Mg-24 > 40,000 cps, < 3% RSD In > 300,000 cps, < 3% RSD Pb-208 >100,000, < 3% RSD Ba/Ba++ and Ce/CeO < 0.03 Bkgd < 30 cps at Mass 220	1)Repeat analysis of DPR 2)Re-optimize instrument tuning parameters 3) Reprepare DPR standard 4) Perform instrument maintenance
Initial Calibration Standards (IC)	Daily, at least 5 calibration points	Correlation coefficient ≥ 0.998 & %RSD ≤ 10. RSDs >10 are acceptable for the CAL2 standard.	1) Repeat analysis of calibration standards 2) Reprepare calibration standards and reanalyze
Initial Calibration Verification (ICV)	Immediately after calibration	Recovery 90-110%, with the exception of Al	1) Repeat analysis of ICV 2) Reprepare ICV standard 3) Recalibrate and reanalyze.
Initial Calibration Blank (ICB)	Immediately after ICV	Absolute value must be ≤ MDL	1) Locate and resolve contamination problems before continuing 2) Reanalyze, recalibrate or flag failing elements for the entire analysis when appropriate
High standard verification (HSV)	After ICB and before ICS	Recovery from 95-105% with the exception of Al	1) Repeat analysis of HSV 2) Reprepare HSV
Interference Check Standard (ICSA/IFA)	Following the HSV, every 8 hours and at the end of each run	Within ±3 times LOQ from zero or from the standard background contamination when present	1) Repeat analysis of ICSA 2) Reprepare ICSA and analyze 3) Adjust correction equation(s) and reprocess entire analysis
Interference Check Standard (ICSAB/IFB)	Following each ICSA	Recovery 80-120% of true value plus standard background contamination when present	1) Repeat analysis of ICSAB 2) Reprepare ICSAB and analyze 3) Adjust correction equation(s) and reprocess entire analysis
Continuing Calibration Verification (CCV)	Analyze before samples, after every 10 samples, and at the end of each run	Recovery 90-110%, with the exception of Al	1) Reanalyze CCV 2) Reprepare CCV 3) Recalibrate and reanalyze samples since last acceptable CCV
Low Calibration Verification (LCV)	At the beginning and end of each analysis, between the CCV and CCB	Recovery 70-130% for Pb only	1) Reanalyze LCV 2) Reprepare LCV 3) Recalibrate and reanalyze samples since last acceptable LCV
Continuing Calibration Blanks (CCB)	Analyzed after each CCV	Absolute value must be ≤ MDL	1) Reanalyze CCB 2) Reanalyze samples since lastacceptable CCB
Laboratory Reagent Blank (LRB/BLK1)	1 per 20 samples, a minimum of 1 per batch	Absolute value must be ≤ MDL	1) Reanalyze 2) If > MDL, but < 5x MDL, sample results for that element must be flagged for the entire analysis 3) If > 5x the MDL then sample results for that element must be blank subtracted
Method Blank (MB/BLK2)	1 per 20 samples, a minimum of 1 per batch	Absolute value must be ≤ MDL. Note: The MB is used only for the purpose of MDL generation	This standard is not required by the method and there is no corrective action

Table 24-3. Summary of Quality Control Procedures for Metals Analysis (cont'd)

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Standard Reference Material (SRM)	1 per 20 samples, a minimum of 1 per batch	Recovery 80-120% for Pb only	1) Reanalyze 2) Flag sample data 3) Re-extract batch
Laboratory Control Sample (LCS/BS and BSD)	1 per 20 samples, a minimum of 1 per batch	Recovery 80-120%, with the exception of Al	1) Reanalyze 2) Flag data if recovery for only one or two elements fail criteria 3) Reprepare sample batch if recovery for most elements fail criteria
Replicates (DUP) (Replicate Analysis)	1 per 20 samples, a minimum of 1 per batch	≤ ±10% RPD for sample and duplicate values ≥ 10 times the MDL	1) Check for matrix interference in the cased of DUP1. 2) Repeat replicate analysis 3) Flag data
Collocated Samples (C1/C2)	10% of samples annually	≤ ±20% RPD for sample and collocate values ≥ 10 times the MDL	1) Flag C2 data if associated replicate analysis are within criteria 2) Repeat analysis if replicate analysis fails.
Post Digestion Spike (PDS)	1 per 20 samples, minimum of 1 per batch	Recovery 75%-125%	1) Flag failed elements for parent sample and PDS 2) Reprepare PDS if preparation issue is suspected reason for failure.
Serial Dilution (SRD)	1 per batch	Recovery 90-110% of undiluted sample if the element concentration is minimally a factor of 50 above the MDL in the original sample	1) Re-prepare dilution if preparation issue is suspected reason for failure. 2) Flag failed analytes
Internal Standards (ISTD)	Every Calibration, QC and Field Sample	Recovery 60-125% of the measured intensity of the calibration blank	1) If drift suspected, stop analysis and determine cause, recalibrate if necessary 2) Reprepare sample 3) If recovery > 125% due to inherent ISTD, dilute sample and reanalyze

Table 24-4. Optimization Procedures

Procedure	When to Perform
Nebulizer Gas Optimization	Daily.
Ion Lens Voltage Optimization	Daily.
Auto Lens Optimization	Daily, when Auto Lens is used in the acquisition method.
Dual Detector Cross Calibration	Cross calibration is necessary if you have selected Dual Mode as your Processing Method. This would only be done when you require extended dynamic range (above 2 million cps). **Note:** This must be performed before each analysis for this method.
Instrument Performance Check	Daily.
X-Y Adjustment	Whenever the cones have been cleaned or replaced, or after any torch maintenance procedure.
Detector Optimization: Pulse Stage Voltage Analog Stage Voltage	When sensitivity cannot be recovered through other cleaning or optimization methods or when the detector is replaced.
Deadtime Correction	This procedure should only be performed if a detector has been replaced, and after the new detector has been optimized.

Table 24-5. Performance Specifications

24Mg Sensitivity	> 40,000 cps	< 3% RSD
In Sensitivity	> 300,000 cps	< 3% RSD
208Pb Sensitivity	> 100,000 cps	< 3% RSD
CeO/Ce	<0.03	N/A
Ba++/Ba+	<0.03	N/A
Background	< 30 cps @ Mass 220	N/A

Table 24-6 Blank Spike Standard (Used for BS/BSD) Preparation (50 mL)

Element	Stock Std. Concentration (µg/mL)	Added Volume (mL)
Al	1000	1.5
Sb	100	0.25
As	100	1.0
Ba	1000	0.5
Be	100	0.25
Cd	100	0.25
Ca	1000	1.25
Cr	100	2.5
Co	100	0.25
Cu	1000	0.5
Fe	1000	0.5
Pb	100	0.25
Mg	1000	0.5
Mn	100	0.5
Hg	10	0.5
Mo	100	0.25
Ni	100	0.5
Rb	1000	0.025
Se	100	1.0
Sr	100	0.25
Tl	10	0.5
Th	10	0.5
U	10	0.5
Zn	1000	0.5

Table 24-7. Analytical Isotopes for Quantitation and Monitoring of Reported Elements

Element	Quantitation Isotope(s)	Monitored/Confirmation Isotope(s)
Aluminum	27	NA
Antimony	121	123
Arsenic	75	NA
Beryllium	9	NA
Barium	137	135
Bismuth (ISTD)	209	NA
Cadmium	111	106, 108, 114
Calcium	43	NA
Chromium	52	53
Cobalt	59	NA
Copper	63	65
Iron	57	54
Gallium (ISTD)	71	NA
Indium (ISTD)	115	NA
Lead	208	206, 207
Lithium (ISTD)	6	NA
Magnesium	25	24
Manganese	55	NA
Mercury	201	200, 202
Molybdenum	98	92, 94, 95, 97
Nickel	60	62
Rubidium	85	NA
Scandium (ISTD)	45	NA
Selenium	82	77, 78
Strontium	88	NA
Thallium	205	203
Thorium	232	NA
Uranium	238	NA
Yttrium (ISTD)	89	NA
Zinc	66	67, 68

NA = Not applicable/none.

Figure 24-8. Quality Control Review Form (Page 1)

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Quality Control Review Form Metals Analysis -- 47mm Filters 2015-1

Sequence ID: _____ **Instrument:** _____ **Batch:** _____
Cal Curve (Method): _____ **Analyst:** _____ **Date:** _____
10% Review Sample IDs: _____ **Reviewer:** _____ **Date:** _____
Optional 1% Review Sample IDs: _____ **Reviewer:** _____ **Date:** _____

Parameter	Acceptance Criteria	Analyst Check (Initials and Date)	Task Lead/Data (Initials and Date)	10% QA Review (Initials and Date)	1% Optional QA Review (Initials and Date)	Comments
Instrument QC						
Daily Performance Report	Mg-24 > 40,000 cps, < 3% RSD In > 300,000 cps, < 3% RSD Pb-208 >100,000, < 3% RSD Ba/Ba++ and Ce/CeO < 0.03 Bkgd < 30 cps at Mass 220					
Initial Calibration Standards (IC)	≥0.998 correlation coefficient & RSD ≤10. RSDs >10 are acceptable for the CAL2 standard.					
Initial Calibration Verification (ICV)	Recovery 90-110%.					
Initial Calibration Blank (ICB)	Absolute value must be ≤ MDL.					
High Calibration Verification (HCV)	Recovery 95-105%.					
Interference Check Standard (ISCA/IFA)	ICSA: ±3 times QL from zero or from the standard background contamination when present					
Interference Check Standard (ICSAB/IFB)	ICSAB: Recovery 80-120% of true value plus standard background contamination when present					
Continuing Calibration Verification (CCV)	Recovery 90-110%.					
Low Calibration Verification (LCV)	Recovery 70-130% for Pb; must be analyzed at the beginning and end of each analysis.					
Continuing Calibration Blanks (CCB)	Absolute value must be ≤ MDL.					
Internal Standard Response	Recovery must be between 60 and 125% of the measured intensity of the calibration blank					

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Revision 10

Figure 24-8. Quality Control Review Form (Page 2)

SOP ERG-MOR-085
Quality Control Review Form Metals Analysis -- 47mm Filters 2015-1 (Continued)

Parameter	Acceptance Criteria	Analyst Check (Initials and Date)	Task Lead/Data (Initials and Date)	10% QA Review (Initials and Date)	1% Optional QA Review (Initials and Date)	Comments
Linear Dynamic Range Check	All sample values must less than 90% of the established linear dynamic range.					
Extraction QC						
Check Sample Volume	Check COC or filter envelope against Bench Sheet to make sure sample volumes are correct.					
Laboratory Reagent Blank (LRB/BLK1)	Absolute value must be ≤ MDL.					
Method Blank (MB/BLK2)	Absolute value must be ≤ MDL.					
Standard Reference Material (SRM)	Recovery 80-120% for Pb.					
Laboratory Control Sample (LCS/BS/BSD)	Recovery 80-120%, with the exception of Al.					
Collocated/Duplicate Samples (D1/D2, C1/C2)	±20% RPD when concentration of either sample is ≥ 10x the MDL					
Replicate Analyses (DUP)	±10% RPD when concentration of the parent sample is ≥ 10x the MDL					
Serial Dilution (SRD)	Recovery 90-110% of undiluted sample if the parent sample concentration is > than 50x the MDL.					
Post Digestion Spike (PDS)	Recovery 75-125%					
Reporting Requirements						
Manual Check of Calculations	Hand calculate an equation - a unit conversion equation, a sample concentration equation, a dilution equation, etc. – to verify equation					
Check LIMS Qualifiers	Check to make sure the LIMS data flags are correct					
Negative Sample Values	Negative sample values must be less than the absolute value of the MDL.					

This review check sheet must be completed by primary data reviewer/TL/QA.

Figure 24-9. Flow Diagram for ICP-MS Preparation and Analysis

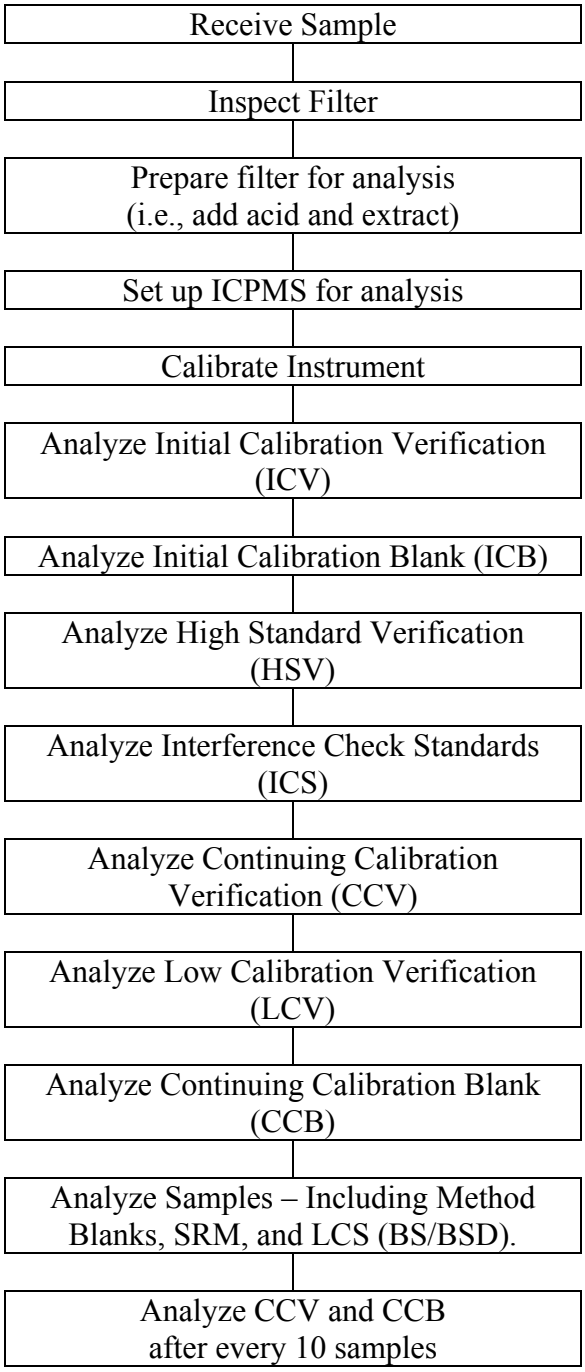

Table 24-10. Teflon Extraction Record

Record for Teflon Extraction Times, Temperatures & H_2O_2 addition 2014-1

Batch: **Date:** **Initials:**_____

Start Time	
Start Block Temperature (°C)*	
Sample Temperature (°C)†/Time	
Time H_2O_2 was added	
Stop Time (Removed from Block)	
Stop Block Temperature (°C)*	
Sample Temperature (°C)†/Time	
Time & Temp. (°C) brought to final volume	

*Block temperature is read from the HotBlock™ controller using an internal thermocouple.
†Sample thermometer serial #: 19587, actual thermometer temperature not the corrected temp.

Thermometer block position # _____

ENGINEERING AND SCIENCE DIVISION

TITLE: SOP for the Preparation of Monitoring Data for AQS Upload	EFFECTIVE DATE: OCT - 1 2014
REFERENCES: N/A	
SATELLITE FILES:	
REASON FOR REVISION: Updates	
WRITER: NAME/DATE Jaime Hansen 10-1-14	PROJECT MANAGER: NAME/DATE Julie C. Swift 10/1/14
QUALITY ASSURANCE COORDINATOR: NAME/DATE Donna Tedder 10/1/14	NEXT SCHEDULED REVIEW: 1/31/15

1.0 IDENTIFICATION AND PURPOSE

The purpose of this document is to define, describe, and present the Standard Operating Procedure (SOP) for the preparation and upload of monitoring data into Environmental Protection Agency's (EPA) Air Quality System (AQS) database. This SOP assumes that the user will have knowledge of how to load data into AQS as well as how to use Microsoft Access. This SOP focuses on how to use the various tools described to translate Laboratory Information Management System (LIMS) data into the correct format for AQS upload.

2.0 MATRIX OR MATRICES

N/A

3.0 METHOD DETECTION LIMIT

N/A

4.0 SCOPE AND APPLICATION

This document outlines the step-by-step process of extracting data from the LIMS, importing and coding the data via a Microsoft Access "Macro" database, and loading the data into EPA's AQS database. Although the intent of this document is to provide instructions on how to extract, code, and load data for the National Monitoring Program, these steps may also be replicated and/or adjusted for any given subset of data for which extracting, coding, and/or AQS loading of the data may be necessary. Not every step or query described in Section 14 is applicable in every situation; some queries may need to be altered or may be skipped entirely. However, translated data sets are not affected by running unnecessary queries from the tools described in this SOP.

5.0 METHOD SUMMARY

N/A

6.0 DEFINITIONS

AQS – EPA's "repository of ambient air quality data" and includes ambient air quality data for criteria pollutants and hazardous air pollutants, as well as meteorological data and metadata information on monitoring locations (http://www.epa.gov/ttn/airs/airsaqs/).

"AQS" Database – a Microsoft Access database where the AQS Tables are exported and parsed out based on various client requests.

AQS RB Template – the table in the Macro database where AQS coding is appended for blank (field blank, trip blank, or lot blank) data; this table is directly loaded into AQS.

AQS RD Template – the table in the Macro database where AQS coding is appended for raw (field sample, primary, or collocate) data; this table is directly loaded into AQS.

AQS RP Template – the table in the Macro database where AQS coding is appended for precision (duplicates and/or replicates) data; this table is directly loaded into AQS.

LIMS – Laboratory Information Management System; the lab's repository of concentration data.

"Macro" Database – a Microsoft Access database where queries are run to convert the data into AQS format; queries are also run to perform QA on the AQS Tables that are generated and loaded into AQS.

POC – Parameter Occurrence Code, used in AQS to distinguish data from different sources for the same site, date, and pollutant.

QCData Template – a table in the Macro database where the QC (or precision) data are appended after they have been quality assured; all queries in the Macro database run on this version of the QCData table because the names are formatted in a specific manner.

"Raw" Database – a Microsoft Access database where data is initially imported and reviewed for completeness.

Sampdata Template – a table in the Macro database where the Sample data are appended after they have been quality assured; all queries in the Macro database run on this version of the Sampdata table because the names are formatted in a specific manner.

Worklist Spreadsheet – a Microsoft Excel table exported from LIMS that provides information related to individual samples not available with the raw concentration data.

Worklist Template – a table in the Macro database where the Worklist data are appended after they have been quality assured; all queries in the Macro database run on this version of the Worklist table because the names are formatted in a specific manner.

7.0 INTERFERENCES

N/A

8.0 SAFETY

N/A

9.0 EQUIPMENT

N/A

10.0 MATERIALS

N/A

11.0 CHEMICALS, REAGENTS, AND STANDARDS

N/A

12.0 COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

N/A

13.0 CALIBRATION AND STANDARDIZATION

N/A

14.0 PROCEDURE

The procedure described in this section produces two results: 1) it transcribes data from LIMS into AQS-coded files with the proper syntax to export and load directly into EPA's AQS database; and 2) it compiles sample data, QC data, and subsequent sample information into a single table in Microsoft Access that is used to perform various data analyses.

It is recommended that notes are taken for each transcription run-through. A log and notes of every data transcription/translation record error or change required to complete the format of the monitoring data shall be kept. A record of the number of records generated from each of the queries in the Macro database (as directed in specific steps in this SOP) shall be kept. It is especially important to note if a sample or its corresponding data are modified for any reason, the reason the change occurred, and how the omission or change was determined.

A detailed, step-by-step list of instructions is provided below.

14.1 Generating a Worklist and Extracting Data from LIMS

Note: Extraction of data from ERG's LIMS requires authorization to access LIMS data and experience using the LIMS system.

14.1.1 In LIMS, go to Laboratory and select Query Analysis Status.

14.1.2 In the "Query For:" drop-down menu, select the appropriate Lab Project Manager (i.e. Julie Swift) and/or work order numbers.

14.1.3 Select the needed sampled date range (i.e. 12/31/12 23:59 through 4/1/13 00:00). Make sure the time for the last date of the range is 00:00 on the next day or data for samples taken on that date may not be included.

14.1.4 In the Status menu, select all status types except "not required."

14.1.5 To the right of the window, order results by project name – analysis – sampled.

14.1.6 Choose Query. When the list appears in the window, select export and save the worklist as an Excel file in the desired C: or L: drive location.

14.1.7 Open the Excel file. Select the Data menu – Filter – Auto Filter.

14.1.8 Sort ascending for sample Status. All statuses marked "Canceled" can be deleted. Sort ascending for Sample Type and delete the following: Audit samples, Filter Blanks, and Passive Blanks.

14.1.9 Review the Sample Type entries to be sure the sample type agrees with the information in the Sample Name and Comments (C1, C2, etc.) entries.

14.1.10 Sort ascending for Status. For samples marked "Invalid," review sample comments and assign AQS null codes using the WorkUser10 column left of the comments. A list of null codes is provided in Table 14-1 (with the most commonly used codes in bold).

14.1.11 With all records showing, sort ascendingly by client (i.e. Region 4) and note the highest and lowest work order number (the first seven digits of the Lab Number) for each client. This will be used to pull the actual concentration data.

14.1.12 To pull the concentration data from LIMS, go to Project Management – Reports.

14.1.13 Choose client (i.e. Region 4).

14.1.14 Select work orders (on right of screen) corresponding to those on the worksheet for this client (find the highest work order noted in Step 14.1.11 and choose, scroll to find the lowest work order, with the shift button held, choose the lowest work order – this will highlight all of the work orders between the two).

14.1.15 Choose destination – C:\ELMT\Userfiles\.

14.1.16 Choose custom – EDD Format – EEDStdExcel_ERG.

14.1.17 Select modified draft – when window opens sort left side of screen by name – then on the right side of the screen, remove (uncheck) everything except the duplicates.

14.1.18 Select continue - report will be generated and saved in the destination chosen.

14.1.19 Email data and worklist Excel files to the person performing the data conversion.

Table 14-1. List of Null Codes

Qualifier Code	Qualifier Description
AA	**Sample Pressure out of Limits**
AB	Technician Unavaliable
AC	Construction/Repairs in Area
AD	Shelter Storm Damage
AE	Shelter Temperature Outside Limits
AF	**Scheduled but not Collected**
AG	**Sample Time out of Limits**
AH	Sample Flow Rate out of Limits
AI	Insufficient Data (cannot calculate)
AJ	**Filter Damage**
AK	**Filter Leak**
AL	Voided by Operator
AM	**Miscellaneous Void**
AN	**Machine Malfunction**
AO	Bad Weather
AP	Vandalism
AQ	Collection Error
AR	Lab Error
AS	Poor Quality Assurance Results
AT	Calibration
AU	Monitoring Waived
AV	**Power Failure**
AW	Wildlife Damage
AX	Precision Check
AY	Q C Control Points (zero/span)
AZ	Q C Audit
BA	Maintenance/Routine Repairs
BB	Unable to Reach Site
BC	Multi-point Calibration
BD	Auto Calibration
BE	Building/Site Repair
BF	Precision/Zero/Span

Qualifier Code	Qualifier Description
BG	Missing ozone data not likely to exceed level of standard
BH	Interference/co-elution/misidentification
BI	Lost or damaged in transit
BJ	Operator Error
BK	Site computer/data logger down
BL	QA Audit
BM	Accuracy check
BN	Sample Value Exceeds Media Limit
BR	Sample Value Below Acceptable Range
CS	Laboratory Calibration Standard
DA	Aberrant Data (Corrupt Files, Aberrant Chromatography, Spikes, Shifts)
DL	Detection Limit Analyses
FI	Filter Inspection Flag
MB	Method Blank (Analytical)
MC	Module End Cap Missing
SA	Storm Approaching
SC	Sampler Contamination
ST	Calibration Verification Standard
TC	Component Check & Retention Time Standard
TS	Holding Time Or Transport Temperature Is Out Of Specs.
XX	Experimental Data

14.2 Getting Started in Microsoft Access with the “Raw” Database.

14.2.1 Copy the Microsoft Access database entitled “QX 20XX RAW” from L:\Jaime\REFERENCES\ and paste into the designated location. Adjust the name of the database accordingly.

14.2.2 Import the Microsoft Excel Worklist spreadsheet (may need to do some “un-formatting”of the file such as removing autofilters, unfreezing panes, unhiding columns, etc.) into the Microsoft Access “Raw” database as a table named “Worklist”.

14.2.3 In the Raw database, review the Worklist for errors such as multiple samples on a single date, missing null codes, data from outside the date range of interest, etc. Make note of any errors, changes, deletions, etc. Resolve any issues with the Sample Log-in Leader or Project Manager and request that the Sample Log-in Leader make corrections in LIMS (if needed). Note any special flags that may be needed in the SampleUser5

column based on the SAMPLECOMMENTS column and available Qualifier Flags for AQS (http://www.epa.gov/ttn/airs/airsaqs/manuals/codedescs.htm). Also note any sites performing manual sampling, running PAMS samples or other samples of a different duration than 24 hours. This is needed for step 14.3.14.

14.2.4 Run the Query0 queries. The "Null Code" query checks to make sure all invalid samples have a null code and the "Check Void" query ensures that all samples with "VOID" in the sample names have an "Invalid" sample status. Run the "Qualifier Flag" query to confirm that the correct qualifier flag has been added to the SampleUser5 field based on the SampleComments field.

14.2.5 Import each of the tabs (SAMPDATA, QCDATA, LNOTE) in the Microsoft Excel raw data spreadsheet files into the Raw database. Do not let Microsoft Access assign a primary key during import. If data were pulled from LIMS in multiple spreadsheets, compile tabs of the same name together in a single table. Note that if the data have been pulled by Region (or method, etc.), a Region field needs to be added to the LNOTE table and updated after each successive import in the format "Region X". The same flag in LIMS can be used to denote different things among different datasets. For example, A-01 is used for manual entry of comments in the LNOTE or ANOTE columns of the raw data. A sample from a site in Region 4 may have an A-01 flag denoting late arrival, while a sample from Region 2 may have an A-01 flag for surrogate recovery issues. Since both samples are denoted with A-01 in the raw data, another aspect of the data, such as Region in this case, must be used to distinguish to what the flag refers. Smaller data sets (data pulled from LIMS in a single spreadsheet) do not need this.

14.2.6 If data were pulled from LIMS in multiple spreadsheets, run the "Confirm All Regions" queries to ensure that data for all of the regions was appended during the import process (for the Sampdata and LNOTE tables.

14.2.7 Run the "missing data" queries in the Raw database (Query1s). They verify that the samples listed in the Worklist match the SAMPDATA and vice versa. If everything is correct, no records will appear in the results. If records appear, there are records in one table that do not match the other; this must be resolved before moving forward.

14.2.8 Resolve any missing data issues with the Project Manager and/or Sample Log-in Leader. Often, data were not "locked" in LIMS and the

data must be re-pulled from LIMS. Be careful with the LNOTEs if additional data are appended into the existing tables. If these are added to the LNOTE table, they must agree with the original Region (or method) they were loaded with. Refer to 14.2.5 for further explanation.

14.3 Coding Raw Data in the "Macro" Database

14.3.1 Print out the AQS Steps Record Sheet spreadsheet (Figure 24-1) located at L:\Jaime\AQS. This is used to note the results from various queries and steps in the coding process.

14.3.2 Once the data are ready in the Raw database, copy the most recent Access MACRO database from L:\Jaime\REFERENCES and paste into the designated location. Adjust the name accordingly.

14.3.3 Delete the following tables in the Macro database (if they exist): D1s, D2s, any "Data X" tables, Dups from QCDATA, Invalids, LNOTE, QA1 Dup Data, QA2 Worklist Data, QCDATA, Qualifiers, SAMPDATA, SAMPDATA + INVALIDS, SAMPDATA + INVALIDS + R1R2, and Worklist.

14.3.4 Delete data from (while leaving the shell table intact) the following six TEMPLATE tables in the Macro database: AQS RA TEMPLATE, AQS RB TEMPLATE, AQS RP TEMPLATE, AQS RD TEMPLATE, QCDATA TEMPLATE, SAMPDATA TEMPLATE, WORKLIST TEMPLATE.

14.3.5 Compact the Macro database. This "deletes" items in Access' memory and reduces the size of the database.

14.3.6 Import the new Worklist, SAMPDATA, LNOTE, and QCDATA tables from the RAW database used in steps 14.2.

14.3.7 In the Macro database, run queries 00A-00C to append the Worklist, QCDATA, and SAMPDATA to their associated template tables (the template tables have formatted column names and data). Note the number of records in the record sheet. From this point forward, all data manipulations are done on the Template tables. This is useful in case there is a need to go back to the "original" versions of the data.

14.3.8 Run queries 00D1 and 00D2. These update the Units column in the QCDATA and SAMPDATA TEMPLATES from "ng/m^3 Air" or "ug/m3 Air" to "ng/m3" or "ug/m3", respectively, which is the format in the reference (or LOOKUP) tables. Note the number of records changed

in the "UPDATE UNITS" slot on the record sheet. Run Query 00D3 to confirm the update in the SAMPDATA Template and check for any other unexpected units of measure.

14.3.9 Run queries 00E, 00F, and 00G. These update the Analysis column in the Worklist, SAMPDATA and QCData TEMPLATES from "Metals Analysis – 47mm" or "Metals Analysis – HiVol" to just "Metals Analysis", which is the format in the reference tables. Note the number of records changed in the "UPDATE ANALYSIS" slot on the record sheet.

14.3.10 Run 01A and 01B. These are similar checks as in step 14.2.7 above. They verify that the samples listed in the Worklist Template match the SAMPDATA TEMPLATE and vice versa. If everything is correct, no records will appear in the results. If results appear, there are records in one table that do not match the other and this must be resolved before moving forward.

14.3.11 Run query 01C. This query looks for possible mislabeled blanks by comparing the SampleType column and the SampleComments column in the Worklist Template. Any results must be resolved before moving forward.

14.3.12 Run query 01D1 and 01D2. These queries put site information for BOMA and TOOK into the SampleInfo1 column. These two sites (for metals only) are collocated and sometimes the Field Samples do not correspond to the primary (C1) sampler; this affects which POC should be used. Note that site info designated with "A" refers to the primary (C1) and "B" refers to the collocated (C2) sampler. Verify that these ran correctly by running query 01D3; a slight deviation in sample log-in sometimes affects the way these are listed. The SampleInfo3 column should say "TOOK A" or "TOOK B" for TOOK samples and "Roxbury A" or "Roxbury B" for BOMA samples. Should a dataset not contain these sites, the queries will simply not update these fields.

14.3.13 Run query 01E1 and 01E2. Query 01E1 trims the SampleName column entries in the Worklist Template table to match the site id in the Project column. Query 01E2 handles sites with names that deviate from the typical four-letter site code (like INDEM). Verify that these queries ran correctly by running query 01E3. Check each trimmed site name to verify that it is correctly formatted.

14.3.14 Run query 01F1 to update start times and durations for any manual samples. If no manual samples are included, a pop-up screen appears

stating that "no sites currently do manual sampling." This should be noted when reviewing the Worklist in Section 14.2 and any sites doing manual samples added prior to running this query. Run query 01F2a to update the duration codes (from 24 to 3 hours) for any PAMS samples; run query 01F2b to update the duration codes for any 1-hour samples. Review the start times and start dates of all manual samples or PAMS samples to ensure that the proper start date and time has been applied to the SampleDate and StartTime fields using query 01F3 to manually update and confirm by running query 01F4.

14.3.15 Run query 01G1 through 01G3 to trim the year from the end of the Methodcode or Analysis columns in the Worklist, Sampdata, and QCData Template tables.

14.3.16 Run query 01H1 and 01H2. These update the POC column of the Worklist Template with the correct POC for TOOK and BOMA (refer to step 14.3.12 for the reason).

14.3.17 Run query 01I1 to verify that there is a POC in the POC Rules table for every site-method-sample type combination. Any results that are returned must either be added to the POC Rules table or QA'ed to make sure a sample type was not mislabeled (such as a site that usually runs duplicates mislabeled as collocates or vice versa). Run query 01I2 to update the POC column in the Worklist Template with the POCs for all other site-method-sample type combinations. Run query 01I3 to confirm that all rows have been updated in the POC column. Any results must be resolved before moving forward.

14.3.18 Run query 01J to verify that the correct number of pollutants are provided for each sample contained in the SAMPDATA Template. Any results returned need to be resolved before moving forward. SNMOC samples have 82 analytes; TO-15 (VOC) samples have 58 analytes; TO-13 (SVOC or PAH) samples have 22 analytes or 25 for the TO-13 plus Phenols list; TO-11A w/ MEK (carbonyl) samples have 13 analytes; IO-3.5 (metal or inorganic) samples have 11 analytes, or in the case of the extended list, 24; and Methane and hexavalent chromium have only one analyte each. Queries 01J2 through 01J4 may be used to resolve exact dups. Run query 01J2 to confirm that there are exact dups; run query 01J3a to make a table of the dups ("Dups to Resolve from Sampdata Template") and then query 01J3b to delete the dups from the Sampdata Template. Lastly, run query 01J4 to group on the dups and append back into Sampdata Template. After completing this sequence of queries, re-run query 01J to confirm that the dups have been removed.

14.3.19 Run query 01Ka to look for any hexavalent chromium samples that have the HT flag in the SampleComments column of the Worklist Template. This flag is used to identify a sample that was exposed to an ambient temperature above a given level (60ºF) when not picked up the day after sampling and will be flagged with a qualifier code in AQS. Run query 01Kb to update the Qualifier column of the Worklist for any of the samples from query 01Ka. Verify that the number of samples updated in 01Kb matched the results from 01Ka. Run query 01Kc to confirm that the flag has been applied.

14.3.20 Run query 01L, which looks for any duplication in the Worklist Template table. Any results that appear must be reconciled before moving forward.

14.3.21 Run query 01M1 through 01M3 to check for numerical results associated with data flagged with the co-elution LIMS flag in the SAMPDATA Template table. Because data flagged with the co-elution flag could not be resolved by the instrument, any such results need to be reported to the Project Manager and likely changed to ND in the table as well as LIMS. Run query 01M1 to look for any such results. If found, run query 01M2 to make a table of the original data for record-keeping purposes. Run query 01M3 to manually update the numerical results to ND. Re-run query 01M1 to confirm that all of the changes have been made.

14.3.22 Run query 01N to confirm that all TNMOC results are numeric. These results are put into LIMS manually and occasionally uploaded incorrectly. Any results that appear must be reconciled before moving forward.

14.3.23 Run query 01O. This updates the SAMPDATA Template with all the information from the Worklist Template. Note the number of records in the record sheet in the 01 slot. This number should match the number from the Import SAMP slot (assuming there have been no data changes such as the removal of dups).

14.3.24 Run query 02a1. This query links the QCDATA Template and the Worklist Template and makes a new table “Dups from QCData”. This query is run to retrieve only duplicate sample data for the samples we’re loading into AQS and not all the other types of QC data that could be in the QCDATA Template table (such as LCS, spikes, etc). Note the number of records in the record sheet in the 02 slot. Run query 02a2 to look for dups in the new Dups from QCData tables; if any are identified, run query 02a3 to make a table of the dups (“Data with Dups in

Precision") and resolve these with the Project Manager. Run query 02a4 to append the correct results back into the Dups from QCData table. After completing this sequence of queries, re-run query 02a2 to confirm that the dups have been resolved.

14.3.25 Run query 02b. This query verifies that the correct number of pollutants is provided for each sample contained in the Dups from QC Data table, similar to step 14.3.18.

14.3.26 Because invalid samples are loaded into AQS but no data is generated from LIMS for invalid samples, records must be created for invalid samples (records with no results for each applicable analyte per method). Run query 03a to ensure all invalid samples have been assigned null codes in the Worklist. Any results that appear must be reconciled before moving forward. Run query 03b to make an Invalids table for non-metal samples, then run query 03c to append in records for metals samples. Note that query 03b must be run first as it sets up the template of the table. Note the number of records from query 03b and 03c in the record sheet in the 03 slot.

14.3.27 Run query 04a to make a new table from the SAMPDATA TEMPLATE called SAMPDATA + INVALIDS. Note the number of records in the record sheet in the 04 slot. Run query 04b to append in records from the Invalids table. The number of records from the 03 slot on the record sheet plus the number of records from the 04 slot should equal the total number of records now in the SAMPDATA + INVALIDS table. Note this total on the record sheet in the "Total in Samp+" slot.

14.3.28 Go into the design of the SAMPDATA + INVALIDS table. Scroll to the bottom and change the "DL-NUMBER" and "RESULT-NUMBER" data types from binary to number and change the field size to double. Run query 04c to update these columns in the SAMPDATA + INVALIDS table. These columns will be used later to assign quantitation flags based on the MDLs and Results. (An error message may pop up when query 04c is run. This is because the query is trying to append "ND"s to a numerical field. Click OK, which will result in a null or blank in the RESULT (or DL)-NUMBER columns.)

14.3.29 Run query 04D to ensure that none of the results are in scientific notation. If results are found, these need to be converted to standard format before moving on.

14.3.30 Skip query 04E and run query 04F. These queries look for results that appear too low based on a few marker analytes. Investigate any results

and resolve with Project Manager. Skip query 04g and run query 04h to check on the number of NDs in a sample. This can be a marker for a mislabeled field blank. Investigate any results and resolve with Project Manager.

14.3.31 Run query 05. This formats the date, in case any unformatted dates get through. Note this in the record sheet under the 05 slot.

14.3.32 Run query 06A1. This puts the Region in the Client column of the Worklist Template by trimming the client name to Region X (this relates back to step 14.2.6). Run query 06A2 to verify that query 06A1 ran properly and resolve any records that appear.

14.3.33 Run query 06b1 to update the LNOTE-ANOTE MERGED column in the SAMPDATA + INVALIDS table. Skip query 06b2 and run query 06b3 to append any instances of multiple flags into the LNOTE table. In the case of multiple flags, manually update the Description column in the LNOTE table to account for both flags. Often, the second flag is just the U flag (Under Detection Limit). Make sure that this description is always listed second in the Description field. Note that these are Region-specific, particularly the A-01x flags, in the case of large data sets.

14.3.34 Run query 06c to verify that all flag descriptions in the LNOTE table appear in the LNOTE Descriptions reference table. If there are no results, move to the next step. If results appear, add the missing description from the LNOTE table to the LNOTE Descriptions table and assign the proper AQS flag, if needed. The Project Manager may need to be consulted to identify the proper description.

14.3.35 The LIMS flag D-F is used to denote any precision results with greater than a method-specific percent difference between a primary and a duplicate/collocate. This flag is applied to the duplicate or the collocate record in LIMS. Because the duplicate data are loaded into AQS in the precision data table (RP or QA), and this table does not accept flags, the flag is essentially missed; thus, the flag needs to be moved to the primary sample for coding purposes in the case of duplicates. (Because both the primary and collocate are loaded into the Raw Data table (RD) in AQS, this is not a problem for collocated pairs). Run query 06d1 to check for D2 results with D-F flags and run query 06d2 to apply the flag to the D1s. Confirm that the number of records is the same for both queries. Run query 06d3 to confirm the flag has been added correctly. Confirm that this combination of Regions and LNOTEs is in the LNOTE and LNOTE Description tables using query 06d4.

14.3.36 Run query 06e1 to count how many results have a D flag applied but the dilution factor is 1. Run query 06e2 to confirm that samples with dilutions greater than 1 have a D flag applied. Run query 06e3 to confirm the total. Resolve any issues with the D flag with the Project Manager.

14.3.37 Run query 06f1 to get a preliminary count on how many records need qualifier codes. Run query 06f2 to create the table Qualifiers. (Note, if this is a small data set, remove the link between the Region field of the LNOTE table and the LNOTE-ANOTE Merged field of the SAMP+INV table in the design of the query.) If the number of records is not the same for query 06f1 and 06f2, run query 06f3 to see where the discrepancies lie and resolve them before moving on. Run query 06f4 to update the Client field in the SAMP + INV table then run query 06f5 to count how many records should have qualifiers as a second QA step. The number of qualifiers from query 06f5 should match the number in the Qualifier table. Note the number of records in the Qualifier table on the record sheet.

14.3.38 Run query 07AA to append non-metal non-detects to the AQS RD TEMPLATE for AQS Raw Data (RD) coding. Note the number of records in the record sheet under the 07A slot. Run query 07AB to append metal non-detects to the AQS RD TEMPLATE. Also note this in the record sheet under the 07A slot.

14.3.39 Run query 07BA to append non-metal detects (and invalids) to the AQS RD TEMPLATE. Note the number of records in the record sheet under the 07B slot. Run query 07BB to append metal detects (and invalids) to the AQS RD TEMPLATE. Also note this in the record sheet under the 07B slot. On the record sheet, sum the four values under 07AA-07BB and enter into the “Total in AQS” slot.

14.3.40 Run query 07C and enter the value in the Total Excluded row of the record sheet. This value represents precision and blank data not converted yet to AQS code as well as excluded internal standards data that are not coded. This value plus the value in the “Total in AQS” slot should equal the value in the “Total in SAMP+” slot. If it does not, there is an error somewhere. Queries have been created to find some common mistakes: Run query 07D (and 07D2) to make sure the pollutants match properly. Run query 07E to verify all site-method-sample type combinations have been assigned a POC in the POC Rules table. Run query 07F to verify if there are any new sites not found in the LOOKUP – Site Info reference table. If there are still errors after these are run, further review is needed.

14.3.41 Run queries 08A and 08B to create tables for D1/C1 data and D2/C2 data, respectively. Note the numbers of records in the 08A and 08B slots on the record sheet. The number of records in each table should be similar, but may not be the same.

14.3.42 Run query 09A1 through 09A3 and note the number of records from each query on the record sheet in slot 09A. Query 09A1 puts D2 data (with a precision id of 1) in the AQS RP TEMPLATE. Queries 09A2 and 09A3 add precision records for C1 and C2 (also with a precision id of 1) for non-metals and metals, respectively.

14.3.43 Run query 09B1 (for nonmetals) and 09B2 (for metals) and note each on the record sheet in slot 09B1/2. These put R1 data into the AQS RP TEMPLATE. R1 data are available for both duplicate and collocated data (and uses a precision id of 2). Run query 09B3 and 09B4 to append replicate data for metals and nonmetals, respectively, to the AQS RP TEMPLATE for precision results for sites that do not run duplicate or collocated events. Note the number of records in the 09B3/4 slot on the record sheet.

14.3.44 Run query 09C and note the number of records on the record sheet in slot 09C. This puts R2 data (with a precision id of 3) in the AQS RP TEMPLATE. These precision data correspond to duplicate data only.

14.3.45 Run query 09D1 (for nonmetals) and 09D2 (for metals) and note each on the record sheet in slot 09D1/2. This puts R2 data into the AQS RP TEMPLATE. These precision data correspond to collocate data only (and uses a precision id of 2).

14.3.46 Total the number of records on the record sheet from slots 09A, B, C, and D and enter into the Total in RP slot.

14.3.47 Run query 10A. This creates a copy of SAMPDATA + INVALIDS (minus blanks) and pastes into SAMPDATA + INVALIDS + R1R2. Note the number of records in the 10A slot on the record sheet. Run queries 10B and 10C. These append the replicate data (for all duplicates and collocates) into the SAMPDATA + INVALIDS + R1R2 table. Note the number of records in the 10B and 10C slots on the record sheet. These should be similar (or the same) as the number of records in the 08A and 08B slots. Run query 10D to append the replicates run on Field Samples, as described in 14.3.43. Note the number of records in the 10D slot on the record sheet. Total the number of records from 10A, B, C, and D and note in the Total in UATMP slot on the record sheet.

14.3.48 Run queries 11A and 11B. These append blank data for non-detect and detect non-metals into the AQS RB TEMPLATE table. Note the number of records in the 11A/B slot on the record sheet.
Run queries 11C and 11D. These append blank data for non-detect and detect metals into the AQS RB TEMPLATE table. Note the number of records in the 11C/D slot on the record sheet. Total the number on the record sheet from slots 11A/B and 11C/D and note in the Total in RB slot. This number may match the number in the Total Excluded column on the record sheet (if the dataset didn't contain any precision data, for example).

14.3.49 If an analyte co-elutes with another, the lab practice is to report it as "ND". However, this is not entirely accurate. All co-eluters have been flagged with a BH in the Qualifier-3 column of the AQS TEMPLATE table. Run query 12A to see if there are any co-eluters in the AQS RD Template table. Because BH is not a flag, but is a null code, AQS will not accept this coding. Run query 12B to 1) move the BH from the Qualifier-3 column to the null code column, 2) remove the 0 representing the ND, and 3) remove the ND flag. Note the number of records updated in the 12 slot on the record sheet and verify that the number of records from 12A match 12B.

14.3.50 Run query 13 to check for any instances of multiple qualifier codes and resolve any results by manually splitting the codes into different Qualifier columns. Note the number of records in the 13 slot on the record sheet.

14.3.51 Run query 14A and 14B to do the same thing to the AQS RB Template table for co-eluters as step 14.3.50. Note the number of records updated in the 14 slot on the record sheet and verify that the number of records from 14A match 14B.

14.3.52 Run query 15a, 15b, and 15c to create data tables for acrolein, dichloromethane, and select GHGs as requested by the Project Manager. These tables need to be exported to Microsoft Excel and emailed to the Project Manager for a separate can study. Note the number of records on the record sheet for the 15 slot.

14.3.53 Run query 16 to add the LK flag to the Oklahoma sites' acetonitrile data. This was requested by the state as they recognize that their acetonitrile data periodically exhibits contamination issues.

14.4 Quality Assurance of the Raw Data in the "Macro" Database

14.4.1 To begin QA of the entire process, perform a manual QA of the data. Select data from the SAMP + INV + R1R2 table and write it down for a representative number of samples. Obtain the appropriate AQS codes for the method, parameter, etc., from the reference tables then use Queries QA 00a-c to visually verify that the coding is correct. These queries put in the site code, which makes it easier to find data by site. Pay special attention to any flags of interest that may have been needed for the dataset. Additionally, Query QA 00 can be used to specifically query blank sample data in the SAMP + INV table.

14.4.2 Skip Queries QA 01-02a/b and run Query QA 04 and 05 (01 through 02 are run by running Query 04-05). If the right two columns are fully populated for Query QA 04 and no results appear in 05, move to step 14.4.3. Otherwise, there is a discrepancy between the number of samples in the WORKLIST TEMPLATE and SAMP + INV + R1R2 tables that must be investigated before proceeding.

14.4.3 Run Queries QA 06-10. These queries make two tables, QA1 Dup Data and QA2 Worklist Data. QA2 is essentially a worklist that includes replicate sample information (WORKLIST TEMPLATE does not). Run Query QA 13 and 16, skipping the ones in between. These compare the number of samples in the new table QA2 Worklist Data to the number of samples in SAMP + INV + R1R2, including replicates. The number of samples for each site/method should match. If they do not, this must be reconciled, and Queries QA 16a-c may be used to try to locate any differences.

14.4.4 Run Query QA 17 and 18. These compare the number of samples in the WORKLIST TEMPLATE to the number of samples in AQS RD TEMPLATE for primary raw data only. The number for each site/method should match. If they do not, this must be reconciled, and Queries QA 16a-c may be used to locate any differences. Note Query QA 18 selects one pollutant from each method to "represent" a sample for each method.

14.4.5 Run Query QA 19 and 20a or 20b. These compare the number of precision samples in the new table, QA2 Worklist Data, to the number of precision samples in AQS RP TEMPLATE. Query 20a includes each individual replicate dates while Query QA 20b provides a count of dates. The number for each site/method should match. If they do not, this must be reconciled; Queries QA 16a-c may be used to locate any differences. Note: Because non-detect results are not included in precision data,

many hex chrome replicates do not go in AQS RP TEMPLATE. Use Query QA 16b to confirm.

14.4.6 Run through Queries QA 21a-e. These queries look for duplicate records in the SAMP + INV + R1R2, AQS RD TEMPLATE, AQS RP TEMPATE, Worklist Template, and AQS RB TEMPLATE tables. Any duplicates must be reconciled before moving forward.

14.4.7 Run Queries QA 22 and 23 or 23b. These compare the number of blank samples in the WORKLIST TEMPLATE to the number of blank samples in AQS RB TEMPLATE. Query QA23 has separate queries, the first pulls all blanks and dates, while query QA 23b performs a count per site and method, similar to step 14.4.5. The number for each site/method should match. If they do not, this must be reconciled, and Queries QA 16a-c may be used to try to locate any differences.

14.4.8 Run Query QA 24. This query verifies that all invalid samples have a null code. Results that appear in the results of the query must be given a null code.

14.4.9 Run Query QA 25a. This query confirms whether the correct MDLs are applied to the VOC and SNMOC samples, which is occasionally a problem at the beginning of a new calendar year. MDLs that are different due to dilutions do not need to be corrected. Query QA 25b can be used to review data for certain pollutants. If changes are needed, run Query QA 25c, which creates a table of all MDLs for these methods. Query QA 25e1 is used to check for samples that need updating and Query 25e2 is used to update the erroneous MDLs to the correct MDLs in the SAMP + INV + R1R2 table. Query QA 25f1 and 25f2 perform similar queries on the AQS RD TEMPLATE table. The counts of these two queries should be identical. Run Query 25g, which is identical to Query 25a, and confirms that there is only one MDL listed per pollutant.

14.4.10 Run Query QA 26a to look for any R2s associated with invalid D2s and valid D1s. These should not be loaded into AQS. Run Query QA 26b to confirm that they were not added to the AQS RP TEMPLATE. If coded properly, no records should appear.

14.4.11 Run Query QA 27 to look for instances of multiple AQS flags in a single Qualifier flag column. Separate any flags that appear by manually adding the second flag to a new Qualifier flag column (such as Qualifier-4, if empty).

14.4.12 Run Query QA 28 to check for results in scientific notation in the Sampdata + Inv + R1R2 table. Step 14.3.29 runs a similar query (Query 04D) on the Sampdata + Invalids table.

14.4.13 Ask another AQS coder to review the files to visually inspect that each file type matches the transaction type (RD, RP, etc). This reviewer shall compare at least one non-ND result for every method contained in each AQS file to the individual reports sent to the clients by the Project Manager to serve as an outside review, per Section 16.0. Both the primary AQS coder and the secondary reviewer should fill out and sign the AQC Quality Control Review Checklist (shown in Figure 24-2) in the AQS binder.

14.5 Creating and Loading Audit Results into AQS

14.5.1 Obtain ERG's quarterly NAAQS FEM Audit Results data in spreadsheet format from the QA Coordinator. Copy and paste the audit results into a new tab. Remove any excess spacing. Inset header information into new columns per the example shown in Figure 24-3.

14.5.2 In the Macro database, delete any data in the AQS RA Template table and the Audit Results table. Import the data from the new tab in the audit spreadsheet into the Audit Results table.

14.5.3 Run Query ZAudit 01 to append the results from the Audit Results table into the AQS RA Template table.

14.5.4 Copy the high-level results from the 1st Actual Value and 1st Indicated Value columns and paste next to the low-level results in the 2nd Actual Value and 2nd Indicated columns.

14.5.5 Run Query ZAudit 02 to delete the high-level result rows that are no longer needed.

14.5.6 Run Query ZAudit 03 to reduce the Indicated results down to three decimal places. Confirm that trailing zeros were not removed; add back in if needed.

14.5.7 Export to text and ask a reviewer to QA the text file.

14.5.8 Load the text files into AQS via the Exchange Network Services Center. Correct any load errors necessary. Update the Black Lab Notebook for AQS.

14.6 Exporting and Loading Raw Data into AQS

14.6.1 Compare and Compact Macro database.

14.6.2 Create a new "QX 20XX AQS" database.

14.6.3 Export the AQS TEMPLATE tables to this database from the Macro database.

14.6.4 Design Make Table and Delete queries to remove any data that doesn't need AQS upload. Design Make Table queries for any sites that want data sent to them directly. There's an electronic copy identifying such data at L:\Jaime\AQS\AQS Special Requests List.xls (Figure 24-4). These queries may be imported from other AQS databases and rerun.

14.6.5 After approval from the secondary review (per Step 14.4.13, export each RD, RP, RB, and/or RA TEMPLATE table to text by right-clicking on each table, selecting EXPORT; select TEXT as the file type and adjust file name as necessary; click on OK; select DELIMITED and then NEXT; choose OTHER and add the "|" character and chose NONE for the TEXT QUALIFIER then select NEXT; then hit FINISH. Review each file.

14.6.6 Load the text files into AQS via the Exchange Network Services Center. Correct any load errors until the data are approved in AQS and post the files for public access.

14.6.7 Update the Black Lab Notebook for AQS (notebook # 00329 as of this revision). Append the WORKLIST TEMPLATE and SAMP + INV + R1R2 tables from the MACRO database into the compiled database for the appropriate NMP reporting year.

15.0 CALCULATIONS

N/A

16.0 QUALITY CONTROL

Greater than 50 queries are located inside the Microsoft Access "Macro" database and are designed to provide a check of common errors (such as duplicate records) that may be encountered during the coding process. The AQS coder shall complete the AQS Quality Control Review Checklist upon completion of the procedures in Section 14.

A reviewer shall inspect the text files to be loaded into AQS by comparing the text files to the original reports sent to the clients by the Project Manager. The reviewer shall inspect one concentration above the detection limit per method per AQS text file and complete an AQS Quality Control Review Checklist after review, as specified in step 14.4.13.

A hardcopy of the AQS Quality Control Review Checklist shall be maintained per the instructions in Section 22.0.

17.0 PREVENTION

N/A

18.0 CORRECTIVE ACTION

N/A

19.0 WASTE MANAGEMENT

N/A

20.0 MAINTENANCE

N/A

21.0 SHORTHAND PROCEDURE

N/A

22.0 DOCUMENTATION AND DOCUMENT CONTROL

The latest version of the Macro and POC Table (for the reference tables) databases shall be posted on the L drive after every update. The current versions are posted at L:\Jaime\REFERENCES. The AQS Special Requests and AQS Record Sheet spreadsheets are also posted and kept up-to-date at L:\Jaime\AQS.

The black AQS laboratory notebook (# 00329) shall be updated whenever data is uploaded into AQS or changes are made to existing data (and associated metadata) in AQS. This notebook shall be maintained per the laboratory's record-keeping procedures.

Hard copies of the AQS Quality Control Review Checklist are maintained in the white AQS binder for a minimum of one year. Afterwards, these hard copies shall be archived per the laboratories archival procedures.

23.0 REFERENCES

Information about EPA's AQS database may be found at the following web address: http://www.epa.gov/ttn/airs/airsaqs/basic_info.htm

24.0 TABLES, DIAGRAMS, FLOWCHARTS, VALIDATION DATA

DATASET						
IMPORT QC						
IMPORT SAMP						
IMPORT WORK						
UPDATE UNITS						
UPDATE ANALYSIS						
01						
02						
03						
04						
TOTAL IN SAMP+						
05						
06						
07A						
07B						
TOTAL IN AQS						
TOTAL EXCLUDED						
08A						
08B						
09A D2/C2						
09B1/2 R1						
09B3/4 R1 for FS						
09C R2 for D2						
09D1/2 R2 for C2						
TOTAL IN RP						
10A						
10B						
10C						
10D						
TOTAL IN UATMP						
11A/B						
11C/D						
TOTAL IN RB						
12						
13						
14						
15						
16						

Figure 24-1. AQS Steps Record Sheet

Data set: _____

Date Coded: _____

AQS Coder: _____

Reviewer: _____

Method/Pollutant Group	Acceptance Criteria	Coder Initials and Date	Reviewer Initials and Date	Comments/Corrections Needed
IO-3.5 (Metals)	Results above detection limit in AQS text file must agree with result reported to the client.*			
Hexavalent Chromium	Results above detection limit in AQS text file must agree with result reported to the client.*			
TO-11A (Carbonyls)	Results above detection limit in AQS text file must agree with result reported to the client.*			
TO-15 (VOC)	Results above detection limit in AQS text file must agree with result reported to the client.*			
TO-13 (SVOC)	Results above detection limit in AQS text file must agree with result reported to the client.*			
SNMOC	Results above detection limit in AQS text file must agree with result reported to the client.*			
Other (Phenols, Methane, Audit Results, etc)	Results above detection limit in AQS text file must agree with result reported to the client.*			

N/A = not applicable to this load

*Reviewer checks 1 concentration per method per upload batch

Figure 24-2. AQS Quality Control Review Checklist

Audit Sample ID	Filter ID	Analyte	ERG Result	Assigned Value	%Recovery	%Diff	Audit	ERG ID	Date Analyzed	Analyst	Result#
RTI-2013-03-001	T2667962	Lead	2.837	2.963	95.8	-4.34	Q1 2014	3022208-10	3/11/2014	RM	1
RTI-2013-03-001	T2667953	Lead	2.703	2.963	91.2	-9.20	Q1 2014	3022208-11	3/11/2014	RM	2
RTI-2013-03-001	T2667955	Lead	2.875	2.963	97.0	-3.01	Q1 2014	3022208-12	3/11/2014	RM	3
RTI-2013-04-001	T2667982	Lead	8.801	8.994	97.8	-2.17	Q1 2014	3022208-22	3/11/2014	RM	1
RTI-2013-04-001	T2667994	Lead	8.894	8.994	98.9	-1.12	Q1 2014	3022208-23	3/11/2014	RM	2
RTI-2013-04-001	T2667996	Lead	8.691	8.994	96.6	-3.42	Q1 2014	3022208-24	3/11/2014	RM	3

Figure 24-3. Sample Lead Audit Header Information

Project	Site	Instructions	Deletion	Contacted or Sent	Separate Load or Performed
Nat'l Program	BTUT	Do not load metals			
Nat'l Program	DEMI	MI loads their data themselves. Export and email the coded text files for VOC, Carbs, SVOC to Debbie Sherrod at SHERRODD@michigan.gov			
Nat'l Program	UNVT	Wait for Robert to approve metals and PAHs data prior to loading, email when completed			
TSAT	MBNV	Code, but hold off on loading for now			
Nat'l Program	PRRI	Load their data then email Melinda Viera at Melinda.Viera@health.ri.gov			
Nat'l Program	BMCO	Waiting on site entry for BMCO; set aside for now			
Nat'l Program	WPFL	Del, Waiting for site to get QAPP completed prior to loading			
Nat'l Program	DECO/PVCO	Delete ERG's "collocated" data (POC E1)			
Nat'l Program	Jaime	Append to compiled database			
Nat'l Program	Julie	Send Acrolein&MeCl& GHG data			

Figure 24-4. AQS Special Requests List

ENGINEERING AND SCIENCE DIVISION

TITLE: SOP for use of the Laboratory Information Management System and Data Progression and Data Reporting	EFFECTIVE DATE: MAY - 6 2015
REFERENCES: ERG-MOR-010, ERG-MOR-022 , ERG-MOR-079, Element Datasystem User's Manual, Promium, LLC., Promium website, www.promium.com	
SATELLITE FILES: Chromatography, Inorganic, Prep, VOC, Mass Spec, Shipping/Receiving and Can Cleaning	
REVISIONS: Added statement about adding QC samples; Updated the sequence naming convention; Added more detail on periodic updates; Added a data qualifier to the qualifier table	
WRITER/EDITOR: NAME/DATE Lana Kronk 5/5/2015	PROJECT MANAGER/TECHNICAL DIRECTOR: NAME/DATE Julie A. Swift 5/6/15
QUALITY ASSURANCE MANAGER: NAME/DATE Donna Tedder 5/5/15	NEXT SCHEDULED REVIEW: 1/31/17

1.0 IDENTIFICATION AND PURPOSE

The purpose of this document is to describe the procedures for using the Laboratory Information Management System (LIMS) to record all sample data, information pertaining to each sample, and data reporting. The LIMS allows historical reconstruction of laboratory activities since the history of each sample is readily available. The LIMS also aids in the verification that the data meets the project needs with pre-set control limits, which allows for straightforward qualification of potential quality impacts in the report.

2.0 MATRIX OR MATRICES

N/A

3.0 METHOD DETECTION LIMIT

The LIMS system DataTool has a template called *MDL Study* that can be used to determine MDLs based on the same method used in ERG-MOR-010. Independent of how the MDLs are determined, the annual MDLs must be entered into LIMS from the QA Admin>Analysis Analyte screen. The entered MDLs are reviewed by QA staff prior to reporting.

The MDL in LIMS will be multiplied by the dilution factor which is entered into the LIMS from the instrument file. If a sample is diluted, the MDL is multiplied by the dilution factor to obtain the actual MDL of the sample, since the concentration of the minimum detectable amount will become higher with each dilution.

4.0 SCOPE AND APPLICATION

All samples at the ERG laboratory are logged, tracked, batched, data uploaded, and reported using the LIMS. Samples received at the laboratory are logged into the LIMS following the procedures in the SOP for Sample Login to the Laboratory Information Management System, ERG-MOR-079. Not every step described in this SOP is applicable to every analytical method.

User access to the LIMS is graduated. People are granted permission only to the tasks they need.

5.0 METHOD SUMMARY

Samples at the ERG laboratory are logged, tracked, batched, data uploaded, and reported using the LIMS. The system records all sample data, information pertaining to each sample, and allows for data reporting. The LIMS also aids in the verification that the data meets the project needs with pre-set control limits.

6.0 DEFINITIONS

COA	Certificate of Analysis
ERG	Eastern Research Group
ID	Identification
LIMS	Laboratory Information Management System
MDL	Minimum Detection Limit
NMP	National Monitoring Program
PM	Project Manager
QA	Quality Assurance
QAPP	Quality Assurance Project Plan

QC	Quality Control
RPD	Relative Percent Difference
SOP	Standard Operating Procedure
TL	Task Lead

7.0 INTERFERENCES

N/A

8.0 SAFETY

N/A

9.0 EQUIPMENT

Promium® Element Laboratory Management Systems (LIMS) for commercial and public sector soil, water, air testing laboratories.

10.0 MATERIALS

N/A

11.0 CHEMICALS, REAGENTS, AND STANDARDS

Information for prepared or commercially-bought standards can be entered and tracked by a LIMS-generated standard ID number in the **Standards** section of the **Laboratory** menu. Vendor certificates of analysis (COA) can be scanned, imported, and linked with the appropriate standards (SOP ERG-MOR-022).

12.0 COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

Collection, preservation, shipment, and storage information for samples received at the laboratory are logged into the LIMS following the procedures in the SOP for Sample Login to the Laboratory Information Management System, ERG-MOR-079.

13.0 CALIBRATION AND STANDARDIZATION

Calibrations can be entered into **Calibration** under the **Laboratory** menu; however, the individual chromatographic software is considered to be more useful than the LIMS calibration section at this time.

14.0 PROCEDURE

Not every step described in this section is applicable to every analysis. With periodic updates from Promium®, this section may not address every possible variation of the LIMS menus. Figure 14-1 shows the general LIMS sample data progression and statuses.

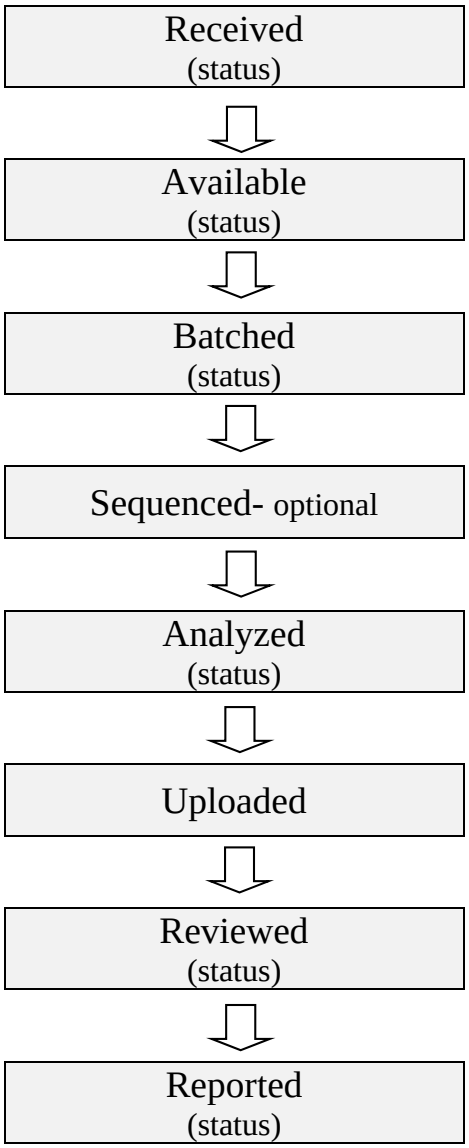

Figure 14-1. LIMS Server and Status Path for Analyses

14.1 LIMS Batch Procedure

14.1.1 Log into Element.

14.1.2 If more than one batch of samples is "Available" use the **Query Analysis Status** tool under the **Laboratory** menu. Query for available samples under the desired analysis, start by clicking **Order Results By** choosing **Sampled** and **LabNumber**. Select the desired number of samples choosing the oldest ones first unless otherwise specified.

14.1.3 From the **Laboratory** menu, select **Batch**. With the desired department selected from the drop-down menu at the left of the screen, click **Add** at the bottom, left-hand corner. A blank batch sheet will appear. (You may choose to press **Copy** instead of **Add**. Use caution here, as the analysis, surrogates, and comments from the copied batch will be included in the new batch and this information may need to be changed.)

14.1.4 Using the drop down menus, fill in or confirm the **Department**, **Preparation Method**, **Batch Matrix**, and any **Surrogates** used. Fill in the **Comments** field to include any additional information required.

14.1.5 Select the appropriate analysis from the **Available** analysis box and press the right-facing arrow button. Be sure to select the analysis denoting the correct year when there are multiple choices, such as "TO-15 yyyy", where yyyy is the year.

14.1.6 Press the **Save** button. The new LIMS-created batch number will be visible in the box to the left of the screen. The numbering scheme BYMDDNN is as follows, the first field is the letter "B". The second field is a number for the year, starting with "1" for 2011 and so on. The third field is a letter for the month of the year starting with "A" for January, the next two fields (fourth and fifth) are for day of the month, and lastly the last two fields (sixth and seventh) are for the batch # on that day.

14.1.7 Select **Bench Sheet** at the bottom of the screen or from the **Laboratory** menu. To make modifications begin by clicking the **Edit** button at bottom of the window.

14.1.8 At the top of the screen, press **Add** and select **Sample by Container**. Select the samples from the list that you would like to include in the batch. Take care to keep all primary and field blank sample pairs as well as duplicate pairs together in the same batch. **Note:** For some analyses, a maximum of twenty samples may be selected for any given batch. If more than 20 samples are selected, additional batch QC must also be added to the bench sheet and extracted to meet the method requirements.

14.1.9 Right click on a sample to bring up a menu, and select **Initial**. Fill in the value for the total collection volume. This will be listed on the sample's corresponding chain of custody, or calculated from the given flow and time values. Repeat this for each sample in the batch. Field blank samples are assigned the same volume as the primary sample collected on the same day.

14.1.10 From the right click menu choose **Comments** and fill in the site code for each sample as it appears on the bench sheet including any C1, C2, or FB designations.

Note: For some analyses two spaces are required before entering comments for formatting reasons.

14.1.11 Each batch will need a number of QC samples included. The exact requirements for batch QC will vary between analyses, but there are three common types that will be used. Each type of QC can be added to a batch using the **Add** command, but the most commonly used QC will be included in the batch automatically after samples are included for most analyses. QC samples will be named by the Batch ID followed by an identifying suffix with a numeral(x).

i. Blank Samples: Each batch will contain at least one Blank Sample (-BLKx). Be sure to confirm the presence of any surrogates used in the analysis using the right click menu.

ii. Spiked Samples: Various types of spiked samples are used in different analyses including Laboratory Control Spikes (-BSx), Matrix Spikes (-MSx), Matrix Spike Duplicates (-MSDx), and Post Spikes (-PSx). As with blank samples confirm any surrogates with the right click menu, but also include the **Spike ID**, **Type** and **Amount** for each spiking solution used.

iii. Duplicate Samples: Include one Duplicate (-DUPx) QC sample for each duplicate or collocated sample in the batch. Using the right click menu assign a **Source** sample to each Duplicate, and change the **Initial** volume to match that of the source sample.

14.1.12 Once all field sample, QC samples have been added and the required information has been updated, print any necessary copies of the bench sheet. If an extraction log is kept, store a copy of the bench sheet in it. A copy of the bench sheet is also kept with the chain of custodies for that batch.

14.2 LIMS Sequence Procedure

14.2.1 From the **Laboratory** menu, select **Sequence**.

14.2.2 Click **Add** at the top right, window labeled **Template ID** will appear. Select the template for the desired method or choose cancel to continue without a template.

14.2.3 Click the pull-down menu for **Source Batch** and select a batch for analysis. Next click **Add** and first select **Batch QC Sample**. This shows a list of all blanks, spikes, and duplicates. Select all the QC samples that will be run in the sequence and double click to add them to the sequence. Repeat this choosing **Add** again but selecting **Batch Sample** to add all desired LIMS samples. It is necessary to keep all primary/field blank pairs and duplicate sample pairs with all corresponding QC samples together in the same sequence.

14.2.4 In addition to Batch QC, Sequence QC must also be included. If using a template the most common sequence QC will be added automatically but any QC sample can be manually added from the Add command.

14.2.5 Once all samples and QC are placed in a sequence they must be placed in the desired run order as per method requirements, typically beginning with QC checks and then sets of samples broken up by additional running QC, and ending with any final QC.

14.2.6 After establishing a desired run order right click on any QC or calibration standards and choose **Standard ID,** then double click on the LIMS standard used in the selected sample. If an internal standard is used select all samples in the sequence and select the correct **Internal Standard ID** using the right click menu. Any sample

prepared from an existing sample (such as PS, BS, or SRD) also needs the **Source Sample** defined using the right click menu.

14.2.7 Once completed, review the sequence for any omissions or errors, make necessary corrections, and click the green **Save** button.

14.2.8 Print a copy of the sequence. File the sequence print out in the appropriate location. The numbering scheme YYMMXXX is as follows, the first field is "YY" for the last two digits of the year. The second field is "MM" for the month number. The third field is "XXX" for the number of sequence in the order they are created starting with 001.

14.3 LIMS Data Upload Procedure

14.3.1 The sample data generated on the instruments is reduced by the analyst via instrument software. When data reduction is complete for a batch or sequence of samples, the analyst will transfer the data from the instrument computer to network server 'bart' (Y:). This server is backed-up daily.

14.3.2 To begin data upload onto LIMS, open **Element**. Go to the **Laboratory** menu and click on **Data Entry/Review.** First choose the department of the analysis being uploaded from the drop down menu on the left, and then in the top left corner choose **Sequence** or **Batch** depending on the analysis. Select the desired sequence or batch from the list and click on **Create** in the **Data Entry** tab in the top right corner. Next click **DataTool**. In DataTool, select the appropriate **File Type** at the top right and choose y: [\\bart\airtoxics] under **Drives**. In the box below choose the folder containing the desired instrument data files.

14.3.5 All of the data files for that sequence will appear in the lower right-hand box. Double-click on the appropriate data file/s or click **Auto Select** for each file that needs to be included in the sequence.

Note: Only undiluted samples and sequence QC should be included here.

14.3.6 Press **Done** when all sample and QC files have been selected to return to the main window. Click **Merge Files** at the bottom of the window.

Data Tool will merge the files and show the data in the Data Transfer window.

Note: Review the content of the top windows in the Data Transfer window for red text indicating unmatched data. If there is any red text, the DataTool cross table requires editing. If possible, match the unmatched data and proceed. If needed, seek the advice of the TL or the LIMS administrator to correct this.

14.3.7 Press **Save** and save this new spreadsheet with any filename.

14.3.8 In Element, at the **Data Entry/Review** window, the merged data will automatically be imported into the data entry table. Press **Save** to save the data to Element and then **Query** in the **Data Review** box. Element will perform all necessary calculations at this point.

14.3.9 In the **Data Entry/Review** window, samples and QC can be reviewed for pass/fails. Any data that does not pass its assigned criteria will have red text. Use the *Summary of Quality Control Procedures* tables in the individual analytical SOPs or in Section 4.0 of the NMP QAPP to decide if criteria have been met and the appropriate corrective action (flagging data, voiding sample, etc.) have been applied. The possible data qualifiers are listed in Table 24-1. Change the Status to "Reviewed".

14.4 After data is uploaded into LIMS, the data package is reviewed by TL using the QA review checklist from the individual analytical SOPs. After which, 10% is reviewed by the QA staff using the same checklist. After the QA staff review, the data is ready for reporting.

14.5 Data reporting is to be done by the Project Manager (PM). The QA staff will notify the PM when their review is complete. Samples marked "Reviewed" are available for final reporting.

14.6 LIMS Data Reporting Procedure

14.6.1 Go to the **Project Management** menu and click on **Reports.**

14.6.2 First choose the client and project of the data being reported from the drop down menu on the top.

14.6.3 Choose a standard **Format** for the report and electronic data deliverable (EDD) or choose a **Custom** format for the report or the EDD.

14.6.4 Choose a **Destination** for the EDD and a printer for the report (PDF995).

14.6.5 On the left side of the screen, select the desired work orders.

14.6.6 Check the appropriate analysis box in the middle screen.

14.6.7 Next click **Modified Final**, if a note to mark the work order as "Closed" comes up, press **No.**

14.6.8 Now choose the samples (and QC, if needed) to be reported in the window that opens up and click **Continue**. The PDF report opens up. Save all but the last page of the report to the desired destination. The EDD, which is an Excel file, is generated at the same time and located in the destination chosen in a previous step.

14.6.9 Invalid samples are listed in the report letter to the client or as a separate excel table.

The reporting formats are templates and have been set up with certain required elements. These reports contain the data qualifiers, footnotes, MDLs, and final units assigned to the reported data. Data reporting is typically done monthly, with a month's worth of samples reported for an individual site. A comprehensive annual NMP data report is prepared each year and includes data statistics, data characterization, and program-wide quality discussion.

15.0 CALCULATIONS

When necessary, standardized procedures for transforming raw data from measured units to final concentrations use calculations listed in the individual analytical SOPs. These calculations were set up in the LIMS and verified annually by QA staff. The TO-15 and SNMOC initial and final units are the same, ppbv and ppbC, respectively. The TO-11A initial units are µg/mL and final units are ppbv. TO-13A has initial units of ng/µL and final units of ng/m^3. The metals analysis has initial units of ng/L and final units of ng/m^3. Hexavalent chromium has initial units of ng/mL and final units of ng/m^3.

Promium® provides a LIMS worksheet to validate algorithms that are utilized in the LIMS system to perform calculations, such the final results from the initial results, standard percent recovery, and RPD between replicate analyses. In the **Print** window,

press **Analysis Info** and choose the template "axi-validation". These calculations are verified with hand calculations biannually by QA staff and documented.

16.0 QUALITY CONTROL

16.1 Each section in LIMS has an "Audit" button. Clicking this button will open a new window that displays the changes made in the applicable section. Element keeps track of the who, when, and what during the editing of information in the LIMS. Right-clicking the mouse in the audit window allows the information to be sorted in various ways and also allows the audit information to be exported or printed.

16.2 Data quality criteria are addressed in the individual analytical SOPs. Data quality and data reduction is reviewed by the TL and 10% of the data is subsequently reviewed by QA staff.

16.3 Data reports are reviewed by the PM prior to being sent to the client.

Note: If requested by a client, uncertainty values can be entered into the Analysis/Matrix screen.

17.0 PREVENTION

N/A

18.0 CORRECTIVE ACTION

Promium® updates are available for the LIMS software automatically and occur often. See the LIMS administrator for any LIMS issues.

19.0 WASTE MANAGEMENT

N/A

20.0 MAINTENANCE

The LIMS system is under an annual service contract with Promium® maintained by the Office Manager. The LIMS administrator is responsible for supporting the periodic updates initiated by Promium®. The Promium updates are first uploaded to an updates folder, then into the LIMS. The updates are uploaded after the monthly reports go out to give the administrator time to fix any potential issues found during testing. The current version number is located at the top of the dashboard.

21.0 SHORTHAND PROCEDURE

N/A

22.0 DOCUMENTATION AND DOCUMENT CONTROL

N/A

23.0 REFERENCES

Element Datasystem User's Manual, Promium®, LLC
Promium website, www.promium.com; also available on the Help menu in the LIMS system.

24.0 TABLES, DIAGRAM, FLOWCHARTS, VALIDATION DATA

Table 24-1. List of LIMS Data Qualifiers

Qualifier	Description
9	Negative value detected – Zero reported
A-01	(Custom Value)
B	Analyte is found in the associated blank as well as in the sample. (CLP B-flag)
B-01	Value is laboratory reagent-blank subtracted.
B-02	Method Blank value exceeds MDL due to background from filter media. Acceptable LRB analysis data indicates the batch was not contaminated.
B-04	Value is laboratory method blank subtracted.
BS-01	Recovery is biased due to high humidity.
C-02	This result was determined using the calibration from the confirmation column.
CE	Not reportable due to a co-eluting compound.
D	This result obtained by dilution.
D-01	This result obtained by diluting and reanalyzing the sample.
D-F	Duplicate exceeds DQO criteria.
D-R	Duplicate RPD greater than 20%; however, parent sample and duplicate values are less than 10 times the MDL.
E	The concentration indicated for this analyte is an estimated value above the calibration range of the instrument. This value is considered an estimate. (CLP E-flag)
GC-BS	Compound exceeds Blank Spike criteria.
I-01	Due to matrix interference, the sample cannot be accurately quantified. The reported result is qualitative.
I-02	This result is outside of the EPA recommended holding time.

Table 24-1. List of LIMS Data Qualifiers (continued)

Qualifier	Description
I-03	Polyatomic interference in ICS standard. Interferent not present in significant levels in samples.
ICS-01	Interference check exceeds criteria.
INT	Not reportable due to interference.
J	Detected but below the Reporting Limit; therefore, result is an estimated concentration. (CLP J-Flag)
L-01	Analyte exceeds HSV criteria. Sample concentrations below the CCV value are accepted based on acceptable CCV recovery.
LK	Analyte identified; Reported value may be biased high.
LL	Analyte identified; Reported value may be biased low.
MS-01	Non-homogeneous matrix interference. Serial Dilution and /or Post spike verifies parent sample value.
NC	Analyte could not be confirmed using the confirmation column.
O-01	This compound is a common laboratory contaminant.
O-02	Due to matrix interference, the sample cannot be accurately quantitated. The reported result is qualitative.
O-03	The concentration reported is an estimated value above the linear quantitation range. Dilution and reanalysis is being performed and an amended report will follow.
O-04	This sample was analyzed outside the EPA recommended holding time.
O-05	This sample was extracted outside the EPA recommended holding time.
PRELIM	Preliminary result. Revised report to follow.
PS-01	Post spike exceeds DQO criteria.
PS-02	Post spike was outside of the control limits due to matrix interference.
QB-01	Compound fails method blank criteria
QB-02	The method blank contains analyte at a concentration above the MRL; however, concentration is less than 10% of the sample results, which is negligible according to method criteria.
QM-01	The spike recovery for this QC sample is outside of established control limits due to sample matrix interference.
QM-05	The spike recovery was outside acceptable limits for the MS and /or MSD due to matrix interference. The LCS and /or LCSD were within acceptable limits showing that the laboratory is in control and the data is acceptable.
QM-06	Due to noted non-homogeneity of the QC sample matrix, the MS/MSD did not provide reliable results for accuracy and precision. Sample results for the QC batch were accepted based on LCS/LCSD percent recoveries and RPD values.
QM-07	The spike recovery was outside acceptance limits for the MS and/or MSD. The batch was accepted based on acceptable LCS recovery.

Table 24-1. List of LIMS Data Qualifiers (continued)

Qualifier	Description
QM-4X	The MS/MSD recovery exceeds criteria because the parent sample concentration is greater than 4 times the spike concentration. Sample results for the QC batch were accepted based on acceptable BS/BSD recoveries.
R-F	Replicate exceeds DQO criteria.
S-01	The surrogate recovery for this sample is not available due to sample dilution required from high analyte concentration and/or matrix interference.
S-02	The surrogate recovery for this sample cannot be accurately quantified due to interference from coeluting organic compounds present in the sample extract.
S-04	The surrogate recovery for this sample is outside of established control limits due to a sample matrix effect.
S-06	The recovery of this surrogate is outside control limits due to sample dilution required from high analyte concentration and/or matrix interference.
S-DUP	Duplicate analysis confirmed surrogate failure due to matrix effects.
S-FS	These surrogates are not spiked in the method blank(s) or blank spike(s).
S-GC	Surrogate recovery outside of control limits. The data was accepted based on valid recovery of the remaining surrogate.
S-HI	High surrogate recovery was confirmed as a matrix effect by a second analysis.
S-LIM	Surrogate recoveries outside method QC limits. Site matrix effects verified by 10% duplicate analysis (including sample duplicate and MS/MSD analysis).
S-LOW	Low surrogate recovery confirmed as a matrix effect by a second analysis.
S-MS	Surrogate recovery outside of acceptance window confirmed as matrix effect by analysis of MS/MSD on this sample.
S-QC	The Surrogate result exceeded the QC limits; however, the percent recovery was acceptable. Sample results for the QC batch were accepted based on percent recoveries of the QC data.
SRD-01	Serial dilution exceeds the control limits.
S-Rec	Sample received by laboratory outside of initial extraction hold time – 14 days.
U	Under detection limit.
Z-01	(Custom Value)

Appendix B

DRI Standard Operating Procedures

DRI STANDARD OPERATING PROCEDURE

X-Ray Fluorescence (XRF) Analysis of Aerosol Filter Samples (PANalytical Epsilon 5)

DRI SOP #2-209.8
Revised October 3, 2014

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1. GENERAL DISCUSSION

1.1 Purpose of procedure

This standard operating procedure is intended to:

- provide a very basic understanding of the principles of X-Ray Fluorescence (XRF) analysis;
- describe a method for the determination of elemental concentrations from ambient and source aerosol filter samples using the PANanlytical Epsilon 5 XRF analyzer;
- detail the concerns and procedures which will ensure a state-of-the-art XRF analysis measurement process.

This procedure will be followed by all analysts at the Environmental Analysis Facility of the Division of Atmospheric Sciences of the Desert Research Institute.

1.2 Measurement principle

Analysis of aerosol filter samples using the PANalytical Epsilon 5 XRF analyzer is based on energy dispersive x-ray fluorescence of elemental components in a thin film sample. The emissions of x-ray photons from the sample are integrated over time and yield quantitative measurements of elements ranging from aluminum (Al) through uranium (U) and semi-quantitative measurements of sodium (Na) and magnesium (Mg). A spectrum of X-ray counts versus photon energy is acquired and displayed during analysis, with individual peak energies corresponding to each element and peak areas corresponding to elemental concentrations. The advantages of XRF analysis include high sensitivity for a number of elements, the ability to analyze small quantities of sample, and the non-destructive nature of the analysis. In addition, because x-ray fluorescence depends on the quantum absorption and emission of photons at the M, L, and K orbitals, the technique is insensitive to the chemical state of the elements. Disadvantages include the subjection of the sample to a vacuum, resulting in loss of some volatile species such as hydrocarbons, ammonia, nitrate, chlorine, and bromine.

The source of x-rays in the PANalytical Epsilon 5 analyzer is a side window dual anode x-ray tube with both Scandium (Sc) and Tungsten (W) anodes. X-rays are focused on one of 11 secondary targets which in turn emit polarized x-rays used to excite a sample. X-rays from a secondary target are absorbed by the sample, exciting electrons to high level orbitals. As the electrons return to their ground state, photons are emitted which are characteristic of the quantum level jumps made by the electron; the energy of the emitted photons are, therefore, characteristic of the elements contained in the sample. The fluoresced photons are detected in a solid state Germanium X-ray detector. Each photon that enters the detector generates an electrical charge whose magnitude is proportional to the photon's energy. The electrical signals from the detector are sorted into energy channels, counted, and displayed. A sample spectrum consists of characteristic peaks superimposed on a background caused by the scatter of x-rays from the tube into the detector. Spectra are collected for a specified length of time and stored on disk for later processing.

DRI uses seven different analysis conditions during a single analysis run to maximize sensitivity to the full range of elements reported. Each of the analysis conditions, which correspond to different

secondary targets, x-ray tube voltage and current, and energy detection range, is designed for a specific group of elements.

1.3 Measurement interferences and their minimization

The XRF is subject to measurement uncertainties from:

- Too much deposit material. Because DRI's XRF analysis and data processing programs for aerosol samples are designed specifically for thin films, x-ray spectra are subject to distortion if unusually heavy deposits are analyzed. This is due to internal absorption of both incident and emitted x-rays within the samples. Optimum loading is ~150 $\mu g/cm^2$ (1 mg/filter for 37 mm filters and 2 mg/filter for 47 mm filters). Adjustments in filter deposit area and sampling time and flow should be made to insure deposits are within this range.

- Too little deposit material. At low concentrations counting statistics and signal noise will dominate the calculations of elemental concentrations. Adjustments in filter deposit area and sampling time and flow should be made to insure deposits are at least 15 $\mu g/cm^2$.

- Inhomogeneous deposits. The x-ray beam is focused on an area ~ 9 x 16 mm in the center of the filter. The results are extrapolated to the entire deposit area of the filter during data processing. Therefore, the center of the filter must be representative of the entire deposit. This effect is minimized by using the sample spinner during analysis which rotates the sample cup at 12 rpm.

- Large particles. Absorption of both incident and emitted x-rays occurs in the presence of large particles. This particularly affects the light elements (Na through sulfur [S]). In addition, large particles may be enriched in certain elements and may bias results in the same matter as inhomogeneous deposits.

- Filter thickness. Increased x-ray scattering is caused by increased filter thickness, increasing in turn the spectral background and causing problems for accurate background subtraction and quantification of elements at low concentrations. Additional uncertainties are introduced if filter thickness varies considerably within a lot, again making accurate background subtractions difficult. The solutions to these problems include using filters from a reputable manufacturer (e.g., Pall, Whatman, MTL), including blanks from each manufacturing lot in the formulation of background/blank spectra, and inspecting each filter over a light table before use.

- Background contamination. While small levels of contaminations may be corrected during blank subtraction, such contaminations rarely are at consistent levels, and uncertainties can be relatively high, particularly if the contaminants correspond to elements of interest. Using filters from reputable manufacturers and performing acceptance tests on all manufacturing lots will reduce the affect of contaminations.

- Filter types. The DRI XRF analysis and data processing procedures are primarily oriented toward Teflon membrane filters, which are analytically clean, are thin to reduce scattering, and have known pore size and particle collection efficiencies. Historically, glass or quartz fiber filters have been used for Total Suspended Particulate (TSP) or PM_{10} monitoring. These filters may be analyzed but, due to their composition, render analysis results for light elements

meaningless. Since particles are trapped within the filter matrix of quartz or glass-fiber filters, x-ray absorption within the filter fibers adds additional uncertainty. In addition, blank contamination levels and variations among manufacturers and manufacturing lots can be orders of magnitude higher for glass or quartz-fiber filters than for Teflon. Recommended filters are Teflon membrane filters from Pall or Whatman.

- Damaged filters. Uncertainties in results from analyzing the damaged portion of a filter are obvious. However, the x-ray signal is heavily dependent upon distance of the filter from the x-ray tube and from the detector. If filter is damaged so as to cause sagging or puckering which changes these distances, analysis results will also be affected.

1.4 Ranges and typical values of measurements obtained by this procedure

A wide range of aerosol concentrations can be measured with this method, provided adjustments to deposit area and sampling flow and time are made to insure optimum loading on the filters (~150 $\mu g/cm^2$). Filter loadings between 15 and 1000 $\mu g/cm^2$ may be used, but results for heavily loaded samples may require manual corrections during data processing and results for lightly loaded filters will have concentrations below detection limits for many elements.

1.5 Typical lower quantifiable limits

The lower quantifiable limits (LQLs) of DRI's XRF analysis depend on a number of factors, including type of filter media, manufacturer of filter media, consistency of filters with respect to thickness and background contaminations, analysis counting time, analysis conditions, and element. Typical three sigma minimum detection limits for Teflon membrane filters are presented in Table 1-1.

Precision is determined largely by the homogeneity of the filter deposit, rather than the analyzer itself. DRI specifications call for ±10% on each element or within ±3 times the analytical uncertainties, whichever is larger. The analytical uncertainties are propagated from the counting statistics of the elemental peaks and background spectra.

1.6 Responsibilities of personnel for carrying out portions of this procedure

All analysts in the laboratory should read and understand the entire standard operating procedure prior to performing XRF analysis, which includes system operation, actual analysis, data processing, and immediate review of the QA data as it is produced to correct system problems.

It is the responsibility of the XRF supervisor to ensure the XRF analyses procedures are properly followed, to examine and document all replicate, QA standards, calibration results, and acceptance test data, to designate samples for reanalysis, to arrange for maintenance and repair, to maintain the supplies and gases necessary to insure uninterrupted analysis, and to deliver the analysis results to the project manager within the specified time period.

Table 1-1. MDLs.

	MDL (µg/cm2)		MDL (µg/cm2)		MDL (µg/cm2)
Na	0.204	Cu	0.002	Sb	0.023
Mg	0.176	Zn	0.004	Cs	0.036
Al	0.038	Ga	0.006	Ba	0.042
Si	0.009	As	0.004	La	0.048
P	0.006	Se	0.002	Ce	0.090
S	0.001	Br	0.002	Sm	0.087
Cl	0.003	Rb	0.001	Eu	0.071
K	0.006	Sr	0.002	Tb	0.071
Ca	0.014	Y	0.002	Hf	0.032
Sc	0.057	Zr	0.006	Ta	0.018
Ti	0.007	Nb	0.005	W	0.013
V	0.001	Mo	0.003	Ir	0.006
Cr	0.002	Pd	0.012	Au	0.007
Mn	0.003	Ag	0.006	Hg	0.006
Fe	0.002	Cd	0.005	Tl	0.004
Co	0.002	In	0.009	Pb	0.004
Ni	0.002	Sn	0.013	U	0.005

1.7 Definitions

MLK Lines: A series of x-ray lines corresponding to electron transitions to the M, L. and K orbitals.

Secondary Target: A metal foil upon which the primary x-rays from the x-ray tube are focused. Emission of "secondary" x-rays are in turn focused on the sample to be analyzed.

1.8 Related procedures

- SOP's related to XRF analysis activities which should be reviewed in conjunction with this document are:
- DRI SOP #6-014r1 Laboratory Ethics.
- DRI SOP #6-015r1 Demonstration of Capability.
- Any SOP's dealing with filter handling and shipping in conjunction with the specific sampling method used.
- DRI SOP #6-013r0 Creation, Revision, Distribution, and Archiving of Standard Operating Procedures.

The programming, maintenance, and troubleshooting manuals for the PANalytical Epsilon 5 system.

2. APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and instrumentation

The PANalytical Epsilon 5 EDXRF analyzer contains two main components, the XRF cabinet (Figure 2-1) and the computer workstation. The XRF cabinet includes an integrated robotic sample changer and a sample chamber that can hold up to 51 samples. The large sample chamber allows almost continuous analysis of samples by allowing operators to load and unload samples in the queue while an analysis is taking place in the isolated analysis chamber.

Figure 2-1. PANalytical Epsilon 5 x-ray cabinet.

2.1.1 Characterization

The PANalytical EDXRF analyzer running under DRI's analysis protocol uses seven different excitation conditions to maximize sensitivity to select groups of elements (see Table 2-1). Each sample is placed in the analysis chamber and analyzed under a vacuum.

Table 2-1. Summary of Epsilon 5 analysis conditions.

Z	Element	Condition	Analysis time	Line	ROI (LL) Kev	ROI (UL) Kev	Secondary target	kV	mA
11	Na	@CaF_2	400	Ka	0.983	1.098	CaF_2	25	24
12	Mg	@CaF_2	400	Ka	1.195	1.313	CaF_2	25	24
13	Al	@CaF_2	400	Ka	1.426	1.547	CaF_2	25	24
14	Si	@CaF_2	400	Ka	1.677	1.802	CaF_2	25	24
15	P	@CaF_2	400	Ka	1.945	2.075	CaF_2	25	24
16	S	@CaF_2	400	Ka	2.242	2.376	CaF_2	25	24
17	Cl	@CaF_2	400	Ka	2.552	2.690	CaF_2	25	24
19	K	@CaF_2	400	Ka	3.239	3.386	CaF_2	25	24
20	Ca	@Fe	300	Ka	3.614	3.767	Fe	40	15
21	Sc	@Fe	300	Ka	4.011	4.170	Fe	40	15
22	Ti	@Fe	300	Ka	4.415	4.603	Fe	40	15
23	V	@Fe	300	Ka	4.853	5.046	Fe	40	15
24	Cr	@Fe	300	Ka	5.310	5.510	Fe	40	15
25	Mn	@Ge	300	Ka	5.792	5.998	Ge	75	8
26	Fe	@Ge	300	Ka	6.292	6.505	Ge	75	8
27	Co	@Ge	300	Ka	6.814	7.033	Ge	75	8
28	Ni	@Ge	300	Ka	7.358	7.585	Ge	75	8
29	Cu	@Ge	300	Ka	7.920	8.153	Ge	75	8
30	Zn	@Ge	300	Ka	8.504	8.747	Ge	75	8
31	Ga	@Mo	300	Ka	9.112	9.363	Mo	100	6
33	As	@Mo	300	Ka	10.390	10.661	Mo	100	6
34	Se	@Mo	300	Ka	11.064	11.344	Mo	100	6
35	Br	@Mo	300	Ka	11.755	12.047	Mo	100	6
37	Rb	@Mo	300	Ka	13.208	13.525	Mo	100	6
38	Sr	@Mo	300	Ka	13.967	14.296	Mo	100	6
39	Y	@Mo	300	Ka	14.748	15.092	Mo	100	6
40	Zr	@Ag	300	Ka	15.554	15.912	Ag	100	6
41	Nb	@Ag	300	Ka	16.382	16.755	Ag	100	6
42	Mo	@Ag	300	Ka	17.233	17.623	Ag	100	6
46	Pd	@CeO_2	300	Ka	20.866	21.331	CeO_2	100	6
47	Ag	@CeO_2	300	Ka	21.833	22.320	CeO_2	100	6
48	Cd	@CeO_2	300	Ka	22.824	23.333	CeO_2	100	6
49	In	@CeO_2	300	Ka	23.839	24.373	CeO_2	100	6
50	Sn	@CeO_2	300	Ka	24.878	25.437	CeO_2	100	6
51	Sb	@CeO_2	300	Ka	25.942	26.528	CeO_2	100	6

Table 2-1. Continued.

Z	Element	Condition	Analysis time	Line	ROI (LL) Kev	ROI (UL) Kev	Secondary target	kV	mA
55	Cs	@CeO_2	300	Ka	4.182	4.375	CeO_2	100	6
56	Ba	@Al_2O_3	300	Ka	31.633	32.379	Al_2O_3	100	6
57	La	@Al_2O_3	300	Ka	32.847	33.630	Al_2O_3	100	6
58	Ce	@Al_2O_3	300	Ka	34.089	34.911	Al_2O_3	100	6
62	Sm	@Al_2O_3	300	Ka	39.319	40.322	Al_2O_3	100	6
63	Eu	@Al_2O_3	300	Ka	40.696	41.750	Al_2O_3	100	6
65	Tb	@Al_2O_3	300	Ka	43.532	44.696	Al_2O_3	100	6
72	Hf	@Mo	300	La	7.739	8.006	Mo	100	6
73	Ta	@Mo	300	La	7.981	8.254	Mo	100	6
74	W	@Mo	300	La	8.227	8.507	Mo	100	6
77	Ir	@Mo	300	La	8.987	9.287	Mo	100	6
79	Au	@Mo	300	La	9.514	9.827	Mo	100	6
80	Hg	@Mo	300	La	9.784	10.104	Mo	100	6
81	Tl	@Mo	300	La	10.057	10.386	Mo	100	6
82	Pb	@Mo	300	La	10.332	10.669	Mo	100	6
92	U	@Ag	300	La	13.309	13.743	Ag	100	6

2.1.2 Safety Systems

Chapter 3 of the "Epsilon 5 EDXRF Spectrometer System User's Guide" contains a complete description of all safety precautions that need to be adhered to while operating the XRF analyzer. The most important of these are described below

Exposure to X-rays:

The X-ray cabinet contains two indicators that tell personnel in the laboratory that x-rays are being produced: the yellow "X-ray emitting lamp" on top of the cabinet will be illuminated and the three yellow "X-rays ON" lamps on the control panel will also be illuminated. If any of these lamps fail the x-ray source is automatically shut off. X-ray dosimeters are placed in the XRF laboratory on the instrument cabinet, at the computer workstation and at the entrance door. These dosimeters are collected quarterly by the UNR Radiation Safety Office for analysis. Exposure reports are kept in the XRF laboratory Radiation Safety Manual and can be reviewed at any time.

Exposure to Beryllium:

The spectrometers x-ray detector and x-ray tube contain toxic Beryllium (Be), but during normal operation these units are sealed within the x-ray cabinet and the operator should have no contact with either assembly. If it is necessary to gain access to one of these assemblies contact the XRF laboratory supervisor first.

2.1.3 Maintenance

Routine maintenance of the Epsilon 5 includes:

Filling the liquid Nitrogen dewar:

The Ge X-ray detector is liquid nitrogen cooled to provide stability. The dewar has a capacity of 20 liters, which under normal operating conditions should last two weeks. To prevent the dewar from ever running dry, it should be refilled at least weekly. Common practice is to fill the dewar on Friday. Refer to section 3.3.3 of the System Users Guide for detailed safety information regarding the handling of liquid nitrogen. The detector temperature and LN2 level are monitored by the instrument and can be checked in the software. To check these parameters, open the "Maintenance Spectrometer", menu then click on the detector symbol (see Figure 2-2). This action will open the detector window from which the level and temperature as well as several other detector parameters are displayed.

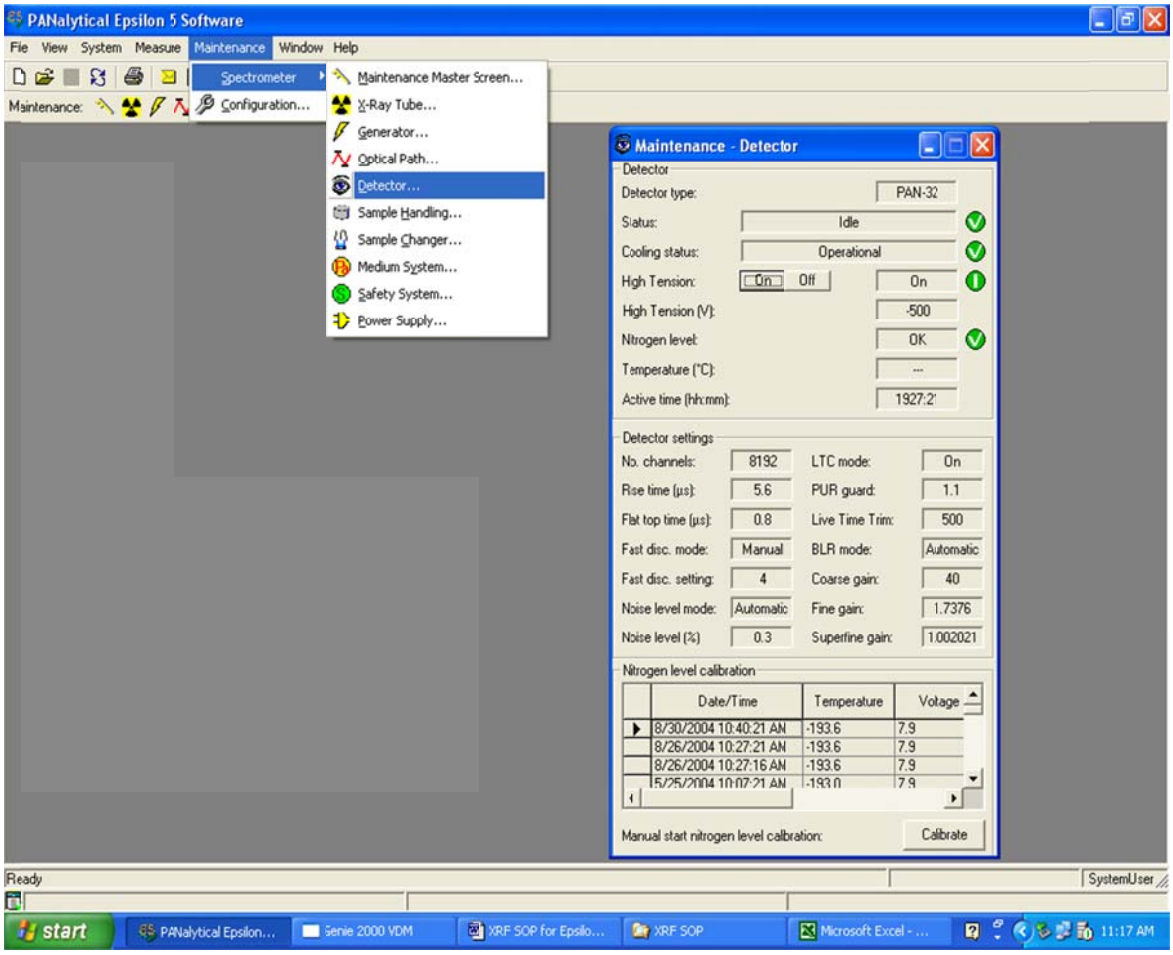


Figure 2-2. Software detector maintenance screen.

Filling the X-ray tube cooling water vessel:

Since the instrument must be shut down prior to filling of the x-ray tube cooling water vessel, this procedure should only be accomplished by the XRF laboratory supervisor. Detailed instructions for this procedure are contained in the Epsilon 5 software Help, under the "User Maintenance", "Routine" menus.

Checking the vacuum pump oil level

Since the instrument must be shut down prior to checking the vacuum pump oil level, this procedure should only be accomplished by the XRF laboratory supervisor. Detailed instructions for this procedure are contained in the Epsilon 5 software Help, under the "User Maintenance", "Routine" menus.

2.1.4 Spare parts list

It is essential that the following spare parts and supplies be kept on hand to insure minimal interruptions in analysis:

- Mylar sheets, 2 X 2" precut squares, 3.6 μm thickness (Somar Spectrofilm, #3615-33).
- Tweezers for handling filters (Millipore flat tipped stainless steel tweezers, #62-000067).
- Kimwipes, large (VWR, #34255) and small (VWR, #34155).
- Copies of current "Epsilon 5 XRF Analysis Logsheet".

2.1.4.1 Reagents

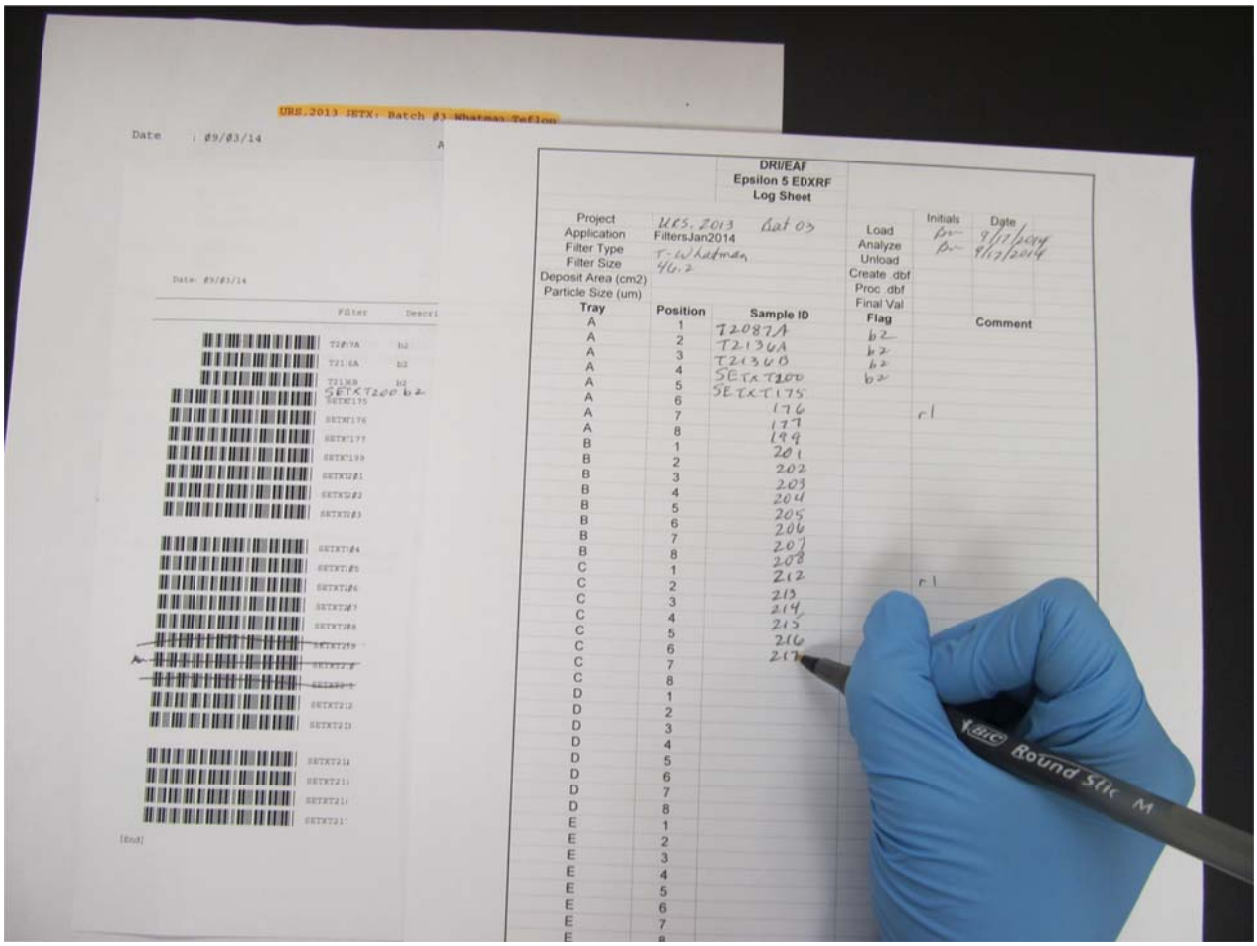
The chemicals required for XRF analysis are:

- methanol in a squeeze bottle for cleaning the sample holders and the filter loading area
- liquid nitrogen for detector cooling

2.1.4.2 Forms

All samples are logged into the EAF LAN upon receipt at the laboratory. A sample analysis list will be prepared by the laboratory or XRF supervisor indicating which samples will be analyzed and any special instructions. Filter IDs from the analysis list are transferred to the XRF analysis log sheet when filters are loaded into the machine for analysis. Figure 2-3 shows an example of analysis list and logsheet.

Figure 2-3. Sample Analysis list.



3. CALIBRATION STANDARDS

3.1 Preparation of working standards, ranges of standard values, and traceability to primary standards

Three types of standards are used with the DRI XRF: elemental thin film standards from µMatter, multiple element thin film standards from µMatter, and NIST certified standards. None of these standards require preparation; they are used as received from the supplier. The µMatter standards are stored in PetriSlides and kept in a cool dark cabinet when not in use to retard oxidation and loss of volatile elements. NIST standards are stored in the XRF room in the sample cabinet at ambient conditions. Certificates of elemental concentrations are provided by the manufacturer and are filed in the XRF lab.

3.2 Use

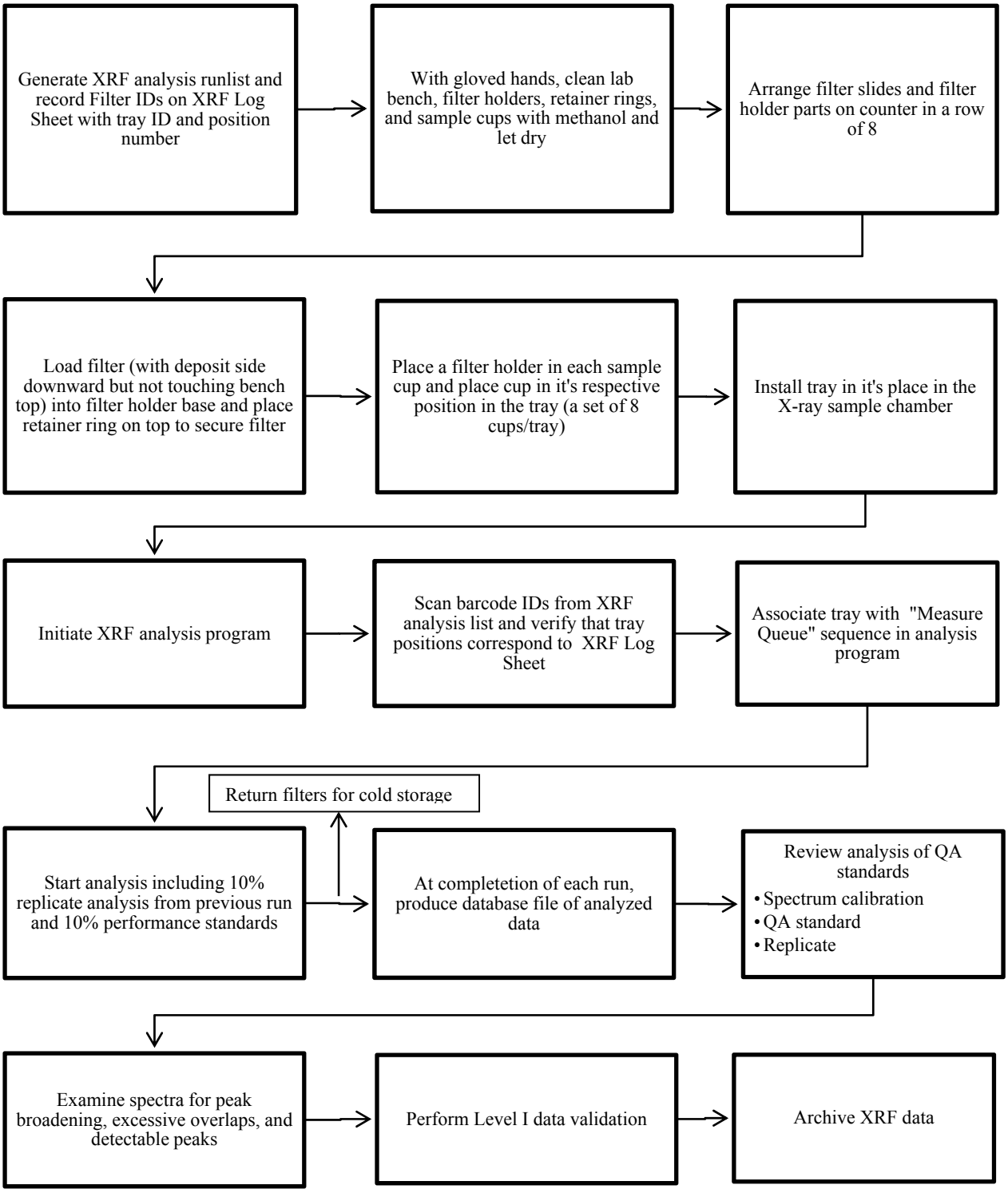
The DRI XRF system is recalibrated approximately every 12 months using the μMatter thin film standards. Recalibration is also performed whenever the QA standard indicated a drift of >±5% in calibration. Standards including elements from Na to U are analyzed in standard 47 mm filter holders under the filter analysis application (Filterxxxyy, where yyy = month and xx = year). Calibration factors in $\mu g/cm^2$ per counts per second per milliamp are calculated for each element using linear regression analysis by the Epsilon 5 software package.

3.3 Typical accuracy of calibration standards

The μMatter standards are accurate to ±5% relative, as stated by the manufacturer.

4. PROCEDURES

The typical flow of samples and data for DRI XRF analysis is depicted in Figure 4-1.


Generate XRF analysis runlist and record Filter IDs on XRF Log Sheet with tray ID and position number
With gloved hands, clean lab bench, filter holders, retainer rings, and sample cups with methanol and let dry
Arrange filter slides and filter holder parts on counter in a row of 8
Load filter (with deposit side downward but not touching bench top) into filter holder base and place retainer ring on top to secure filter
Place a filter holder in each sample cup and place cup in it's respective position in the tray (a set of 8 cups/tray)
Install tray in it's place in the X-ray sample chamber
Initiate XRF analysis program
Scan barcode IDs from XRF analysis list and verify that tray positions correspond to XRF Log Sheet
Associate tray with "Measure Queue" sequence in analysis program
Return filters for cold storage
Start analysis including 10% replicate analysis from previous run and 10% performance standards
At completetion of each run, produce database file of analyzed data
Review analysis of QA standards
• Spectrum calibration
• QA standard
• Replicate
Examine spectra for peak broadening, excessive overlaps, and detectable peaks
Perform Level I data validation
Archive XRF data

4.1 Start-Up

Normally the Epsilon 5 XRF is left running at all times and requires no special startup procedure. If the x-ray cabinet has been turned off, simply press the main power switch on the front panel to the "ON" position (Figure 4-2). If the power has been interrupted the x-ray cabinet will come back on when power is restored, however the computer program will likely require initialization before analysis may begin. To start the Epsilon 5 software, simple double click its icon on the desktop. The software will start and connect automatically to the spectrometer hardware

Figure 4.2. Epsilon 5 front panel display and controls.

4.1.1 Detector Calibration

The detector contains a Digital Signal Processor (DSP) that must be calibrated for the signals coming from the detector in order that they be placed in the proper energy channels. The calibration process consists of repeated measurements of the Tungsten (W) beam stop permanently installed in the Epsilon 5, therefore no standard loading is required. The calibration is performed on a weekly basis, typically on Friday afternoon. From the Epsilon 5 software main screen, choose the system drop down menu, then choose "Detector Calibration", select "Calibrate All" (Figure 4-3). The iterative process will begin and when finished the "Hours since cal" should be near zero for all three detector settings. Simply close the window when this is finished.

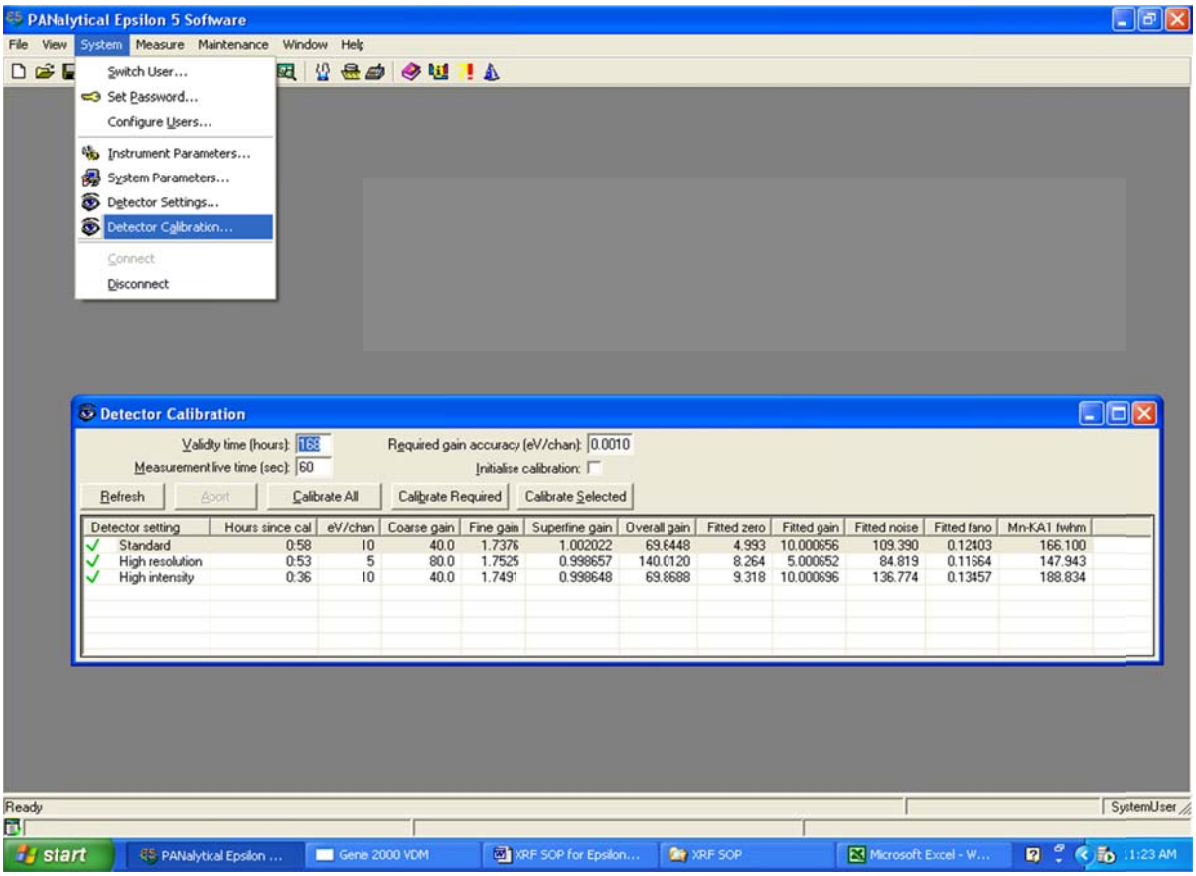


Figure 4-3. Software detector calibration window.

4.1.2 Routine Operation

Figure 4-4a-f shows the typical flow of events that takes place during an XRF analysis.


a)
Computer generated analysis list with barcodes
XRF Log Sheet
b)
Retaining ring
Filter holder
Loaded filter deposit side downward
Petri slide with filter sample
c)
Loaded filter in each metal cup
Metal sleeve
Sample tray of 8 cups
Tray ID
d)
Mechanical arm
X-ray light on during analysis
X-ray sample changer chamber
Sample Tray
e)
Measure Queue
Identification for sample during analysis
Tray ID
Filter sample ID
XRF Protocol
Position ID
Sample tray in queue for analysis
QA Standards
f)
Mechanical arm
Lid of X-ray vacuum chamber
QA Standard loaded by mechanical arm
X-ray Chamber
Additional QA Standard

Figure 4-4. Typical flow of events during an XRF analysis.

4.1.3 Filter Loading

The filter loading procedure depends on the filter media to be analyzed (1) quartz- or glass-fiber filters or (2) Teflon-membrane filters. The procedures are different for these two options. The XRF Supervisor may designate special handling and loading procedure for unusual samples or project requirements. The notes at the top of the analysis list should be read carefully before handling the samples.

Glass-fiber or quartz filters are infrequently analyzed at DRI by XRF for elements heavier than sulfur. Sulfur and lighter elements cannot be measured quantitatively on glass fiber or quartz filters due to high, variable background levels of these elements on these filter media and due to high absorption and backgrounds resulting from the relatively thick filter media.

Glass fiber and quartz filters are most frequently in the form of 8" X 10" sheets used in hi-vol samplers. Sample punches are taken from these large sheets for analysis.

Teflon membrane filters analyzed at DRI are generally 25, 37, or 47 mm diameter ring-mounted filters. The sample holders used in the DRI XRF are custom-designed holders for 25, 37 or 47 mm filters Sample punches of glass fiber or quartz filters using DRI's sample punch are placed into 47 mm holders. Other sizes of filters may be accommodated; refer to the analysis list or XRF Supervisor for additional instructions.

The 25, 37 and 47 mm holders are designed to fit in the solid sample cups in the XRF sample trays. All three styles consist of two parts: a holder base and a friction-fit retainer ring.

The holders are labeled on the side with a number between 1 and 8 which corresponds to a position in the sample tray; the retainer rings are not numbered. Select a complete set of holder bases and retainer rings for positions 1 through 8. Each sample tray can accommodate up to eight sample cups and the sample exchanger can hold up to six sample trays, so a maximum of 48 samples can be loaded at any one time.

Filters are loaded in the following manner:

- Wipe the work area clean with a methanol-dampened Kimwipe.
- Using latex gloves which have been carefully wiped with a methanol-dampened Kimwipe after being slipped on (to remove loose particles from the gloves), carefully wipe each sample holder base and retainer ring with methanol-dampened Kimwipes. Insure that all surfaces are free of particles, particularly the inner lip of the holder bases and the side of the retainer ring which will be contacting the filter. Place the holder bases on the clean Kimwipe in rows of 8 holders each; place the cleaned retainer rings on top of the holder bases. Carefully wipe the surface of eight sample cups with a second methanol-dampened Kimwipe place them in a row above the eight holders. Figure 4-5 shows the 47mm filter holder and the solid sample cup used for the analysis of filters.

- Referring to the XRF analysis list, select filters for analysis. The first two analysis trays for a particular project will include 16 first-time analyses and no replicates. Subsequent trays will include replicates at the rate of 1 per tray. The goal is to run approximately 10% replicates. Final adjustments in the number of replicates run are made in the final tray for a given project.

- Retrieve the samples to be analyzed from the XRF sample cabinet and lay the selected filters evenly across the Kimwipe, in rows of 8 filters each, beneath each filter holder. (The filters are still in their labeled containers at this step).

- Locate a current Epsilon 5 XRF Analysis Logsheet (Figure 2-4). Note: the QA gross counts ranges on the Analysis Logsheets change slightly when the XRF is recalibrated; make sure the latest version of the Analysis Logsheet is used. Complete the project, run ID (as specified in the analysis list), filter type and size, and sample load date and technician's initials sections as shown in Figure 2-4.

- Complete the sample IDs positions with the filter IDs selected for this run, referring to the XRF Analysis List and making sure that the correspondence of holder number and sample ID is the same on the XRF Analysis Logsheet as on the loading table.

- Check the filters for visual defects, large particles, filter damage, or other abnormalities which may affect the quality of the analysis. Note any problems in the comments section of the Analysis Logsheet.

- Teflon Membrane Filter Loading

  The following steps are followed to load ring-mounted membrane filters into the filter holders:

  — After wiping a pair of tweezers clean with a methanol-dampened Kimwipe, remove the filter from the first petri dish or PetriSlide. Examine the deposit closely for defects not previously noted. Remove carefully all large or loose particles which may fall off during analysis.

  — Carefully move the retainer ring from the corresponding holder base (avoid touching the lower surface which will contact the filter). Turn the filter over (face down) and place it into the holder base.

  — Place the retainer ring over the filter, squeeze it slightly to reduce its circumference, and place it over the filter to hold it flat. Insure that the opening in the retainer ring is oriented toward the right. Note: the filters must be completely flat against the inner lip of the holder bases: the x-ray signal is sensitive to distance traveled, and slight changes in the distance between the x-ray tube, the filter, and the detector will have measurable effects.

  — Proceed in a similar manner for the remaining samples.

  — Each loaded filter holder must now be carefully loaded into the corresponding sample cup. The filter holders must lay flat in the sample cup, so take extreme care to ensure that you lower the filter holders straight down into the cup. The sample cups can now be loaded into a sample tray. Each sample tray has a letter designation that corresponds with its position in the XRF sample changer.

— After all samples are loaded, double check that the sample ID on the Logsheet matches the ID on the empty filter container for each position.

— If samples will not be loaded immediately into the XRF sample chamber, place a large, clean Kimwipe over the holders and place the Analysis Logsheet on top.

- Quartz or Glass Fiber Filter Loading

The following steps are followed to load glass fiber or quartz filters into the filter holders:

— Locate the box of Mylar sheets (3.6 μm, 2 X 2 inch squares) in the XRF sample cabinet.

— Open the box of Mylar and carefully remove the top tissue paper; a sheet of Mylar should accompany the tissue paper due to static attraction.

— Carefully move the retainer ring from the corresponding holder base (avoid touching the lower surface which will contact the filter).

— Place the Mylar over the first holder base. Holding one corner of the Mylar with tweezers, remove the tissue paper, leaving the Mylar draped over the filter holder.

— After wiping a pair of tweezers clean with a methanol-dampened Kimwipe, remove the filter from the first petri dish or PetriSlide. Examine the deposit closely for defects not previously noted. Remove carefully all large or loose particles which may fall off during analysis.

— Turn the filter over (face down) and place it into the holder base. Center the punch in holder base opening.

— In a similar manner, place a second Mylar square over the filter punch. Although the two Mylar sheets are not electrostatically attracted to one another, they are attracted to most other objects, including tweezers, fingers, sample holder bases, and the tissue paper. Some caution is necessary to insure both Mylar squares are lying flat.

— Place the retainer ring over the filter, squeeze it slightly to reduce its circumference, and place it over the filter to hold it flat. Note: the bottom Mylar sheet and the filter must be completely flat against the inner lip of the holder bases: the x-ray signal is sensitive to distance traveled, and slight changes in the distance between the x-ray tube, the filter, and the detector will have measurable effects. The bottom Mylar must be as free as possible of wrinkles. Careful tension on alternate corners of the Mylar will generally remove residual wrinkles. Caution: take care that the retainer ring does not pop out as tension is applied to the Mylar.

— Each loaded filter holder must now be carefully loaded into the corresponding sample cup. The filter holders must lay flat in the sample cup, so take extreme care to ensure that you lower the filter holders straight down into the cup. The sample cups can now be loaded into a sample tray. Each sample tray can hold up to eight sample cups and has a letter designation that corresponds with its position in the XRF sample changer.

— Proceed in a similar manner for the remaining samples.

— After all samples are loaded, double check that the sample ID on the Logsheet matches the ID on the empty PetriSlide for each position.

If samples will not be loaded immediately into the XRF sample chamber, place a large, clean Kimwipe over the holders and place the Analysis Logsheet on top.

4.1.4 Loading the sample chamber

Before opening the sample changer cover, check the front panel to ensure that the green "Free to Open" lamp is lit. The cover is interlock protected to prevent the robotic sample changer arm from moving while the cover is open thereby preventing damage to the arm and/or the operator. If the cover is open when the sample changer arm is ready to change the sample, the software will show a warning window on the computer screen requesting that the operator close the sample chamber cover. It is good practice to check the progress of the current analysis, if it is nearly complete, the operator should wait until the sample is finished and the next one is loaded before proceeding with the reloading of the sample chamber. If you are in the middle of loading the sample chamber and the software requests that you close the sample chamber cover, simply finish what you are doing to a convenient point and close the cover to allow the machine to change samples.

Sample trays are loaded into the sample changer with the letter written on the sample tray (A-F) matching the etched letter in the sample chamber (Figure 4-4 d). The trays are keyed to prevent them from being loaded backwards in the sample chamber; this ensures samples one through eight are in the proper order. When all trays have been loaded, close the sample chamber lid.

4.2 Filter Analysis

Once sample trays are loaded into the X-ray cabinet sample chamber, analysis can begin. To start an analysis go to the computer workstation and ensure that the Epsilon 5 software is currently running (it should always be running) and choose the "Sample Changer Measurements" option under the "Measure" menu (Figure 4-5).

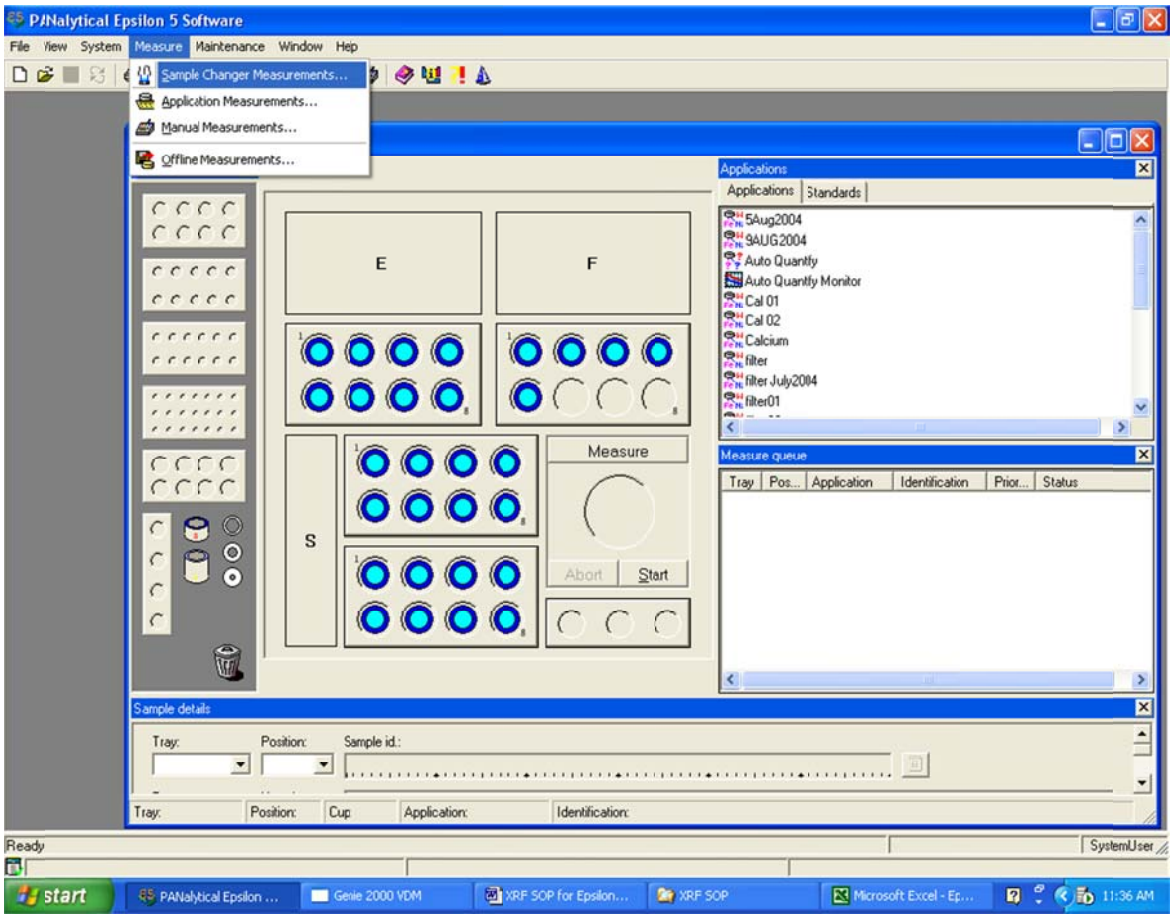


Figure 4-5. Software sample changer measurements window.

From this window sample IDs can be added to the analysis queue by clicking on its position in the tray, this will enable the "Sample id:" window at the bottom of the screen. Once the ID has been entered the sample position color should be blue indicating all is well and analysis can begin. Next the operator simply drags the samples over to the "Measure queue". This action will change the color to yellow. See Figure 4-6 for an explanation of the sample colors.

If these are the first samples added to the queue the Start button must be selected, otherwise if these samples are being added to a queue that has analysis in progress they will automatically be added to the end of the queue.

For analysis of filters (47mm, 37mm or 25mm) the sample trays used are the "2x4" sample cups (the bottom horizontal tray on the left hand side of Figure 4-5). The application for analysis is chosen from the list of applications, usually the application setup for the measurement of Teflon membrane filters is set as the default application.

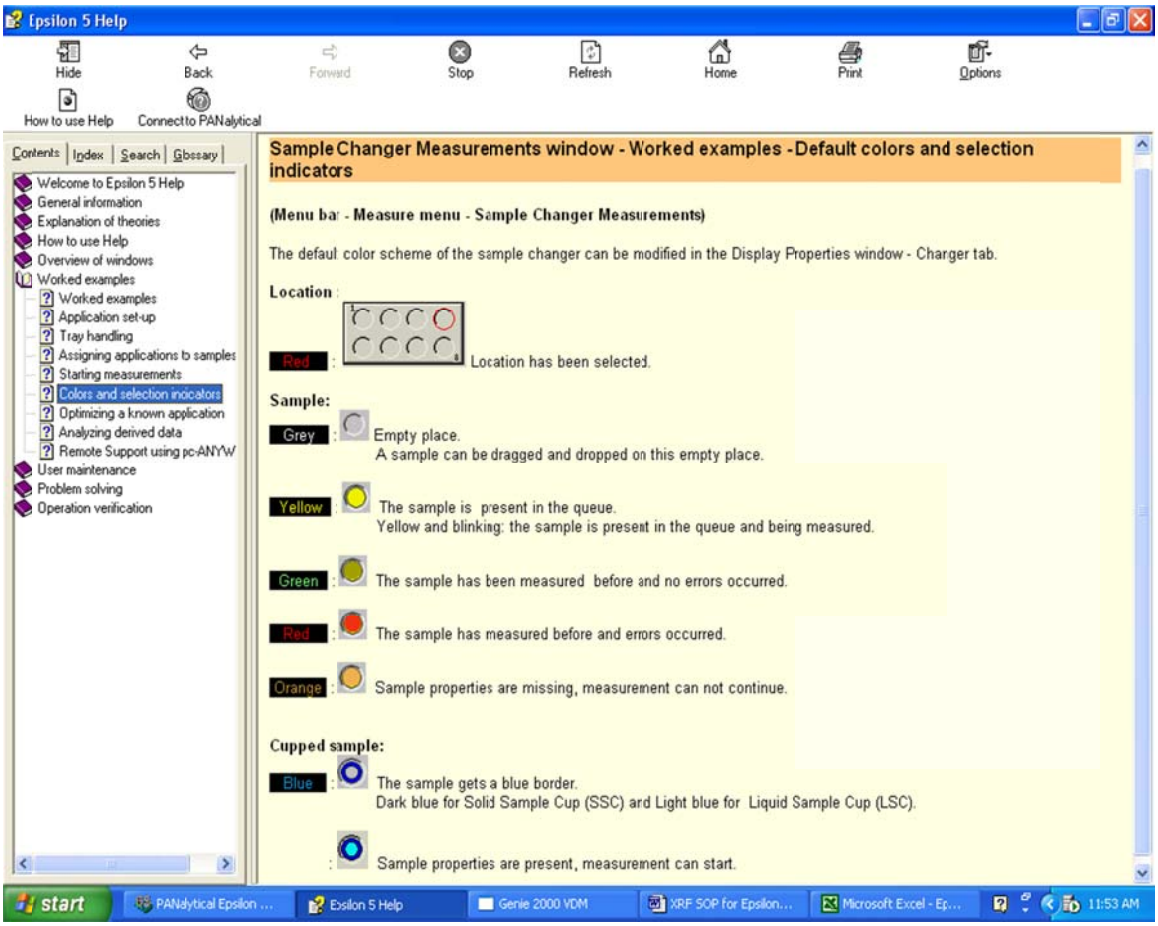


Figure 4-6. Software Help screen defining sample changer window colors.

When the analysis of a sample is successfully completed the sample indicator will be green. If any problems were encountered during analysis the sample will be red. If any samples are red immediately notify the XRF laboratory supervisor.

4.5 Shut-Down

Typically the Epsilon 5 system is left running at all times, but in the event of an emergency the X-ray cabinet can be shut down by simply pressing the "Power On" switch on the control panel to the "Off" position.

When power is removed from the Epsilon 5 or when the software is shut down, immediately notify the XRF laboratory supervisor or his/her designee. The x-ray detector is protected from damage due to liquid nitrogen depletion by the software (the software will shut down the detectors high voltage power supply if the liquid nitrogen runs too low), therefore if the software is shut down and the x-ray cabinet is left on, it is imperative that the liquid nitrogen level be closely monitored.

5. QUANTIFICATION

5.1 Calibration procedures

Calibration of the Epsilon 5 XRF analyzer is achieved by analyzing μMatter thin film standards. The software package calculates a linear regression line for each element using Nuclepore blanks and at least two standards for each element. The calibration line for Cu is shown in Figure 5-1. The results of the calibration for each element are stored with the application and a hardcopy is filed in the XRF laboratory.

For elements where no standards are available a calibration factor is obtained by plotting instrument response versus atomic number and interpolating the factor for the missing element. This operation is performed by the XRF laboratory supervisor using Microsoft Excel spreadsheet software. Electronic copies of the calibration curves for each condition are saved in Excel spreadsheets and posted in the laboratory information management system.

Full calibrations are performed when the QA standard that is analyzed daily falls outside acceptable limits or when any significant repair or parts replacement is performed on the instrument.

5.2 Calculations

The Epsilon 5 software integrates the peaks for each element, performs the deconvolution routine (to account for interelement interferences) and then uses the calibration data for each element to convert the raw counts data to micrograms per square centimeter for reporting. All sample data is stored in the results database on the XRF computer. In order to process batches of filters the data must be saved via the results window to a text file that is converted into a database file for final processing. To select filter results for export, open the results window for the application and highlight the samples, then click the show report button to create the report. To save the data as an exportable text file, print the report to a comma delimited file. This operation is illustrated in Figure 5-2.

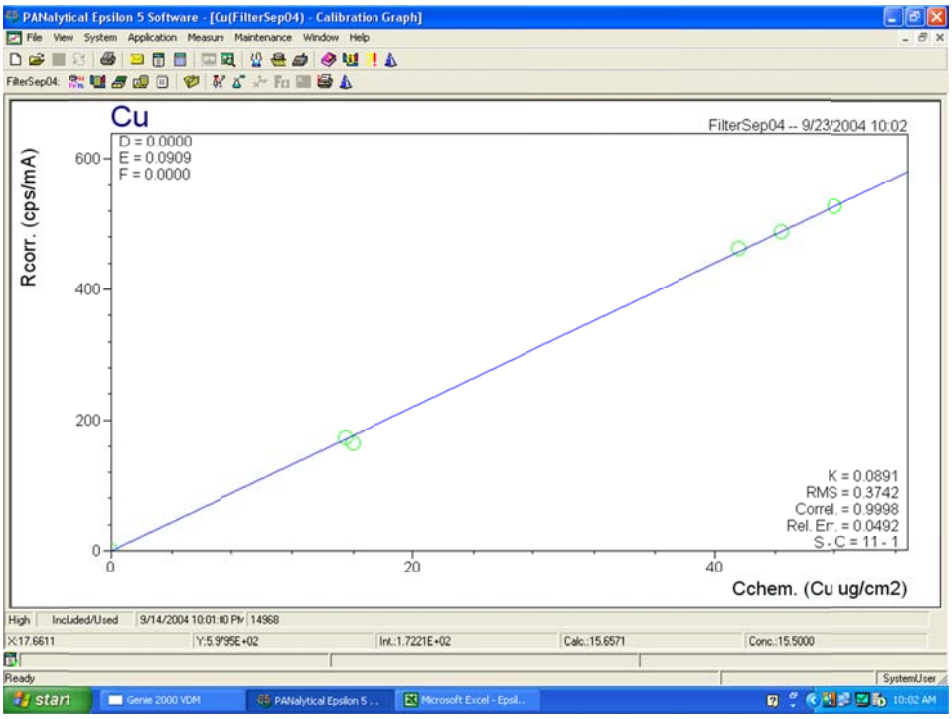


Figure 5-1. Software calibration graph window.

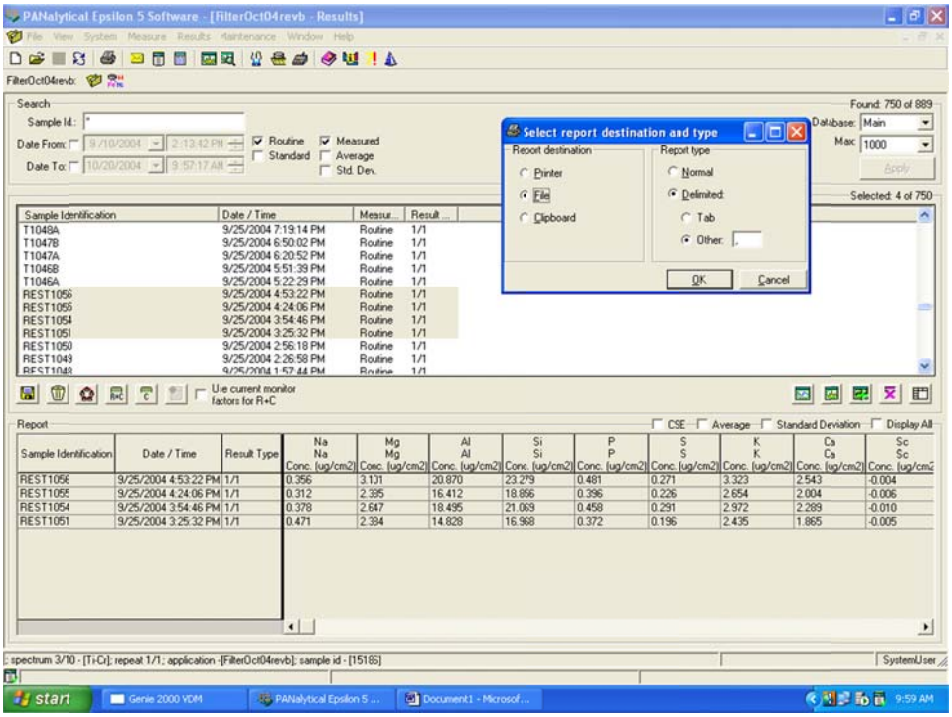


Figure 5-2. Software Analysis Results window.

6. QUALITY CONTROL

Quality control for the XRF analyzer consists of checking the performance of the analyzer against a QA standard which is analyzed every day and looking at replicate analyses.

6.1 Performance testing

A multi-element Micromatter thin film standard is run daily to monitor for instrument drift. Using the Epsilon 5 software the latest results can be displayed while the instrument is still processing the analysis queue. Each day check the results for the QA standard and record the concentrations in micrograms per square centimeter on the XRF Micromatter Multielement QA Standard analysis logsheet. Upper and lower bounds (± 5%) are listed on the logsheet. If the concentration is between these bounds no action is necessary, if it is out of bounds the XRF supervisor must be immediately notified and the problem must be fixed before analysis continues.

6.2 Reproducibility testing

Replicates of analyzed samples are performed at the rate of 10%. This corresponds to one replicate per analysis tray after the first tray. The general pattern to be followed is one tray with two replicates, followed by three trays with one replicate each. This generally corrects for the changing number of original samples which can be analyzed in each batch due to the number of replicates. The total number of replicates is compared to the total number of filters prior to the last run for a given project, and additional replicates are placed in the last tray to insure a 10% replicate rate.

Replicate data is examined during the data validation and spectra review step. In general, the replicate $\mu g/cm^2$ data should be within ± 10% or within 3 times the reported analytical uncertainties. Exceptions to these criteria may be made for such species as chlorine and bromine, which may vaporize under the high vacuum and decrease between the first and second analyses.

6.3 Validation Codes

Flags for all laboratory chemical analysis are defined in Table 6-1. During loading and unloading of the filters from the analyzer the operator should record and flags on the analysis logsheet.

Table 6-1. Validation codes and their meanings.

Flag	Meaning
b	Blank.
b1	Field/dynamic blank.
b2	Laboratory blank.
b3	Distilled-deionized water blank.
b4	Method blank.
b5	Extract/solution blank.
b6	Transport blank.
c	Analysis result reprocessed or recalculated.
c1	XRF spectrum reprocessed using manually adjusted background.
d	Sample dropped.
f	Filter damaged or ripped.
f1	Filter damaged, outside of analysis area.
f2	Filter damaged, within analysis area.
f3	Filter wrinkled.
f4	Filter stuck to PetriSlide.
f5	Teflon membrane separated from support ring.
f6	Pinholes in filter.
g	Filter deposit damaged.
g1	Deposit scratched or scraped, causing a thin line in the deposit.
g2	Deposit smudged, causing a large area of deposit to be displaced.
g3	Filter deposit side down in PetriSlide.
g4	Part of deposit appears to have fallen off; particles on inside of PetriSlide.
g5	Ungloved finger touched filter.
g6	Gloved finger touched filter.
h	Filter holder assembly problem.
h1	Deposit not centered.
h2	Sampled on wrong side of filter.
h4	Filter support grid upside down- deposit has widely spaced stripes or grid pattern.
h5	Two filters in PetriSlide- analyzed separately.
i	Inhomogeneous sample deposit.
i1	Evidence of impaction - deposit heavier in center of filter.
i2	Random areas of darker or lighter deposit on filter.
i3	Light colored deposit with dark specks.

Flag	Meaning
i4	Non-uniform deposit near edge - possible air leak.
m	Analysis results affected by matrix effect.
m1	Organic/elemental carbon split undetermined due to an apparent color change of non-carbon particles during analysis; all measured carbon reported as organic.
m2	Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit.
m3	A non-typical, but valid, laser response was observed during TOR analysis. This phenomena may result in increased uncertainty of the organic/elemental carbon split. Total carbon measurements are likely unaffected.
n	Foreign substance on sample.
n1	Insects on deposit, removed before analysis.
n2	Insects on deposit, not all removed.
n3	Metallic particles observed on deposit.
n4	Many particles on deposit much larger than cut point of inlet.
n5	Fibers or fuzz on filter.
n6	Oily-looking droplets on filter.
n7	Shiny substance on filter.
n8	Particles on back of filter.
n9	Discoloration on deposit.
q	Standard.
q1	Quality control standard.
q2	Externally prepared quality control standard.
q3	Second type of externally prepared quality control standard.
q4	Calibration standard.
r	Replicate analysis.
r1	First replicate analysis on the same analyzer.
r2	Second replicate analysis on the same analyzer.
r3	Third replicate analysis on the same analyzer.
r4	Sample re-analysis.
r5	Replicate on different analyzer.
r6	Sample re-extraction and re-analysis.
r7	Sample re-analyzed with same result, original value used.
s	Suspect analysis result.
v	Invalid (void) analysis result.
v1	Quality control standard check exceeded ± 10% of specified concentration range.

Flag	Meaning
v2	Replicate analysis failed acceptable limit specified in SOP.
v3	Potential contamination.
v4	Concentration out of expected range.
w	Wet Sample.
w1	Deposit spotted from water drops.

Analysis results are categorized as valid, suspect, or invalid. Unflagged samples, or samples with any flag except 's' or 'v' indicate valid results. The 's' flag indicates results of suspect validity. The 'v' flag indicates invalid analysis results. Chemical analysis data validation flags are all lower case.

Data validation feedback

Begin data validation by verifying that all data entry is correct: sample ID's, deposit areas, and flags on the Logsheet and the printouts should match. If there are any discrepancies, note them on the XRF Validation Summary.

Next, examine the results for internal consistency and "reasonableness" of the XRF data. Categories to check are presence of elements whose concentrations are usually below the detection limit for typical ambient air samples, unusual elemental ratios, and replicate analysis results. Since data from the QA standard has already been checked, and since its composition is unlike aerosol samples, do not apply these checks to the QA standard.

The XRF Analysis Logsheet and results data file are reviewed by the XRF Supervisor or his designee. Any samples with incorrect or questionable data are noted on the XRF Validation Summary, record the filter ID, analysis condition, problem, along with steps taken to resolve any problems. Once all data has been validated and any necessary corrections are made in the database, the line labeled "QA Chks" on the XRF Analysis Logsheet is initialed. Hardcopies of all data validation summary sheets are filed in the XRF laboratory.

7. REFERENCES

PANalytical , *Epsilon 5 EDXRF Spectrometer System User's Guide*, First Edition March 2003

8. DOCUMENT CHANGES

7/30/07: r3 – minor formatting changes. Added signature blocks to title page. Note that original SOP started as r1 and not r0.

10/12/09: r4 – Changed to reflect the installation of the new dual anode Sc/W x-ray tube.

12/10/09: r5 Updated MDL table

12/17/10 r6 Updated XRF logbook example

07/09/12: r7 Updated MDL table and conditions table to reflect changes to analysis protocol made during the March 2012 calibration. Deleted section 6.3 regarding control charts.

10/03/14: r8 Updated SOP with pictures and flow chart figures.

DRI STANDARD OPERATING PROCEDURE

General EAF Internal Audit Procedures

DRI SOP #4-117r1
March 17, 2014

Desert Research Institute
Division of Atmospheric Sciences
2215 Raggio Parkway
Reno, NV 89512

(775) 674-7094

Prepared By: _____ **Date:** 3/17/14

Reviewed By: _____ **Date:** 3/17/14

Approved By: _____ **Date:** 3/17/14

1. GENERAL DISCUSSION

1.1 Purpose of Procedure

This procedure outlines the general procedures to be followed when preparing for, conducting, and reporting the results of internal systems audits of Environmental Analysis Facility (EAF) operations.

Internal audits of EAF operations are technical/management systems audits to assess the following:

- Compliance with requirements in QA/QC-related documents
- Documentation of compliance by review of records (forms, log books, etc.)
- Determination of compliance by observing performance of tasks
- Conformance with general quality system practices
- Correction of deficiencies through corrective actions

1.2 Measurement Principle

Depends on the specific EAF operation being audited.

1.3 Measurement Interferences and Their Minimization

Depends on the specific EAF operation being audited.

1.4 Ranges and Typical Values

Depends on the specific EAF operation being audited.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

Depends on the specific EAF operation being audited.

1.6 Personnel Responsibilities

All EAF employees are responsible for adhering to the procedures and documentation requirements contained in the EAF Quality Manual, Quality Management Plans, Quality Assurance Plans, and Standard Operating Procedures. For internal EAF audits, laboratory personnel are responsible for demonstrating procedures as they are normally conducted and responding to auditor questions.

Laboratory supervisors and coordinators are responsible for ensuring that all procedures and documentation are followed properly and that any deviations are quickly resolved. For the internal EAF audits, supervisors/coordinators are responsible for seeing that the audit can be conducted on the agreed date(s), that necessary staff and documents are available, observing the proceeding and responding to questions as needed, reviewing audit findings with the auditor and agreeing to or commenting corrective actions to resolve audit deficiencies.

The QA Officer is responsible for ensuring that all QA/QC requirements for EAF operations are being met. For the internal EAF audits, the QA Officer is responsible for conducting the audit personally or through a designee. The detailed responsibilities of the auditor are given in this SOP.

1.7 Definitions

Audit – A systematic, independent examination of facilities, equipment, personnel, training, procedures, record-keeping, data validation, data management, and reporting aspects of a system to determine whether QA/QC activities are being conducted as planned and whether these activities effectively achieve quality objectives..

1.8 Related Procedures

Demonstration of Capability – DRI SOP #6-015.

Specific SOPs relevant to the particular operation being audited.

Specific EAF internal audit procedures for particular EAF operational areas.

2. APPARATUS, MATERIALS, AND FORMS

2.1 Apparatus and Instrumentation

Depends on the specific EAF operation being audited.

2.2 Reagents

Depends on the specific EAF operation being audited.

2.2 Forms

Each specific EAF internal audit procedure will have an audit form for that particular operation. Figure 2-1 shows excerpts of an audit form used for an EAF internal audit of $PM_{2.5}$ FRM gravimetry operations. Major deficiencies are tracked through Corrective Action Requests (CARs). An example form is shown in Figure 2-2.

3. CALIBRATION PROCEDURES

Depends on the specific EAF operation being audited.

4. PROCEDURES

4.1 General

Internal EAF audit procedures are to be developed for all EAF operations as time and resources permit based on the following priorities:

1. All operations for which NELAC accreditation is sought and to be retained.
2. Other EAF operations in priority order based on the fraction of the EAF workload that each represents.

DRI Internal Audit of EAF PM2.5 Gravimetry Operations

Auditor(s) Richard Tropp

Date(s) 7/31/09, 8/3/09, 8/4/09, & 8/26/09

Purpose: Conduct a technical/management systems audit to assess the following
- Compliance with requirements contained in documents listed in References
- Documentation of compliance by review of records (forms, log books, etc.)
- Assessment of compliane by observing performance of tasks
- Conformance with general Quality System practices (see References)

References:
1. DRI, SOP #2-114r6, *PM2.5 FRM Gravimetric Analysis* (12/2/08)
2. DRI, SOP #6-015r0, *Demonstration of Capability* (6/13/08)
3. DRI, SOP #6-014r0, *Laboratory Ethics* (6/13/08)
4. DRI, *Quality Assurance Project Plan PM2.5 Filter Laboratory Analysis Program* - Rev. 1 (8/08)
5. EPA, *Quality Assurance Handbook for Air Pollution Measurement Systems - Volume II Ambient Air Monitoring Program*, EPA-454/B-08-003 (12/08)
6. DRI, *Quality Manual - Environmental Analysis Facility (EAF)* - Rev. 1 (6/08)

Personnel Interviewed
Supervisor/Coordinator: Brenda Cristani
Others: Gail Martin

General Information
No. of Technicians: BC + 4
Comments: Observed Gail / Martin

Documents Examined

Item	Location	OK (Y/N)
1. Demonstrations of Capability	Weighing Room (PM2.5)	N
2. Laboratory Ethics Agreements	Weighing Room (PM2.5)	Y
3. SOP #2-114r6	Weighing Room (PM2.5)	Y
4. Weighing Logbooks	Weighing Room (PM2.5)	Y see comments
5. Environmental Condition Charts	Weighing Room (PM2.5)	Y
6. Weight Room Audits/Services Book	Weighing Room (PM2.5)	Y
7. Filter Media Acceptance Logsheets	Lab Technician Room	Y
8. Filter Assignment Logsheets	Weighing Room (PM2.5)	Y

Comments: Item 1 – 4 DOCs, but 3 fr 6/08 & need to be renewed. Item 2 – looked at random pages from 7/08 on in Current Projects (A-C, D-H, I-P, Q&R-Z) & TCEQ Mass (Shipments 110-) Discuss Guidelines 11/5/09 w BC & JMP 4/16/09 SERPP 12/2/08 FN; Technician 8/6/08 FLD, & TCEQ & TSS 5/15/09. Item 4 – Need additional comments/codes to explain unusual items (e.g., un weighed final filters, >30% replicate on final filters). Be careful to indicate where in sequence T/C taken as go from one sheet to another

Figure 2-1a. Excerpts of EAF Internal Audit Form for $PM_{2.5}$ FRM Gravimetry

DRI Internal Audit of EAF PM2.5 Gravimetry Operations (Continued)

Specific Items Checked

Calibration/Verification/Service/Preventive Maintenance Frequency

Item	Freq.	Criteria	Found	OK (Y/N)
Balance Cal.	1/yr	Manuf.	Back two 2005-2009	Y
Lab Temp	1/6 mos	± 2 °C	last done in June '09	N
Lab RH	1/6 mos	± 2 %RH	not in book	N
Working Mass Stds (w Primary)	1/3 mos	< ± 25 µg	only 200 mg	N
Primary Mass Stds	1/yr	< ± 25 µg		Y see comment
Calibration Stds	All	NIST-tr C1		Y
Replace P210 Source	1/6 mos	NA	not changed 1/2005	N
Balance Internal Cal	B	NA	not checked	N
Balance Check - Span	B/10/E	≤ ± 3 µg	not check	Y

QC Checks

Item	Freq.	Criteria	Found	OK (Y/N)
Filter Conditioning (Pre-Use)	All filters	> 4 wks		Y
Fiter Conditioning (Pre/Post Wgt)	All filters	> 24 hrs		Y
Env Conds - Tavg	All filters	20-23 °C		Y
Env Conds - Tsd	All filters	± 2 °C		Y
Env Conds - RHavg	All filters	30-40 %RH		Y
Env Conds - RHsd	All filters	± 5 %RH		Y
Lab blanks	2%	± 10 µg diff		Y
Field Blanks	>10%	NA		Y
Replicate Wgts - Pre	100%	± 10 µg diff		Y
Replicate Wgts - Post	30%	± 15 µg diff		Y

Operational

Item	Found	OK (Y/N)
Plastic forceps for std wgts	yes	Y
Petri-slides open	2 on start	Y
Time in neutralizer	~ 30 sec	Y
Reading stabilized	3 secs	Y
Record on weight sheet	yes	Y
Replicates done by another tech	yes	Y

General QC

Item	Found	OK (Y/N)
Handwritten records clear & in ink	Not always	N
Errors crossed & corrections near	Usually at bottom sheet	N
Correction maker ID'ed	Usually at top by sheet or bottom	N
Critical data corrections w. reason	Not always	N
Computer correction - audit trail	done by DRI in 3625 db	Y

Comments: Lab Temp & RH - not consistently done every 6 mos
Next scheduled one should be December
Working mass - 1/yr - needs 1/6 mos only 200 mg need to do 50 & 100 mg too
Primary mass - past 1 yrs needs to go back (was due in '09)
P210 source - no available documentation on changeout included in service book. Long term note to do this from now on.

Page 2 of 4

Figure 2-1b. Excerpts of EAF Internal Audit Form for $PM_{2.5}$ FRM Gravimetry

EAF CORRECTIVE ACTION REQUEST

CAR No. _____ **Date** _____

To **From**
How Identified
Reported (Nonconformance) Conditions **Answer Due Date** **Signature**
Root Cause
Corrective Action (Give Steps & Expected Completion Dates)
Preventive Action
Completed by **Date**
Accepted by **Date**
Follow-up Results **Performed by** **Date**
Closed Out (Y/N) _____ If not closed out on follow-up, issue a new CAR **New CAR No.** **Date**

Figure 2-2. Corrective Action Request (CAR) Form

Separate internal EAF audits (with separate audit forms) may be conducted for particular aspects of a general operation. For example, for $PM_{2.5}$ gravimetry operations, separate audits (and forms) may be performed for gravimetry, shipping and receiving, and cold storage. Internal EAF audits will also review all elements of the quality management system, including corrective actions, calibration and check procedures for balances, sensors, purchasing, and complaints. Usually such audits will be conducted at approximately the same time. However, an audit for one particular portion of a general operation may be conducted separately if only that particular portion of the general operation has changed significantly.

Once initiated, internal EAF audits for a particular operation will be conducted at least annually or within 3 months of a major change in related SOPs. Internal audits will be suspended or stopped if a particular operation is performed rarely (i.e., less than yearly) or has been discontinued.

The following sections describe the general procedures to be used when creating (or revising), conducting, reporting, and following up on an internal EAF audit.

4.2 Creating or Initiating a Specific Internal EAF Audit Procedure

4.2.1 First review relevant reference documents and make sure that they are the most recent approved versions available. Example documents may include:

- EAF Quality Manual (NELAC)
- Quality Management Plans (QMPs)
- Quality Assurance Project Plans (QAPPs)
- EAF Standard Operating Procedures (SOPs)
- EPA (or other agency) requirements and guidance documents such as volume II of the EAP QA Handbook
- The Code of Federal Regulations (CFR), especially 40 CFR Parts 50, 53, and 58
- Specific client contract requirements

4.2.1 Prepare or revise a list of references and applicable requirements. Look for potential conflicts in the requirements. If necessary, resolve conflicts by choosing the most stringent requirement.

4.2.3 Prepare or revise the audit form. The audit form should include the following items:

- Title with area being audited
- Date(s) of the audit
- Purpose of the audit
- References
- Personnel interviewed

- General information
- Documents examined
- Specific items to be checked based on requirements in references
- Comments
- Minor deficiencies
- Major deficiencies
- Follow-up and corrective actions
- Next audit schedule and type
- Closing meeting signoff

If there are revisions to an existing audit procedure document the changes in the audit workbook along with the date and reason.

4.2 Conducting the Audit

4.2.1 Notify the area supervisor/coordinator of the upcoming audit about 1-2 weeks in advance to make sure that the operational tasks to be observed will take place on an agreed date and that laboratory personnel and the supervisor will be present.

4.2.2 Prior to the agreed date of the observational portion of the audit, check the location and contents of documents to be reviewed.

4.2.3 The EAF QA Officer or his designee conducts the audit according to the specific procedures and criteria outlined in the workbook and form for the audit of a particular operational area.

4.2.3.1 The auditor again checks documents in the presence of the supervisor and discusses any related issues.

4.2.3.2 The auditor checks whether or not the audit criteria and requirements listed are being met or not. Clarification may be sought from the supervisor or other laboratory personnel where questions arise. Results are documented on the audit form.

4.2.3.3 The auditor observes the performance of tasks in a specific operational area by laboratory personnel that normally conduct them. The auditor may ask questions or to determine if requirements are met and how certain situations are handled. Results are documented on the form and may be discussed with the laboratory personnel involved and the supervisor.

4.2.3.4 The auditor reviews the results documented on the audit form and then lists minor and major deficiencies.

4.2.3.5 The audit findings are reviewed with the supervisor/coordinator at the end of the audit at which the supervisor's comments are noted for the record. Minor deficiencies or changes that can be implemented immediately are to be implemented within the next few days.

4.2.3.6 Major deficiencies or those that require equipment, software, or facility modifications, purchase, or installation are to be listed in Corrective Action Requests (CARs) with, dates established for their implementation and a follow-up schedule created to check on their timely completion.

4.3 Audit Report and Follow-up Actions

4.3.1 The auditor shall present a written report to the supervisor/coordinator, EAF Executive Director and to the EAF QA Officer (if the audit was performed by a designee).

4.3.2 Archive a hardcopy of the audit report in the audit book and an electronic copy in the SOP section of the LAN.

4.3.3 Schedule, track, and document follow-up progress of the CARs.

4.3.4 Enter a tentative date (typically 1 year later) on the calendar for the next audit.

5. QUANTIFICATION

Depends on the

6. QUALITY CONTROL

Depends on the specific EAF operation being audited. In addition, internal audit reports and CARs are archived in an audit book and on the LAN.

7. QUALITY ASSURANCE

Depends on the specific EAF operation being audited.

8. REFERENCES

Refer to the oven's owner's manual for additional information concerning its operation.

9. DOCUMENT CHANGES

08/09/12: New SOP – r0.

03/17/14: r1 – Replaced CAR Form (Figure 2-2) with updated version.

DRI STANDARD OPERATING PROCEDURE

Demonstration of Capability

DRI SOP #6-0015r1
August 15, 2012

Desert Research Institute
Division of Atmospheric Sciences
2215 Raggio Parkway
Reno, NV 89512

(775) 674-7094

Prepared By: Richard Snopp **Date:** 8/15/12

Reviewed By: John G. Watson **Date:** 8/15/2012

Approved By: Judith Chow **Date:** 8/15/2012

1. GENERAL DISCUSSION

1.1 Purpose of Procedure

This procedure describes the method used for performing, approving, and documenting the initial and continuing demonstration of capability (DOC) for Environmental Analysis Facility (EAF) procedures.

This procedure is performed prior to an employee using a test method or standard operating procedure, any time there is a significant change in instrument type, personnel or test method, or if a new analyte is added to an existing accredited method. In the absence of significant changes, it is repeated annually.

1.2 Measurement Principle

As specified in the SOP for which capability is to be demonstrated.

1.3 Measurement Interferences and Their Minimization

As specified in the SOP for which capability is to be demonstrated.

1.4 Ranges and Typical Values

As specified in the SOP for which capability is to be demonstrated.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

As specified in the SOP for which capability is to be demonstrated.

1.6 Personnel Responsibilities

Technician/Analyst - Person responsible for completing training and demonstration of capability studies.

Laboratory Supervisor – Person responsible for certifying that an employee has demonstrated competence for a certain method/analyte/matrix and for ensuring that training and DOCs are performed when needed, per this SOP. A supervisor who also performs the tasks of a technician analyst is also responsible for a demonstration of his/her capability by his/her supervisor or the QA Officer or designee.

Quality Assurance Officer – Person or designee responsible for ensuring and certifying that employees have documented training and demonstration of capabilities on file, and for annual reviews and updates of DOCs.

1.7 Definitions

Demonstration of Capability (DOC) – A procedure to establish the ability of the analyst/technician to generate acceptable accuracy.

Relative Standard Deviation (RSD) – The absolute value of the coefficient of variation expressed as a percentage.

1.8 Related Procedures

None

2. APPARATUS, MATERIALS, AND FORMS

2.1 Apparatus and Instrumentation

As specified in the SOP for which capability is to be demonstrated.

2.2 Reagents

As specified in the SOP for which capability is to be demonstrated.

2.2 Forms

EAF Demonstration of Capability Form (Figure 2-1).

3. CALIBRATION PROCEDURES

Not applicable

4. PROCEDURES

4.1 General

4.1.1 Upon hire, employees receive initial DRI new employee orientation training. Once completed, the employee then receives EAF orientation and training in specific standard operating procedures.

4.1.2 Prior to approval for the performance of any method, training and a satisfactory demonstration of capability must be performed for that method.

4.1.3 Any time there is a change in instrument type, personnel or test method, a DOC must be performed.

4.1.4 If a method is added to an accreditation or if an analyte is added to an existing accredited method, training and a DOC study must be performed by affected analysts and technicians before routine analysis begins

4.1.5 Demonstration of Capability (DOCs) studies are used as documented evidence of competence. Individual DOCs are recorded on the EAF Demonstration of Capability Form.

4.1.6 DOCs are performed only after proper documented training for the method is complete. The person performing the DOC must have a solid understanding of the content, QA of the method, and of the equipment and/or instrumentation to be used.

EAF DEMONSTRATION OF CAPABILITY
CERTIFICATION STATEMENT

Date:_____

Environmental Analysis Facility (EAF)
Desert Research Institute
2215 Raggio Parkway
Reno, NV 89512

Name: _____

Job Title: _____

Method/Matrix/Analyte(s):

_____

SOP Number and Revision: _____

We, the undersigned, CERTIFY that:

1. The person identified above, using the cited test method(s), which is used at this facility for the analyses of samples under the National Environmental Laboratory Accreditation Program, have met the Initial Demonstration of Capability.
2. The test method was performed by the person identified on this certification.
3. A copy of the laboratory-specific SOPs is available for all personnel on-site.
4. The data associated with the initial demonstration of capability are true, accurate, complete and self-explanatory (1).
5. All raw data (including a copy of this certification form) necessary to reconstruct and validate these analyses have been retained at the facility, and, the associated information is well organized and available for review by authorized inspectors.

_____	_____	_____
Laboratory Supervisor	Signature	Date
_____	_____	_____
Quality Assurance Officer	Signature	Date

(1)True: Consistent with supporting data.
Accurate: Based on good laboratory practices consistent with sound scientific principles/practices.
Complete: Includes the results of all supporting performance testing.
Self-explanatory: Data properly labeled and stored so that the results are clear and require no additional explanation.

Figure 2-1. EAF Demonstration of Capability Form

4.1.7 In the absence of significant changes, a continuing DOC is to be conducted annually.

4.1.8 Employee training files are annually reviewed and continuing DOC studies may be selected for employees on a random basis.

4.1.9 A continuing DOC may also be performed as part of a corrective action due to suspected sub-standard performance by an individual.

4.2 Performance of Demonstration of Capability (DOC) Studies

4.2.1 DOC studies are not performed with customer samples, instead, proficiency samples or laboratory-spiked samples (prepared from clean matrices) are used.

4.2.2 All DOC studies are considered blind to the analyst, as they are unaware of the content of the sample. All sample preparations and analyses are performed in accordance with the specified method, with no deviations or modifications.

4.2.3 Laboratory samples are prepared from clean matrices, in which no target analytes or interferences are present, and stock standards. The stock standards must be prepared independently from those used in the instrument calibration.

4.2.4 No less than five (5) replicate samples are prepared using the specified method.

4.2.5 For a bulk sample, at least 5 different sample weights will be recorded. For a liquid sample, at least 5 aliquots will be taken and diluted to the specified concentration.

4.2.6 The final sample concentration should be 1-4 times the reporting limit for each analyte.

4.2.7 The 5 preparations and 5 analyses may be prepared and analyzed concurrently, or over a period of days.

4.2.8 When complete, the report (in appropriate reporting units) and raw data (or a copy of the raw data) is reviewed by Laboratory Management and/or QA.

4.2.9 Proficiency studies may be used to satisfy the ongoing DOC requirements.

4.3 Evaluation of DOC Results

4.3.1 Laboratory management and/or QA reviews the laboratory results and the raw data is reviewed to ensure that the results of the QA and calibration standards meet the requirements, as specified by the method.

4.3.2 The analyses results are compared to the certified or spiked values, as appropriate.

4.3.3 Percent recovery and relative standard deviation (RSD) are calculated for each analyte of interest.

4.3.4 To consider a DOC study acceptable using a proficiency sample, the reported results for all 5 analyses (and the average of the 5 results) must be within the published acceptable limits of the proficiency study.

4.3.5 To consider a DOC study acceptable using a laboratory-prepared sample, percent recovery (for each analyte) must be within ±20% of the spiked value for all 5 analyses (and the average of the 5 results) or meet the specifications within the SOP, whichever is more stringent.

4.3.6 The relative standard deviation (RSD) for the 5 results must be <10%, for the DOC to be considered acceptable.

4.3.7 If all parameters meet the acceptance criteria identified in section 4.3, the DOC is considered acceptable, the EAF Demonstration of Capability Form is approved by laboratory management and QA, and analysis of actual customer samples may begin.

4.3.8 If any of the parameters (for one or more of the analytes) do not meet the acceptance criteria, the DOC is considered unacceptable for that parameter and the analysis of actual samples cannot begin. Refer to section 4.4 below for handling of unacceptable DOC results.

4.4 Handling of Unacceptable DOC Results

4.4.1 If any of the tested parameters fail to meet the acceptance criteria, the source of the problem is identified, corrected, and the test is repeated for all failing parameters.

4.4.2 In the case of repeated failure, the steps in Section 4.3 are repeated and the study is conducted with supervision and/or the study is performed concurrently with an approved individual.

4.5 Documentation and Record Control

4.5.1 The EAF Demonstration of Capability Form is used as a record of approval for Demonstration of Capability Studies

4.5.2 DOC forms are signed by the individual (or work cell participants), the department manager and the QA officer.

4.5.3 Training and DOC records are maintained in employee training files.

4.5.4 Training and DOC records are reviewed no less than annually to ensure that they commensurate with the employee's current job description.

4.5.5 Training and DOC records are maintained for no less than 5 years from the date of employee termination or separation.

5. QUANTIFICATION

See section 4.3 and relevant sections of the SOPs for which the DOC is being obtained.

6. QUALITY CONTROL

Signed *EAF Demonstration of Capability* forms are maintained as quality and management records for a minimum of five years from the date of employee separation.

7. QUALITY ASSURANCE

See Section 6, Quality Control.

8. REFERENCES

National Environmental Laboratory Accreditation Conference (NELAC). Quality Systems. Appendix C - Demonstration of Capability. 2003 NELAC Standard. Approved June 5, 2003. Effective July 1, 2005

NELAC Institute. Management and Technical Requirements for Laboratories Performing Environmental Analysis – Module 2: Quality Systems General Requirements. TNI Standard. EL-V1M2-2011. Adopted September 8, 2009. Effective September 1, 2010.

9. DOCUMENT CHANGES

06/13/08: New SOP – r0.
08/15/12: r1 – Clarified that 2) supervisors/coordinators are to perform demonstrations of capability if they perform the tasks of a technician/analyst and 2) that in the absence of significant changes continuing DOCs are performed annually. Also added TNI Standard as reference.

DRI STANDARD OPERATING PROCEDURE

Corrective Action

DRI SOP #6-017r0
August 15, 2012

Desert Research Institute
Division of Atmospheric Sciences
2215 Raggio Parkway
Reno, NV 89512

(775) 674-7094

Prepared By: _____ **Date:** 8/15/12

Reviewed By: _____ **Date:** 8/15/2012

Approved By: _____ **Date:** 8/15/2012

1. GENERAL DISCUSSION

1.1 Purpose of Procedure

This procedure outlines the corrective action system and use of the Corrective Action Request (CAR) system within the Environmental Analysis Facility (EAF) to document major changes made to procedures, systems, facilities, instruments, and computer programs occur after the item has been completed and accepted.

1.2 Measurement Principle

Not applicable

1.3 Measurement Interferences and Their Minimization

Not applicable

1.4 Ranges and Typical Values

Not applicable

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

Not applicable

1.6 Personnel Responsibilities

All EAF employees are responsible for being aware of the potential for operational and data quality issues and to report any problems to their supervisors, including those that may initiate a CAR.

The supervisor/coordinator for the affected operation is responsible for assigning personnel, assisting in setting completion deadlines, and reviewing and approving the CAR to be acted upon. The EAF Executive Director and QA Officer may need to be included in allocating resources and establishing deadlines, especially when a major, costly effort involving multiple groups may be indicated.

The EAF QA Officer or designee acts as the administrator for CARs, reviews each regularly, provides assistance as needed, tracks the progress of each, and follows up if a CAR's completion is overdue.

1.7 Definitions

Corrective Action Request (CAR) system – A process by which specified operational and data quality issues are addressed, especially if major resources or time or data has been delivered to a client.

1.8 Related Procedures

None

2. APPARATUS, MATERIALS, AND FORMS

2.1 Apparatus and Instrumentation

Not applicable

2.2 Reagents

Not applicable

2.2 Forms

EAF Corrective Action Request (CAR) Form (Figure 2-1).

3. CALIBRATION PROCEDURES

Not applicable

4. PROCEDURES

4.1 Applicability

4.1.1 Typical circumstances in which the CAR process may be used may include the following

- Correcting major bugs in software (especially if the software has been used to deliver data to EAF clients).
- Making major changes to improve procedures and corresponding SOPs or other quality documents (especially when the revisions involve equipment, facility, or software revisions)
- Purchasing, installing, and testing new equipment or software to solve specific performance deficiencies
- Developing new training materials to remedy specific staff performance issues
- Investigating and correcting systematic data quality or quality system deficiencies in the EAF

4.1.2 A CAR must be used if any of the following conditions apply:

- A major effort is needed to solve a specific operational or data quality issue
- Significant costs (e.g., labor hours, equipment, or materials) are involved
- Corrected data needs to be redelivered to the client
- A client is aware of the issue and expects status updates
- The corrective effort will take a relatively long period of time (i.e., more than about two weeks)
- Approved validation and QA criteria are affected
- Information about the corrective action needs to be formally documented

EAF CORRECTIVE ACTION REQUEST

CAR No. _____ **Date** _____

To **From**
How Identified
Reported (Nonconformance) Conditions **Answer Due Date** **Signature**
Root Cause
Corrective Action (Give Steps & Expected Completion Dates)
Preventive Action
Completed by **Date**
Accepted by **Date**
Follow-up Results **Performed by** **Date**
Closed Out (Y/N) _____ If not closed out on follow-up, issue a new CAR **New CAR No.** **Date**

Figure 2-1. EAF Corrective Action Request (CAR) Form

4.1.3 A CAR may be used when none of the circumstances in 4.1.2 apply and the laboratory supervisor/coordinator agrees that the corrective action can be handled within the normal scope of operations. Isolated, limited problems that typically arise during routine operations should not require CARs.

4.2 Procedure

4.2.1 Administration - The CAR forms are issued and logged by the EAF Quality Assurance Officer or a designee. Numbers are assigned to the CARs and are distributed as requested. CARs are logged in the Internal EAF Audit Book, log sheets updated, and forms and (related information) filed.

4.2.2 Initiation – Any EAF personnel may report a problem that initiates a CAR. Often, CARs may arise from internal EAF audit, external audits and ongoing data validation and QA/QC review. The originator of the CAR works with the supervisor/coordinator and EAF QA Officer (or designee) to complete the first two sections of the CAR form.

4.2.3 Assignment and Approval - The supervisor/coordinator for the affected operation is responsible for assigning personnel, working with the EAF QA Officer or designee to set a completion deadline and approving the CAR to be acted upon. CARs requiring significant resources or time to complete must be approved by the EAF Executive Director and the EAF QA officer.

4.2.4 Tracking – Once the CAR has been scheduled and approved, copies of the form are distributed to the initiator, supervisor/coordinator, and any other persons listed at the bottom of the form. The CAR form is maintained by the administrator, who enters due dates into a tracking calendar. The administrator reviews the CAR log, and each CAR regularly, provides input as necessary, and reports delays or concerns to the EAF Executive Director and QA Officer.

4.2.5 Implementation – Assigned personnel and the area supervisor/coordinator are responsible for carrying out the corrective action. The CAR file is updated whenever significant modifications to the approach, costs, resources, or deadlines are necessary.

4.2.6 Completion – When the corrective actions are completed, the successful completion of a CAR should be approved by the area supervisor/coordinator, Quality assurance officer or designee, or the EAF Executive Director.

4.2.7 Archiving – When the corrective action has been completed and approved, the approved CAR form and copies of related material and documentation shall be archived with their location given in the CAR log book.

5. QUANTIFICATION

Not applicable

6. QUALITY CONTROL

Expected due dates and completion are tracked using a schedule calendar.

7. QUALITY ASSURANCE

Not applicable

8. REFERENCES

None

9. DOCUMENT CHANGES

08/15/12: New SOP – r0.