

Quality Assurance  
Guidance Document

Revision 1.0

Laboratory Analysis and  
Data Processing/Validation for  
Chemical Speciation of PM<sub>2.5</sub> Filter Samples

Quality Assurance Project Plan

OAQPS Category 1 QAPP

Prepared for:

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Office of Air Quality Planning and Standards  
Research Triangle Park, NC 27711

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Prepared by:

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## LIST OF ACRONYMS AND ABBREVIATIONS

ADQ	audit of data quality
AMTIC	Ambient Monitoring Technology Information Center (US EPA)
AQRC	Air Quality Research Center
AQS	air quality system database
cm <sup>2</sup>	square centimeter
CASAC	Clean Air Scientific Advisory Committee
CDMS	Chemical Speciation Network data management system
COC	chain-of-custody
cps	counts per second
CSN	Chemical Speciation Network
CV	coefficient of variation
DART	data analysis and reporting tool
DAS	Division of Atmospheric Sciences
DDW	distilled-deionized water
DOPO	Delivery Order Project Officer
DQI	data quality indicator
DQO	data quality objective
DRI	Desert Research Institute
EDXRF	energy dispersive X-ray fluorescence
EAF	Environmental Analysis Facility
EC	elemental carbon
EPA	U.S. Environmental Protection Agency
FID	flame ionization detector
GC/MS	gas chromatography/mass spectrometry
IC	ion chromatography
IMPROVE	Interagency Monitoring of Protected Visual Environments
KHP	potassium hydrogen phthalate
L	liters
L/min	liters per minute
LAN	local area network
m	meter
m <sup>3</sup>	cubic meter
mA	milliamp
MDL	method detection limit
ME-RM	multi-element reference material
min	minute
MQO	measurement quality objective
MS	mass spectrometry

NAAQS	National Ambient Air Quality Standard
NAREL	National Air and Radiation Environmental Laboratory
NDIR	nondispersive infrared
NIST	National Institute of Standards and Technology
NSHE	Nevada System of Higher Education
OAQPS	EPA Office of Air Quality Planning and Standards
OC	organic carbon
ORIA	EPA Office of Radiation and Indoor Air
PE	performance evaluation
PI	principal investigator
PM	particulate matter
PMc	coarse particulate matter (with aerodynamic diameter less than 10 $\mu\text{m}$ and greater than 2.5 $\mu\text{m}$ )
PM <sub>2.5</sub>	particulate matter (with aerodynamic diameter less than 2.5 $\mu\text{m}$ )
PM <sub>10</sub>	particulate matter (with aerodynamic diameter less than 10 $\mu\text{m}$ )
PM <sub>10-2.5</sub>	PM <sub>10</sub> – PM <sub>2.5</sub>
PTFE	polytetrafluoroethylene
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
QMP	quality management plan
r	correlation coefficient
RM	reference material
RMSRE	reference material standard relative error
SIP	state implementation plan
SLT	state, local, and tribal
SOP	standard operating procedure
SRM	standard reference material
SVOC	semi-volatile organic compound
TOR	thermal optical reflectance carbon combustion analysis
TOT	thermal optical transmittance carbon combustion analysis
TSA	technical systems audit
UC Davis	University of California at Davis
UCD	University of California at Davis
$\mu\text{g}$	micrograms
$\mu\text{m}$	micrometers
Urel	relative expanded uncertainty
XRF	X-ray fluorescence
Z-score	standard score

## LIST OF TABLES

Table 1. Summary of Model 2015 and Model 2001 carbon analyzers differences. ....	10
Table 2: QC criteria summary.....	19
Table 3. Management records.....	23
Table 4. QA/QC records. ....	23
Table 5. Laboratory records.....	24
Table 6. DRI QC criteria for ion chromatography (anions and cations). ....	31
Table 7. UC Davis QC criteria for XRF (elements). ....	34
Table 8. DRI QC criteria for OC/EC analysis using the IMPROVE_A TOR/TOT carbon analysis method. ....	37
Table 9. Average MDL and proportional uncertainty estimates along with the number of collocated data pairs that were included in the uncertainty estimation for each reported parameter. ....	41
Table 10. Inspection criteria for DRI ion chromatography laboratory. ....	44
Table 11. DRI ion chromatography maintenance schedule. ....	44
Table 12. Inspection criteria for the XRF laboratory.....	45
Table 13. XRF laboratory maintenance schedule & responsibility. ....	45
Table 14. DRI carbon analysis laboratory maintenance schedule. ....	45
Table 15. Standard reference materials used for calibration of Epsilon 5.....	47
Table 16: Concentration ranges for XRF element standards.....	48
Table 17. DRI carbon laboratory instrument calibrations and frequencies. ....	49
Table 18. Types of audits of data quality.....	55


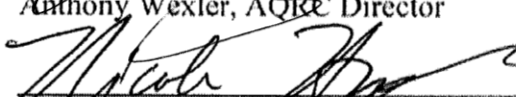
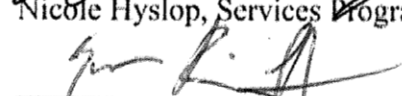
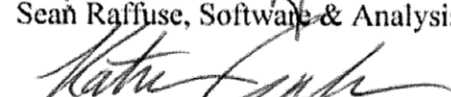
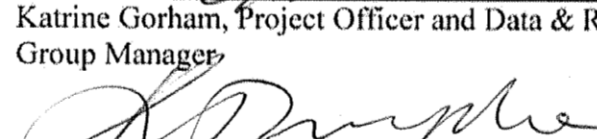
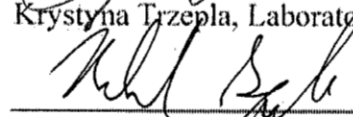
## LIST OF FIGURES

Figure 1. UC Davis Organizational Chart.....	2
Figure 2. DRI Organizational Chart.....	3
Figure 3. Improved analytical MDLs for Model 2015 vs. Model 2001. ....	10
Figure 4. Analytical MDLs for OC and EC at 7 wavelengths. ....	11
Figure 5. Comparison of replicate carbon analysis results between Model 2015 and Model 2001 carbon analyzers. ....	12
Figure 6. Flowchart of sample receiving and inventorying at UC Davis. ....	27
Figure 7. DRI sample flow diagram. ....	28
Figure 8. General flow diagram for CSN quartz-fiber IMPROVE_A carbon analysis. ....	30

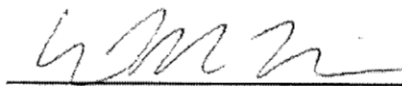
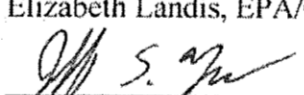
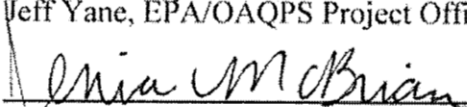
## 1. TITLE AND APPROVAL SHEET

The following signatures indicate agreement with the procedures specified within this plan and a commitment to deliver the details of this plan.

### Air Quality Research Center

 _____ Anthony Wexler, AQRC Director	12/3/17 _____ Date
 _____ Nicole Hyslop, Services Program Manager	11/29/17 _____ Date
 _____ Sean Raffuse, Software & Analysis Group Manager	11/29/17 _____ Date
 _____ Katrine Gorham, Project Officer and Data & Reporting Group Manager	11/29/17 _____ Date
 _____ Krystyna Trzepla, Laboratory Manager	11/29/17 _____ Date
 _____ Nicholas Spada, UC Davis QA Manager	11/29/17 _____ Date

### Environmental Protection Agency

 _____ Elizabeth Landis, EPA/OAQPS Program Manager	11/29/17 _____ Date
 _____ Jeff Yane, EPA/OAQPS Project Officer	11/29/17 _____ Date
 _____ Jenia McBrian, EPA/OAQPS Quality Assurance Officer	11/29/17 _____ Date

## 2. TABLE OF CONTENTS

List of Acronyms and Abbreviations .....	ii
List of Tables .....	iv
List of Figures .....	v
1. Title and Approval Sheet .....	1
2. Table of Contents .....	1
3. Distribution List .....	3
4. Project Management .....	3
4.1 Project/Task Organization .....	3
4.1.2 The Role of DRI in the Program .....	8
4.1.3 Position Responsibilities: DRI .....	12
4.2 Problem Definition/Background .....	16
4.3 Project/Task Description .....	16
4.3.1 Schedule .....	17
4.3.2 Sample Types and Quantities .....	17
4.4 Quality Objectives and Criteria for Measurement Data .....	17
4.4.1 Data Quality Objectives Process .....	17
4.5 Measurement Quality Objectives .....	18
4.6 Special Training and Certification.....	20
4.6.1 Purpose / Background .....	20
4.6.2 Training .....	20
4.6.3 Certification.....	21
4.7 Documents and Records .....	22
4.7.1 Management Records .....	23
4.7.2 QA/QC Records .....	23
4.7.3 Analytical Laboratories' Records.....	24
5. Data Generation and Acquisition.....	25
5.1 Sampling Process Design (Experimental Design).....	25
5.2 Sampling Methods Requirements.....	25
5.3 Sample Handling and Custody .....	26
5.3.1 Sample Handling and Chain of Custody .....	26
5.3.2 Internal Tracking of Analytical Samples .....	28
5.3.3 Archiving of Filters and Extracts .....	29
5.4 Analytical Methods Requirements .....	29
5.4.1 XRF Analysis for Elements.....	29
5.4.2 Extraction and Analysis of Anions and Cations.....	29
5.4.3 Carbon Analysis .....	29
5.5 Quality Control Requirements.....	30
5.5.1 Quality Criteria for Ion Analysis.....	30
5.5.2 Quality Criteria for XRF .....	33

5.5.3	Quality Criteria for OC/EC Analysis .....	35
5.5.4	Disaster Recovery Plan for Data .....	39
5.5.5	Uncertainty Determination .....	39
5.5.6	Method Detection Limits .....	42
5.5.7	Programmatic Uncertainty .....	43
5.6	Instrument/Equipment Testing, Inspection, and Maintenance Requirements .....	44
5.6.1	Ion Chromatography Laboratory .....	44
5.6.2	XRF Laboratory .....	44
5.6.3	OC/EC Laboratory .....	45
5.7	Instrument Calibration and Frequency .....	46
5.7.1	DRI Ion Chromatography Laboratory .....	46
5.7.2	XRF Laboratory .....	46
5.7.3	OC/EC Laboratory .....	49
5.8	Inspection/Acceptance of Supplies and Consumables .....	50
5.8.1	Filters .....	50
5.8.2	Criteria for Other Materials .....	50
5.9	Data Acquisition Requirements (Non-direct Measurements) .....	50
5.10	Data Management .....	50
5.10.1	Data Integrity .....	51
5.10.2	Data Flagging .....	52
5.10.3	Validation of the CDMS .....	52
5.10.4	Facility Recovery .....	53
5.10.5	Hardware Recovery .....	53
5.10.6	Software and Data Recovery .....	53
5.10.7	Data Security .....	54
6.	Assessments and Response Actions .....	55
6.1	Audits of Data Quality .....	55
6.2	Data Quality Assessments .....	56
6.3	External Quality Assurance Assessments .....	56
6.4	Reports to Management .....	56
7.	Data REVIEW And Validation .....	57
7.1	Validation .....	58
7.1.1	Level 0 Validation .....	58
7.1.2	Level 1 Validation .....	59
7.1.3	DART Validation .....	60
7.1.4	Validation of Subcontractor Data .....	60
7.2	Data Corrections .....	61
7.2.1	Elemental Analysis .....	61
7.2.2	Ions .....	61
7.2.3	OC/EC .....	61
7.3	Reconciliation with User Requirements .....	62



8. References.....	62
9. Appendix.....	63
9.1 Appendix A: List of DRI SOPs.....	63
9.2 Appendix B: List of UC Davis SOPs .....	64

### **3. DISTRIBUTION LIST**

#### Air Quality Research Center (AQRC)

Anthony Wexler, AQRC Director  
Nicole Hyslop, Services Program Manager  
Sean Raffuse, Software & Analysis Manager  
Katrine Gorham, Project Officer and Data & Reporting Group Manager  
Krystyna Trzepla, Laboratory Manager  
Nicholas Spada, UC Davis QA Manager

#### Desert Research Institute (DRI)

Judith Chow, Principal Investigator and EAF Director  
Richard Tropp, EAF QA Manager  
Steve Kohl, EAF Laboratory Manager  
Dana Trimble, EAF Laboratory Manager

#### Environmental Protection Agency (EPA)

Elizabeth Landis, EPA/OAQPS Program Manager  
Jeff Yane, EPA/OAQPS Project Officer  
Jenia McBrian, EPA/OAQPS Quality Assurance Officer

### **4. PROJECT MANAGEMENT**

#### **4.1 Project/Task Organization**

This QAPP describes quality planning for contract number EP-D-15-020 with the U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS). Work on this contract in support of the PM Chemical Speciation Network (CSN) program is performed by staff from the Air Quality Research Center (AQRC) at the University of California at Davis (UC Davis). UC Davis will perform x-ray fluorescence (XRF) analysis and will process, validate, and deliver the final concentration data. Desert Research Institute (DRI), a subcontractor to UC Davis, will perform ions analysis by ion chromatography and will perform organic/elemental carbon (OC/EC) analysis using the same method

used in the Interagency Monitoring of Protected Visual Environments (IMPROVE) program.

Organizational charts for project personnel at UC Davis and DRI are shown in Figure 1 and Figure 2, respectively.

UC Davis coordinates its laboratory and data management activities with EPA/OAQPS. Lab QA auditing and technical assistance are also provided by EPA/OAQPS.

Figure 1. UC Davis Organizational Chart

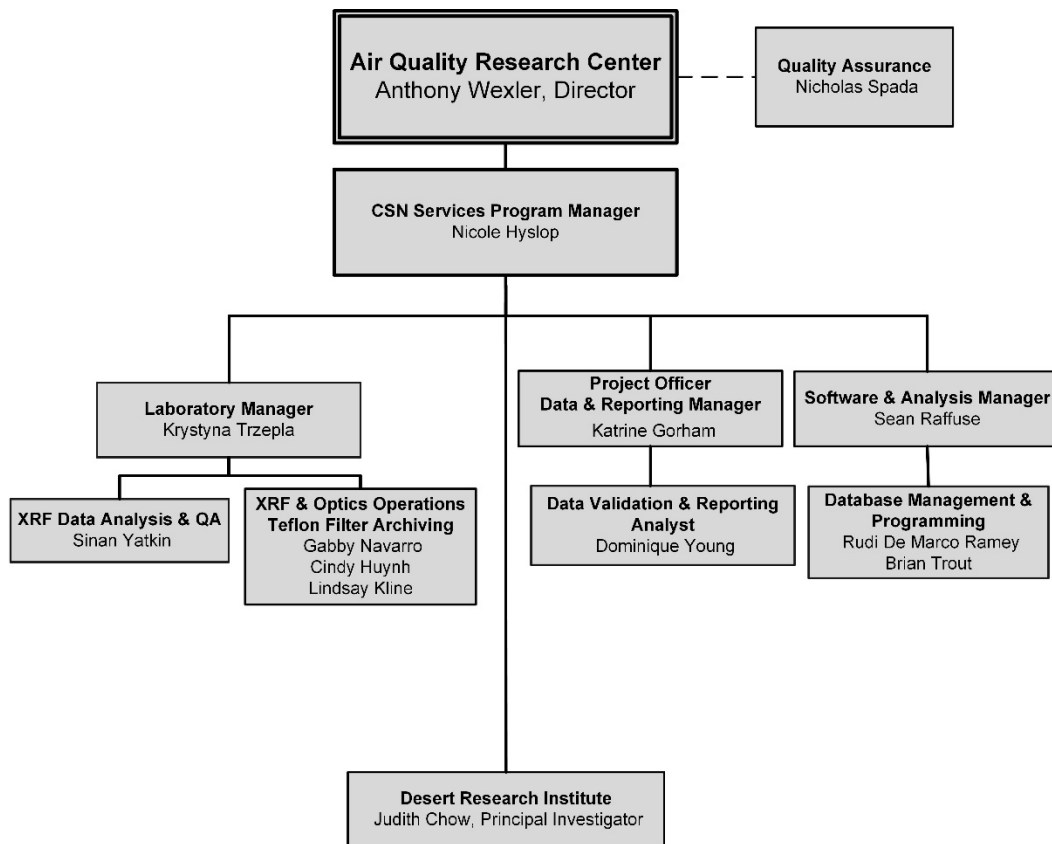
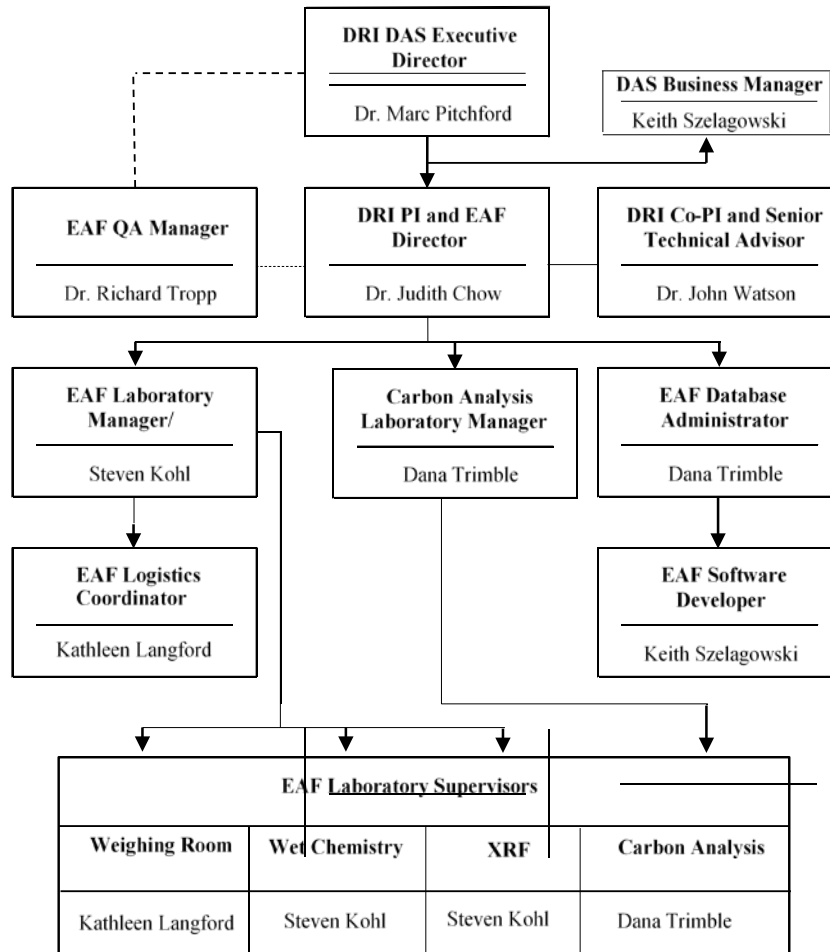


Figure 2. DRI Organizational Chart



Position Responsibilities: UC Davis

4.1.1.1 Director of AQRC, Dr. Anthony Wexler

The Director of the AQRC has the overall responsibility, accountability, and authority for all programs operating through the department. Responsibilities include:

1. Determining that the research program adheres to its budget,
2. Facilitating interaction with other AQRC programs, as well as other programs on UC campuses,
3. Overseeing personnel performance reviews, and
4. Representing AQRC in any fiscal inquiries.

Dr. Wexler is an aerosol scientist and professor of Mechanical and Aerospace Engineering, Civil and Environmental Engineering, and Land, Air and Water Resources. His work focuses on the role of atmospheric particles in human health and climate change. He works on mathematical modeling of atmospheric aerosol dynamics, development of advanced instrumentation for particle collection and analysis, and response of airways to particle deposition. He has 30 years of experience in the field of atmospheric science with 17 years at UC Davis. Contact information: [aswexler@ucdavis.edu](mailto:aswexler@ucdavis.edu) and 530-754-6558.

#### 4.1.1.2 Services Program Manager, Dr. Nicole Hyslop

The CSN program at UC Davis is led by the Services Program Manager, who provides overall supervision to ensure that the technical program is being performed in accordance with the EPA statement of work and according to this QAPP. Responsibilities include:

1. Maintaining cooperative working relationships with the EPA Project Manager, Delivery Order Project Officers (DOPO), and UC Davis QA Manager in the following ways:
  - a. Conference calls to be held as frequently as needed,
  - b. Meetings with EPA staff as-needed ,
  - c. Written communications and e-mails to document planning and decisions,
2. Facilitating interaction among team personnel,
3. Ensuring that proper techniques and procedures are followed,
4. Ensuring the quality and timely delivery of data,
5. Ensuring that reporting requirements are satisfied,
6. Maintaining cost and schedule control,
7. Adjusting schedules to meet client needs, and
8. Reviewing and approving deliverables submitted to the client.

Dr. Hyslop is a principal investigator and operations manager for the Air Quality Monitoring group at UC Davis. She is responsible for managing IMPROVE and CSN operations at UCD including managing the laboratory, field, data validation, and applications development staff. Dr. Hyslop has BS and MS degrees in Chemical Engineering from the University of Wisconsin – Madison and University of Texas – Austin. She has 21 years of experience in the field of atmospheric science with 13 years at UC Davis and 5 years at Sonoma Technology, Inc. Contact information: [nmhyslop@ucdavis.edu](mailto:nmhyslop@ucdavis.edu) and 530-754-8979.

#### 4.1.1.3 UC Davis QA Manager, Dr. Nicholas Spada

The UC Davis QA Manager monitors quality assurance/quality control (QA/QC) for the CSN program at UC Davis, and in this role Dr. Spada reports to the Director of Air Quality Research Center. As such, the UC Davis QA Manager can report problems to AQRC's highest level of management, independent of the CSN project structure. In practice the UC Davis QA Manager will work closely with the Services Program Manager with the expectation that most problems can be solved without involvement from the Director of the Air Quality Research Center. Responsibilities include:

1. Reviewing the results of routine monthly data validation checks performed at AQRC before the data are distributed to the SLTs for review,
2. Reviewing the efforts of other AQRC staff to investigate problems identified during data review and to recommend corrective actions,
3. Reviewing control charts and other data quality reports from AQRC and DRI to assess the achievement of MQOs for uncertainties and MDLs,
4. Performing periodic in-lab and data review audits of data quality for the AQRC and DRI laboratories,
5. Conducting an annual review of the SOPs, QAPP, and QMP for both AQRC and DRI,
6. Hosting external auditors during anticipated visits, and
7. Distributing EPA-provided Performance Evaluation (PE) samples within AQRC and summarizing PE analysis results.

Dr. Spada is a post-doctoral scholar with the Air Quality Group at UC Davis. His work focuses on the role of metallic species in atmospheric particles in human health and climate change. He works on development of measurement techniques and instrumentation as well as performs local and long-transport field studies. He has 11 years of experience in the field of environmental science with 6 years at UC Davis. Contact information: njspada@ucdavis.edu and 530-752-0933.

#### 4.1.1.4 Project Officer and Data & Reporting Group Manager, Dr. Katrine Gorham

The CSN Project Officer will report directly to the Services Program Manager and will assist with several facets of the project. Responsibilities include:

1. Preparing monthly, quarterly, and annual reports for the EPA, with input from other project staff,
2. Preparing and editing various project-related documents such as position descriptions, technical reports, and meeting summaries,
3. Assisting in the editing of the SOPs, QAPP, and QMP,
4. Tracking project budgets and submitting a monthly budget summary to the Services Program Manager,

5. Tracking the number of samples analyzed under each Delivery Order as input to the monthly invoices,
6. Coordinating the purchasing of supplies and equipment,
7. Coordinating the recruitment and hiring of new staff, as needed, and
8. Tracking the flow of data through DART and on to final submittal to ensure that schedules for each monthly submittal are met.

The AQRC Data & Reporting Manager Group Manager oversees data validation and delivery operations, and oversees technical staff (including Dr. Dominique Young) responsible for data validation and submission (see Section 7).

Responsibilities include:

1. Reviewing the components of the measurements (flow rates, elemental concentration, etc.) in preparation for final data validation,
2. Working with others in laboratory operations to resolve problems or discrepancies encountered during data review,
3. Validating the final data set, with input as needed from data analysts,
4. Submitting the data set to the DART system for SLT review,
5. Communicating with SLT data validators to resolve discrepancies,
6. Formatting the data to meet AQS standards, and
7. Submitting the final data sets to AQS.

As the AQRC Project Manager and Data & Reporting Group Manager, Dr. Gorham manages the data validation process, data deliverables, reporting, documentation, internal/external communication, and financial tracking. She has a background in atmospheric chemistry, and 8 years of experience in the field of research management with one year at UC Davis. Contact information: kgorham@ucdavis.edu and 530-752-7119.

#### 4.1.1.5 Laboratory Manager, Krystyna Trzepla

The AQRC Laboratory Manager is responsible for overseeing all aspects of the laboratory, including handling samples, analyzing samples by EDXRF and optical absorption, and validating analytical data. Responsibilities include:

1. Maintaining a smooth flow of filters through the laboratory,
2. Coordinating work with DRI for ions and carbon analysis,
3. Maintaining a schedule for sample analysis, quality control tests, data processing, and progress tracking to ensure that schedules are met and sample identification and integrity are not compromised,
4. Reviewing each data set in the context of historical data and of current system conditions, reviewing control charts, identifying abnormalities, and providing recommendations for understanding and rectifying them,
5. Reviewing the SOPs, QAPP, and QMP,
6. Training and mentoring new staff, and

7. Managing tests comparing the UC Davis laboratory with other EDXRF laboratories (through PE sample comparisons or other round-robin studies), working with the other laboratories to establish test protocols, overseeing the analysis of samples at UC Davis, analyzing the results, and working with the other laboratories to prepare reports and publications for external distribution.

The AQRC Laboratory Manager oversees technical staff, including:

A spectroscopist (Dr. Sinan Yatkin) reviews all of the EDXRF data and performs QC checks, with responsibilities including:

1. Reviewing the EDXRF analysis results and related spectra,
2. Processing and reviewing the data from all EDXRF quality control tests and providing the data to other analysts in final form, and
3. Providing recommendations to the data validation analyst regarding EDXRF data quality.

Three laboratory technicians (Gabby Navarro, Cindy Huynh, and Lindsay Kline) share the following responsibilities:

1. Organizing the PTFE filters received for analysis and recording filter identification information in the database,
2. Operating the EDXRF and optical absorption systems,
3. Maintaining a record of the parameters and conditions associated with each analysis for each analytical system, processing the data, and providing the data to other analysts in final form, and
4. Placing PTFE filters in a permanent archive and maintaining a cataloging system to allow efficient retrieval of archived filters (see Section 5.3.3).

Ms. Trzepla is the Laboratory Manager for the Air Quality Monitoring group at UC Davis. She is responsible for managing daily laboratory operations including sample preparation, gravimetric analysis, X-ray fluorescence (XRF) analysis, and light absorption measurements. She has been the Laboratory Manager since 2010. She led several laboratory changes related to new instrumentation (XRF systems, balances) including research, testing and implementation. Ms. Trzepla is also leading the efforts to develop XRF calibration materials specifically for particulate matter analysis. She has 31 years of experience in the field of atmospheric science with 27 years at UC Davis. Contact information: [ktrzepla@ucdavis.edu](mailto:ktrzepla@ucdavis.edu) and 530-752-4232.

#### 4.1.1.6 Software & Analysis Group Manager, Sean Raffuse

The AQRC Software and Analysis Group Manager oversees development of the CSN SQL database and software for laboratory operations, validation, and data analysis. The Software & Analysis Group Manager has two technical staff:

The AQRC Software & Analysis Group Manager oversees technical staff (including Rudi De Marco Ramey and Brian Trout) who share responsibilities for database management and programming. Responsibilities include:

1. Maintaining and upgrading the data management system (see Section 5.10) including the SQL Server database, data processing and visualization tools, and data reporting and data input forms,
2. Working with staff to identify, map, design and implement improvements to the data management system,
3. Testing, verifying, and documenting modifications to the system,
4. Importing and processing new data and associated metadata into the database system, and
5. Designing and maintaining an archival system for all data and metadata records and source files.

As the AQRC Software & Analysis Group Manager, Mr. Raffuse oversees data processing and software development for laboratory operations, validation tools, and data analysis. In addition, his research focuses on developing, improving and applying fire and smoke models through the use of data sets, research, and information systems, and developing and using satellite-derived data products. He has 15 years of experience in the field of atmospheric science with 4 at UC Davis. Contact information: sraffuse@ucdavis.edu and 530-752-4225.

#### 4.1.2 The Role of DRI in the Program

UC Davis has engaged DRI as a subcontractor for ions and OC/EC analysis. As a subcontractor laboratory providing analytical services, DRI has contributed to this QAPP and provided their SOPs and QMP for EPA approval.

The data quality requirements specified in the UC Davis prime contract with EPA flow down contractually through the subcontract to DRI. DRI initially qualified for ions and carbon analysis by passing the performance evaluation (PE) samples sent by the EPA to all contract bidders in December 2014. Throughout the course of this contract UC Davis will regularly review DRI's quality control test data to ensure quality of the subcontracted work. DRI's ions and carbon data will also be subject to data validation prior to submittal to AQS (see Section 7). UCD will arrange technical systems audits of the DRI facilities every two to three years.

DRI is a nonprofit environmental research institute that is an autonomous division of the Nevada System of Higher Education (NSHE). DRI's environmental research programs are directed from three core divisions (Atmospheric Sciences, Earth and Ecosystem Sciences, and Hydrologic Sciences) and several interdisciplinary centers. DRI's Environmental Analysis Facility (EAF) in Reno, Nevada, was established in 1985 by its current director.



DRI will provide ions analysis for nylon filter samples collected in CSN. Each filter will be extracted in distilled-deionized water (DDW) and then analyzed for anions and cations by ion chromatography (IC). The anions to be reported are sulfate, nitrate, and chloride. The cations to be reported are ammonium, sodium, and potassium. Ion chromatography will be performed using any of three Dionex ICS-5000+ systems with two Dionex ICS-3000 systems as backup. Detailed description of DRI methods for ions analysis, along with references to the applicable SOPs, can be found in Sections 5.4.2.

An inter-comparison test between the older ICS-3000 and the new ICS-5000+ systems at EAF showed excellent agreement of concentrations for all anions based on a complete batch (n = 34) of TCEQ samples. A comparison between the three new ICS-5000+ systems was conducted as well, revealing comparable results for all ions, with a slightly lower correlation for chloride. Additional inter-comparison tests were performed on a batch of CSN samples (n = 116), again showing excellent correlations for all anion species with linear regression slopes between 0.94 and 1.0, and correlation coefficients ranging from 0.998 to 1.00.

Moreover, the inter-comparison demonstrated superior performance of the ICS-5000+ systems, reflected in three important parameters: 1) higher sensitivity; 2) better chromatographic resolution; and, 3) ability to measure carboxylic acids. The higher sensitivity is reflected in the lower detection limits, e.g., a factor of four improvement for sulfate and a factor of two improvement for ammonium. Another improvement is the location of the chloride peak in relation to the water dip. Moreover, the utilization of a hydroxide eluent on the ICS-5000+ systems allows for separation, identification, and quantification of organic acids, i.e., carboxylate and dicarboxylate ions.

DRI will provide OC/EC analysis for quartz filter samples following the same method as currently employed by the IMPROVE program. This analytical protocol, known as IMPROVE\_A, was developed by DRI using the DRI Model 2001 Thermal/Optical Carbon Analyzer (manufactured by Atmoslytic, Calabasas, CA). It was placed in service on the IMPROVE program beginning January 1, 2005 and phased into the CSN program between 2007 and 2010. The method is based on the technical requirements given in DRI's SOP. UC Davis and DRI have defined data transfer formats and procedures and have developed SOPs for OC/EC analysis (described below). Detailed description of DRI methods for carbon analysis, along with references to the applicable SOPs, can be found in Sections 5.4.3.

Data generated by the IMPROVE\_A method is reported using both the Thermal Optical Transmittance (TOT) and Thermal Optical Reflectance (TOR) methods.

TOT and TOR results for certain OC fractions differ, so both will be reported to EPA’s Air Quality System (AQS) database under separate parameter codes.

Multi-wavelength Carbon Analyzer

The Model 2015 multi-wavelength carbon analyzer replaced the Model 2001 single wavelength carbon analyzer for analysis of samples collected on or after January 1, 2016. The Model 2001 reached the end of its useful life – maintenance time and effort were increasing and replacement parts were increasingly difficult to find. The Model 2015 is designed with more readily available parts and simpler maintenance. In addition, the multi-wavelength capability of Model 2015 provides information useful for determining carbon origins. Table 1 summarizes some the differences between the Model 2015 and Model 2001 carbon analyzers.

Table 1. Summary of Model 2015 and Model 2001 carbon analyzers differences.

Model 2001 Carbon Analyzer	Model 2015 Carbon Analyzer
FID (uses methanator)	Nondispersive infrared (NDIR, no need for methane gas)
632 nm laser	405, 455, 532, 635, 780, 808, and 980 nm Lasers
No ability to measure brown carbon	Pyrolyzed carbon at multiple wavelengths will allow for brown carbon measurements and improved black carbon measurements
Visual Basic Program Architecture	LabVIEW Program Architecture
Microsoft Access data storage with 2 GB total storage limit	Microsoft SQL Server data storage with 10GB storage limit per database (free version)
Real time values for FID and Laser	Real time data for flow meters (5), ovens (2), NDIR, and lasers (7)
Proprietary, outdated, and unavailable parts	Off-the-shelf, current parts
Maintenance requires partial deconstruction	Easier maintenance due to sliding shelves and hydraulic lifts

With its improved design, the Model 2015 can also achieve better performance, including better Method Detection Limits (MDLs; Figure 3). Additionally, the MDLs are similar among the 7 wavelengths (Figure 4). Replicate analyses indicate good agreement between the Model 2015 and Model 2001 for IMPROVE\_A carbon analysis parameters OC, EC and TC (Figure 5).

Figure 3. Improved analytical MDLs for Model 2015 vs. Model 2001.

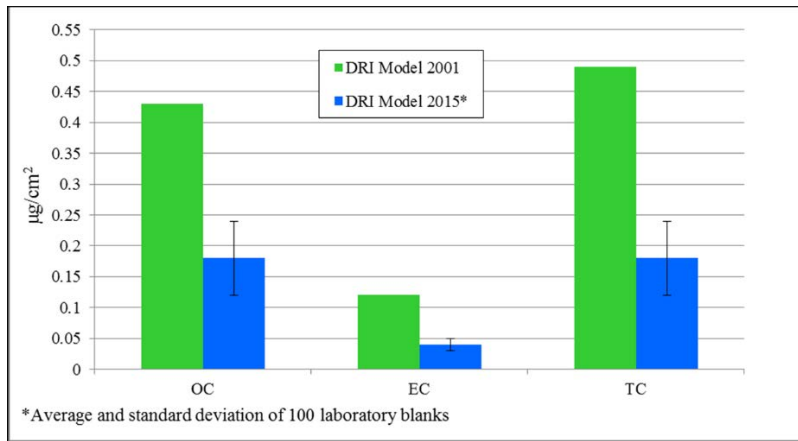


Figure 4. Analytical MDLs for OC and EC at 7 wavelengths.

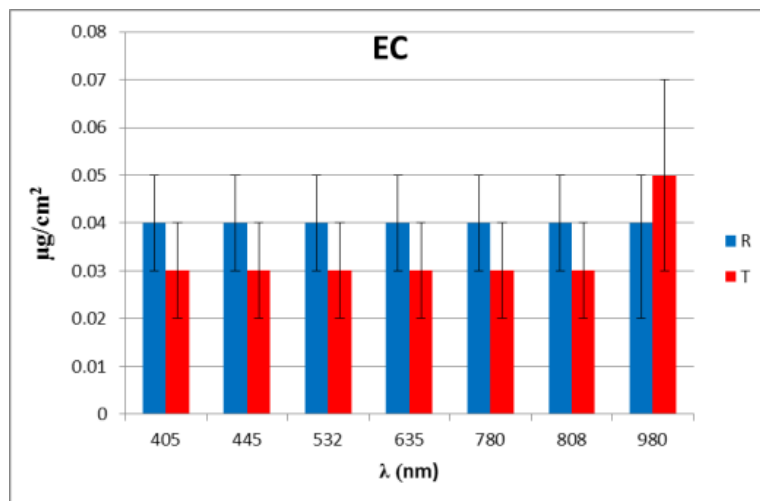
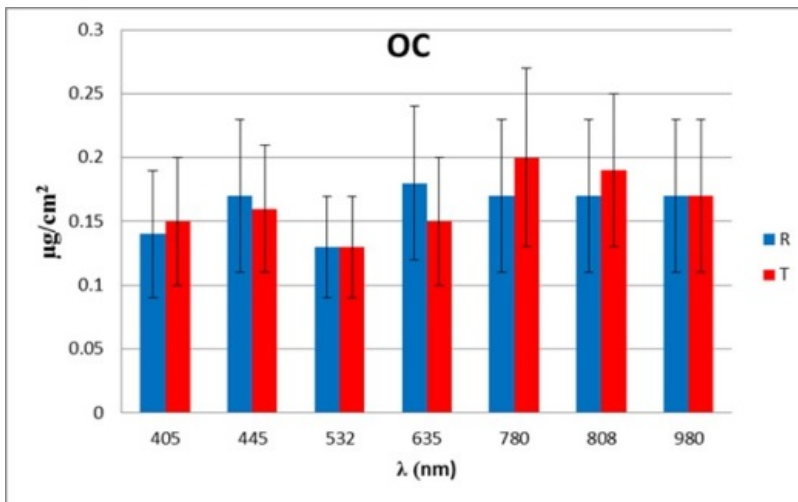
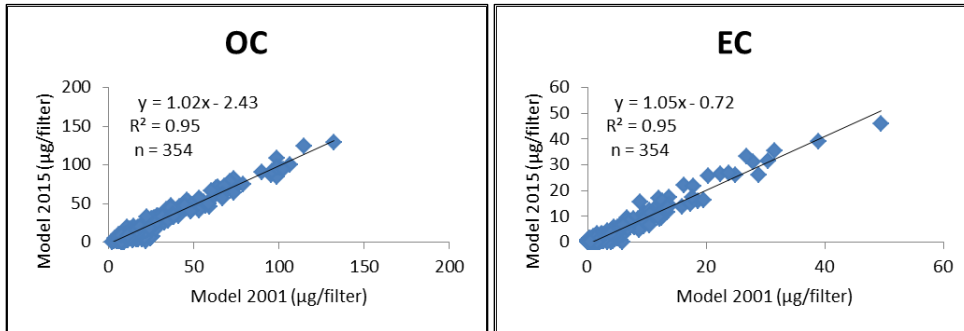
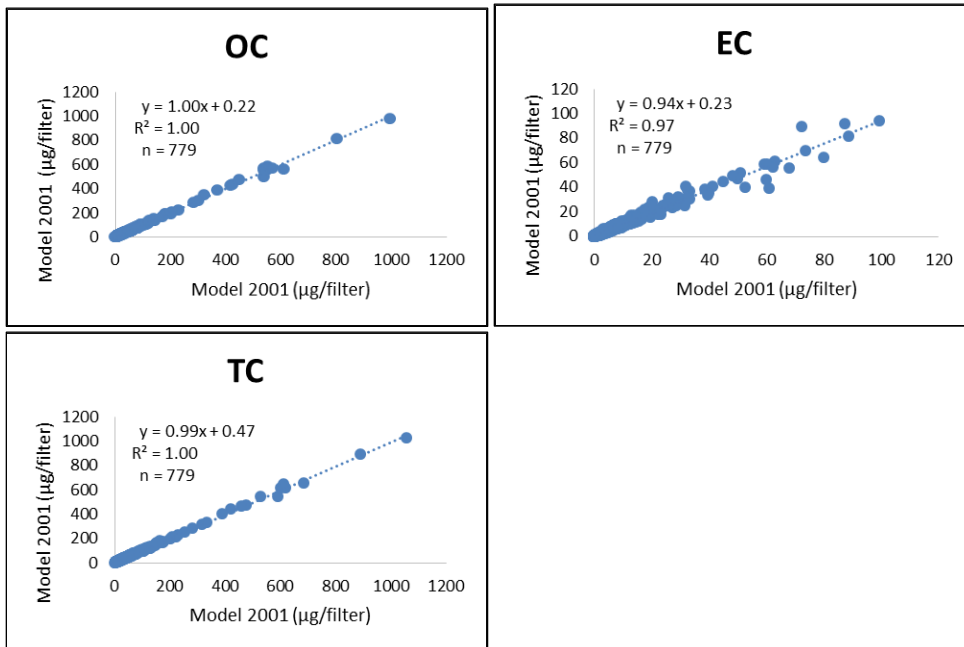


Figure 5. Comparison of replicate carbon analysis results between Model 2015 and Model 2001 carbon analyzers.

(a) Model 2015 versus Model 2001; 354 samples analyzed 2/8/15 – 7/29/15.



(b) Model 2001 versus Model 2001; 779 samples analyzed 2/8/15 – 7/29/15.



#### 4.1.3 Position Responsibilities: DRI

##### 4.1.3.1 DAS Executive Director, Dr. Marc Pitchford

The Division of Atmospheric Sciences (DAS) Executive Director provides overall guidance and oversight of the DAS. The Executive Director approves EAF Quality Management Plans and has the authority to see that project QA/QC issues reported by the EAF QA Manager have the resources to be expeditiously resolved.

Dr. Pitchford has been involved in air quality monitoring and assessment research since 1974. In particular his interests and experience has been in leading technical teams responsible for the design and management of extensive aerosol and visibility monitoring studies and networks. Among his achievements is the design and oversight of the IMPROVE aerosol and visibility monitoring network which started with 20 sites in 1986 and continues to operate over 160 sites nationwide; the design and technical leadership of Project MOHAVE (1991 – 1996) and the BRAVO Study (1997 – 2004), both involved extensive field monitoring programs with ambient measurements and tracer release and monitoring followed by deterministic and receptor modeling for source attribution; and co-technical leader of the EPA PM Super Sites program that funded five university research partnerships to develop and operate sophisticated aerosol monitoring sites various urban areas. Dr. Pitchford has also acted as a visibility subject matter expert adviser to the US Environmental Protection Agency for the development and implementation of policy for visibility protection of national parks and wilderness areas, and for the review/revisions of the Secondary Particulate Matter National Ambient Air Quality Standards. Contact information: marc.pitchford@dri.edu and 775-674-7127.

#### 4.1.3.2 Principal Investigator and EAF Director, Dr. Judy Chow

The EAS Director and DAS Principal Investigator (PI) for this project oversees, coordinates, and tracks progress of the PM<sub>2.5</sub> carbon and ions analyses, monitors feedback from the EAF QA Manager, ensures completion of delivery of monthly data to UC Davis, and tracks expenses and invoices.

Dr. Chow has more than 38 years of experience in atmospheric sciences, environmental health, research, and education. As founder and director of the Desert Research Institute's (DRI) EAF, she heads a group of ~30 research scientists and technicians in developing and applying advanced analytical methods to characterize suspended atmospheric particles for source attribution and evaluate their effects on visibility, air pollution, ecosystems, and health. Dr. Chow has served on a number of monitoring and research advisory committees for PM<sub>2.5</sub>, including the National Academy of Sciences/National Research Council Committee on "Research Priorities for Airborne Particulate Matter". She serves on the U.S. EPA's Clean Air Scientific Advisory Committee (CASAC) Ambient Air Monitoring and Methods Subcommittee (now the Air Monitoring and Methods Subcommittee) since 2004. Contact information: judy.chow@dri.edu and 775-674-7050.

#### 4.1.3.3 Co-PI and Senior Technical Advisor, Dr. John Watson

The Co-PI and Senior Technical Advisor provides assistance if unusual sample deposits or abnormal peaks are detected in CSN samples, initiates extra testing or optional special studies to resolve discrepancies as necessary, and ensures the consistency of long-term measurements.

Dr. Watson has over 43 years of experience in the field of atmospheric sciences. His research includes: 1) designing and conducting regional- urban-, and neighborhood-scale aerosol characterization and source apportionment studies; 2) developing and applying real-world, multipollutant emission measurement technologies; and 3) evaluating, characterizing, and advancing methods to measure carbonaceous material in suspended particles. Contact information: john.watson@dri.edu and 775-674-7046.

#### 4.1.3.4 EAF QA Manager, Dr. Richard Tropp

The EAF QA Manager ensures that carbon and ions analysis procedures conform to the QA/QC and contract requirements. The EAF QA Manager also prepares, and/or reviews and approves quality-related documents such as this QAPP and the DRI SOPs and QMP. The EAF QA Manager conducts internal audits, including audit of data quality, coordinates external system and performance audits, participates in inter-laboratory comparisons, and oversees the EAFs quality system. The EAF QA Manager has the independence and authority to report issues directly to the EAF Director or DAS Executive Director, as needed, for resolution.

Dr. Tropp has more than 37 years of management and research experience in the areas of ambient air quality monitoring, aerosol and particulate measurements, visibility, acid deposition, data analysis, quality assurance, regulation development, and air pollution control. His experience includes university research, management of state agency regulation development and research, and management and participation in more than 60 ambient air monitoring projects. These projects included particulate measurements for advanced aerosol models, visibility, acid deposition, wet and dry depositions, ozone precursors, air toxics, air quality monitoring, and revised National Ambient Air Quality Standards and monitoring guidance, most recently for PM<sub>2.5</sub>. Contact information: richard.tropp@dri.edu and 775-674-7094.

#### 4.1.3.5 EAF Laboratory Managers, Coordinators, and Supervisors

The EAF Laboratory Manager (Steven Kohl) coordinates routine PM<sub>2.5</sub> laboratory operations among the different EAF laboratories and oversees the anion and cation analyses for the CSN samples. The EAF Carbon Laboratory Manager (Dana Trimble) oversees the carbon laboratory operations. Both Laboratory Managers conduct Level I data validation and data reporting. The EAF Logistics Coordinator and Weighing Room Supervisor (Kathleen Langford) is responsible for: 1) coordinating the logistics of shipping, receiving, handling and distribution of samples, and 2) gravimetric analyses. Additionally, the EAF Laboratory Manager and EAF Carbon Laboratory Manager have professional, technical, and hourly staff members reporting to them for performing carbon and ions analyses.

#### 4.1.3.6 EAF Database Administrator, Dana Trimble

The EAF Database Administrator, oversees the maintenance of EAF laboratory, back-ups and security for EAF databases, and special retrievals of database information. The EAF Database Administrator also coordinates the collection and reporting of information for project deliverables and billings.

Ms. Trimble has over 21 years of experience in managing laboratory operations and computer and database administration. As EAF's Carbon Laboratory Manager, she is responsible for the day-to-day operations of the carbon laboratory and supervises the carbon analysts. She also performs Level I and Level II carbon data validation. She is responsible for compiling and reporting IMPROVE carbon analysis data for both the EPA's Chemical Speciation Network and NPS's IMPROVE network and all to other sponsors requiring carbon analysis. Additionally, Ms. Trimble serves as EAF's computer systems manager and supervises the administrative and technical staff that support EAF. Contact information: dana.trimble@dri.edu and 775-674-7114.

#### 4.1.3.7 EAF Software Developer and Support, Keith Szelagowski

The EAF Software Developer and Support Manager provides software development and network and systems support, as well as develops database structure, entry screens, and report formats based on user and EPA requirements and guidance. In addition, this position develops programs to implement and enhance database design and data processing, and provides technical support to troubleshoot and maintain the EAFs local area networks (LANs) and backup and recovery systems.

Mr. Szelagowski has 4 years of experience in software support at DRI and has developed many of the software and database structures in use with supporting

analytical results. Contact information: keith.szlagowski@dri.edu and 775-674-7174.

#### 4.1.3.8 EAF Business Manager, Keith Szlagowski

The EAF Business Manager tracks deliverables and accounts payable and submits monthly invoices. This position also ensures that contract administrative and reporting requirements are met.

Mr. Szlagowski has 2 years of experience in business management at DRI. Contact information: keith.szlagowski@dri.edu and 775-674-7174.

## 4.2 Problem Definition/Background

In 1997, the EPA promulgated the new National Ambient Air Quality Standards (NAAQS) for particulate matter (PM). The regulations (40 CFR Parts 50, 53, and 58) apply to the mass concentrations ( $\mu\text{g}/\text{cubic meter of air}$ ) of particles with aerodynamic diameters less than 10 micrometers (the  $\text{PM}_{10}$  standard) and to particles with aerodynamic diameters less than 2.5 micrometers (the  $\text{PM}_{2.5}$  standard). To support these standards, a 1500-site mass measurements network and a smaller  $\text{PM}_{2.5}$  CSN were established.

The CSN consists of a set of core sites and non-core sites. Chemically speciated data are used to serve needs associated with development of emission mitigation approaches to reduce ambient PM concentration levels. Such needs include emission inventory establishment, air quality model evaluations, and source attribution analysis. Other uses of the data sets will be regional haze assessments, estimating personal exposure to PM and its components, evaluating potential linkages to health effects, and support for setting a secondary NAAQS for PM.

## 4.3 Project/Task Description

The UC Davis laboratory contract involves three broad areas:

1. Receiving field samples from the filter handling contractor (Amec Foster Wheeler) and analyzing the sample media for chemical constituents including elements, soluble anions and cations, and carbonaceous species.
2. Assembling validated sets of data from the analyses, preparing data reports for EPA management and SLT, and entering data into the AQS.
3. Establishing and applying a comprehensive QA/QC system. The UC Davis and DRI CSN SOPs and QMPs and this QAPP provide the documentation for the quality system for this study.



UC Davis will provide all the staff, facilities, analytical instrumentation, computer hardware and software, and consumable supplies necessary to carry out tasks from these work areas and will ensure that all contractual specifications are met. The contractual requirements for UC Davis flow down to DRI through the subcontract that UC Davis has established with DRI.

#### 4.3.1 Schedule

The current contract is active September 16, 2015 to September 15, 2020. After receipt of all filters and associated filter data, the analysis laboratories have 30 calendar days to analyze the filters for elements, ions, and carbon. Levels 0 and 1 data validation will be conducted within 30 calendar days prior to delivering the data set to an interim password protected web site or ftp site. After the data has returned from the interim site, UC Davis will upload the data into AQS within 30 calendar days.

#### 4.3.2 Sample Types and Quantities

Samples will be analyzed on three types of filters: polytetrafluoroethylene (PTFE), nylon, and quartz. PTFE filters (elements) are shipped to UC Davis and the nylon (ions) and quartz (carbon) filters are shipped directly to DRI (see Section 5.3). At the beginning of the contract period in 2015 approximately 13,000 filters of each type are anticipated to be analyzed each year. This level of activity is expected to continue for the remainder of the contract unless program funding is reduced.

### 4.4 Quality Objectives and Criteria for Measurement Data

#### 4.4.1 Data Quality Objectives Process

The data quality objectives (DQO) process is a strategic planning approach used to achieve data of adequate quality to support decision making. The DQO process helps to ensure that the type, quantity, and quality of environmental monitoring data will be sufficient for the data's intended use, while simultaneously ensuring that resources are not wasted collecting unnecessary, redundant, or overly precise data. The formal DQO process consists of seven steps for development of an experimental design to meet decision criteria specified by stakeholders, as described in EPA QA/G-4, *Guidance for the Data Quality Objectives Process* (EPA, 1994).

A DQO Workgroup was established by the EPA to develop and document DQOs for the PM<sub>2.5</sub> CSN. The primary DQO, detection of trends in the chemical

speciation data, was defined as follows  
(<http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/dqo3.pdf>):

“To be able to detect a 3%–5% annual trend in the concentrations of selected chemical species with 3–5 years of data on a site-by-site basis after adjusting for seasonality, with power of 0.80.” (EPA, 1999a)

The DQO study concluded that with sampling every third day for five years, trends greater than 5% (or less than –5%) per year can be detected for sulfate, calcium, and total carbon on a single-site basis. For nitrate, however, the annual trend must exceed  $\pm 6.3\%$  to be detected with a power of 80%. The workgroup members concluded that this was not sufficiently different from the 5% goal to require adjustment to the sampling design. Sampling daily instead of every third day provides little improvement in the ability to detect trends; however, the model showed that cutting the sampling rate to every sixth day begins to impair the ability to detect concentration trends within five years.

Several secondary objectives for data collected at the CSN sites and other chemical speciation sites were identified, but these were not evaluated quantitatively by the workgroup. Five important secondary data uses are as follows:

1. Model evaluation, verification, and/or validation
2. Emission inventory
3. Source attribution
4. Spatial and seasonal characterization of aerosol distributions
5. State Implementation Plan (SIP) attainment and strategy development

The desirable data quality characteristics for these secondary objectives are significantly different from those applicable to trend assessment.

Further development of quantitative DQOs will inform refinement of quality objectives for CSN; subsequent versions of this QAPP will include updates as they become available.

#### **4.5 Measurement Quality Objectives**

Development of quantitative Measurement Quality Objectives (MQOs) is contingent upon further development of DQOs by the EPA. These MQOs are specified by the following data quality indicators (DQIs): precision, bias, representativeness, comparability, completeness, and detectability.

**Precision** – is a measure of the “repeatability of the measurement process under specified conditions” (EPA, 1983). Precision represents the random component of the error term.

**Bias** – is a measure of a systematic offset which skews data results in a single direction, either positive or negative, from an accepted value.

**Representativeness** – is the extent to which measurement results represent the locations, conditions, and times of sampling. This aspect is controlled by network design, siting, and probe locations.

**Comparability** – is the agreement between similar and related data sets. Comparability can be determined using collocated sampling techniques with the same or similar analytical methods and quantifying the difference for a statistically significant number of collocated sample pairs.

**Completeness** – is the yield of valid measurement results from an expected set of measurements under normal conditions. The data completeness goal for each parameter reported is 75%, consistent with 40 CFR Part 50.

**Detectability** – is the lowest result value that a specific analytical method can reliably discern.

The DQIs that are used to assess MQOs for laboratory analyses are discussed in detail in Section 5.5 and shown in Tables 6 through 8. DQI criteria are summarized in Table 2. The existing CSN DQOs were based on IMPROVE data, and the MQOs for CSN are specified by the same DQIs as for IMPROVE.

Table 2: QC criteria summary.

QC Activity	Frequency
<b>Ion Chromatography (Anions and Cations)</b>	
Multipoint Calibration	Daily or every batch of ~100 samples, whichever comes first
MDL (Nylon Lab Blank)	Initially, then annually or after major instrument change (e.g., conductivity detector or column change)
Distilled Deionized Water Blank	Four initially to establish background, followed by one every 10 samples
Method Blank	One for every 40 samples
QC Standards	Daily or every run
Check Standards	Every 10 samples
Replicates	10% of samples
<b>XRF (Elements)</b>	
Calibration Verification (SRM2783)	Following calibration
Calibration Verification (SRM2783)	Monthly
PTFE Blanks, Instrument Stability/Precision (repeatability)	Daily
Multi-element RMs, Instrument Stability/Precision (repeatability)	Daily & weekly
Reproducibility (reanalysis)	Monthly
<b>IMPROVE A TOR/TOT (Carbon)</b>	
Laboratory Blank Check	Beginning of analysis day

Leak Check	Beginning of analysis day
Laser Performance Check	Beginning of analysis day
Calibration Peak Area Check	Every analysis
Auto-Calibration Check	Alternating beginning or end of each analysis day
Manual Injection Calibration	Four times a week (Sun, Tue, Thu, and Sat)
Sucrose Calibration Check	Thrice per week (began March, 2009)
Potassium Hydrogen Phthalate (KHP) Calibration Check	Twice per week (Tue and Thu)
System Blank Check	Once per week
Sample Replicates (on the same or a different analyzer)	Every 10 analyses
Multiple Point Calibrations	Every six months or after major instrument repair
Temperature Calibrations	Every six months, or whenever the thermocouple is replaced
Oxygen Level in Helium Atmosphere (using GC/MS)	Every six months, or whenever leak is detected
Inter-laboratory comparisons	Once per year
External systems audits	Initiated by UC Davis once every two to three years

## 4.6 Special Training and Certification

### 4.6.1 Purpose / Background

This section describes any specialized training requirements necessary to complete the project and the procedures are summarized to ensure that specific training skills can be verified, documented, and updated as necessary.

### 4.6.2 Training

The Laboratory Manager trains laboratory technicians in sample handling and preparation for analysis at the time of employment. Physical records of training are maintained by the laboratory manager, who closely oversees all operations.

Analysts new to the CSN program are required to have experience with basic measurement techniques relevant to the analyses being performed. These techniques include operation of an XRF spectrometer, ion chromatograph, and OC/EC analyzer.

Prior to training, analysts will read and understand the relevant SOP(s). Under the direction the Laboratory Manager or experienced technician, the analyst will follow the SOP and to analyze samples and, if available, samples that have been analyzed previously by an experienced analyst. The Laboratory Manager or mentor will audit performance of the analyst, checking operations such as calibration, data treatment, system maintenance, and record keeping. With both acceptable analytical results and a successful audit, the analyst will be approved to perform program sample analyses. Ongoing performance will be monitored by the Laboratory Manager through review of analytical data.

#### 4.6.2.1 Experience and Training of Current Personnel

Permanent employees at UC Davis and DRI are eligible to attend training courses relevant to this program. Both in-house and extramural training opportunities are available to employees. Project staff are encouraged to attend courses such as manufacturers' training sessions or method-specific courses.

#### 4.6.2.2 Training and Qualification of New Personnel

New personnel will be hired as necessary to meet the needs of this program. Both UC Davis and DRI utilize student employees who are replaced by new employees when they graduate. These personnel are typically involved with routine, but important, activities such as receiving exposed samples and data entry. It is critical that errors in these areas be held to an absolute minimum; therefore, an in-house training program is used to ensure full proficiency.

The approach for assessing and training new hires (and cross-training of existing employees) is as follows:

- Candidate credentials are carefully assessed with regard to prior experience and aptitude, and are interviewed by a panel including at least one senior-level project participant.
- Candidates are assessed on a case-by-case basis by the Laboratory Manager, and are expected to have experience or aptitude equivalent to two years of experience. Many student employees have science or engineering majors and have gained laboratory experience through their studies. References are contacted to verify that candidates have appropriate laboratory skills and aptitude.
- For permanent employee hires, there is a six month probationary period, during which time the employee may be terminated for failing to meet required job standards; temporary employees may be dismissed at any time.
- All SOPs are written in sufficient detail to provide new employees with the requisite training and experience to perform the task. Any departures from the written SOPs require consultation with the Laboratory Manager. Departures from SOPs necessitated by systematic or recurring problems result in corrective actions, which may include revision of the SOP.
- All new employees work under close supervision.

#### 4.6.3 Certification

University regulations require that staff who operate XRF instrumentation are certified in radiation safety by the UC Davis Environmental Health and Safety

Department. Records are maintained by UC Davis Environmental Health and Safety. This has no impact on the quality of the CSN data.

#### **4.7 Documents and Records**

The following sections describe the required documentation for the program. Data records associated with all field sampling and analytical results will be retained for a minimum of five years following sample analysis. Documents related to data quality and training are listed in Table 3. These documents will be retained for a period of ten years after contract completion as specified in *EPA Records Schedule 1035 Item c* (EPA, 2017). If additional contracts are awarded, all of the documentation will be retained as specified in the contract. All of the electronic records will be maintained on servers dedicated to the AQRC at UC Davis. Records and documentation for the subcontract laboratory will be obtained from DRI and maintained on the UC Davis servers.

Some of the documents listed in Table 3 will be made available to UC Davis and DRI project staff for training and reference. These include this QAPP, the QMPs (UC Davis and DRI), SOPs, and forms and logbooks related to each analytical method or data processing function. Documents will be made available to staff in hardcopy and/or shared drive electronic versions.

The QAPP, QMPs, SOPs, and forms will be reviewed annually and revised as needed, as scheduled by the UC Davis Project Officer. Documents that are maintained and revised at DRI will be sent to UC Davis for archiving. Project staff will be notified when new/updated documents are available.

##### Document Management at DRI

Hardcopies of controlled project documents such as this QAPP and SOPs are limited and managed by the EAF QA Manager. All controlled documents, however, are available on the EAF LAN. Current versions are available in both .pdf and .doc format, with the signed PDF version as the official one. To the extent possible, DRI maintains copies of all SOPs, project-related documents such as reports and deliverables, QA-related documents, such as QAPPs, QMPs, audit of data quality (ADQ) results, and technical systems audits (TSAs) for at least ten years after project completion and generally, indefinitely.

The EAF QA Manager reviews relevant project material annually as part of internal audits of quality systems.

#### 4.7.1 Management Records

A summary of the management documentation and records maintained for this program is shown in Table 3.

Table 3. Management records.

Document Name	Description	Format	Storage Location
Monthly Reports	Monthly progress reports to EPA, indicating data delivered and problems encountered.	Electronic; delivered to EPA	AQRC
Quarterly Metadata Reports	Changes and issues that impact data quality. Dates for samples affected or invalidated.	Electronic; delivered to EPA	AQRC
Annual Data Quality Report	Annual summary of data quality and analysis issues	Electronic; delivered to EPA	AQRC
Correspondence	Contractual correspondence with EPA & DRI	Electronic & hardcopy	AQRC
Purchase Requisitions	Copies of all approved purchase requisitions and purchase orders	Electronic & hardcopy	AQRC
Conference Call Notes	Notes made during conference calls and other project-related calls	Electronic & hardcopy	AQRC
E-mail	All project-related e-mail correspondence	Electronic	UCD server

#### 4.7.2 QA/QC Records

Table 4 shows the QA/QC records that are maintained.

Table 4. QA/QC records.

Document Name	Description	Format	Storage Location
Training Files	Records of training for lab analysts	Hardcopy; web based records for online training	AQRC & DRI
Internal audits, questionnaires, & results	Results of internal QA surveys & audits	Electronic & hardcopy	AQRC & DRI
External audits, questionnaires, & results	Results of audits conducted by outside parties (ADQs, TSAs, audits of sample custody)	Electronic & hardcopy	AQRC & DRI
QAPP	Master version of QAPP, including pending revisions	Electronic & hardcopy	AQRC
QMPs	Master versions of UCD and DRI QMPs, including pending revisions	Electronic & hardcopy	AQRC & DRI

SOPs	Current versions of all SOPs	Electronic & hardcopy	AQRC & DRI
Intercomparison Study Results	Results of comparisons of two or more laboratories	Electronic & hardcopy	AQRC & DRI
Corrective Action Response Memos	Results of identified QA problems & their resolutions	Electronic and Hardcopy	AQRC & DRI

#### 4.7.3 Analytical Laboratories' Records

UC Davis and DRI analytical laboratories maintain the records listed in Table 5.

Table 5. Laboratory records.

Document Name	Description	Format	Storage Location
<b>XRF Laboratory Records</b>			
Laboratory Notebooks	Analysts' comments, instrument operations and maintenance logs	Electronic & hardcopy	XRF Lab
Calibration & Instrumentation Certificates & Records	Certificates of analysis, NIST traceability, and instrument testing & maintenance	Electronic & hardcopy	XRF Lab
Method Specific Application	Includes x-ray generation information and other information required to automate the XRF analyses	Computer files on each XRF instrument	XRF Lab
Instrument User's Manual and SOP	Information for setting up, using, and troubleshooting the XRF instrument	Electronic & hardcopy	XRF Lab
SOPs	Current copies of SOPs and associated TI documents	Electronic & hardcopy	XRF Lab
QAPP	A current copy of this QAPP	Electronic & hardcopy	XRF Lab
Analytical Results Database (Raw Data Records)	Results of XRF elemental analyses	Electronic (database)	XRF Lab
Analytical QC Records	Results of calibrations, SRM recoveries, QC checks, replicate analyses	Electronic	XRF Lab
<b>IC Laboratory Records</b>			
Laboratory Notebooks	Analysts' comments, instrument operations and maintenance logs	Electronic & hardcopy	IC Lab
Calibration & Instrumentation Certificates & Records	Certificates of analysis, NIST traceability, and instrument testing & maintenance	Electronic & hardcopy	IC Lab Network project files
Method Database	Information for automating the analyses	Computer files	IC Lab Database
Instrument User's Manuals	Information for setting up, using, and troubleshooting the instruments	Electronic & hardcopy	IC Lab



SOPs	Current copies of SOPs and associated TI documents	Electronic & hardcopy	IC Lab
QAPP	A current copy of this QAPP	Electronic & hardcopy	IC Lab
Analytical Results Database (Raw Data Records)	Results of ions analyses	Electronic (database)	Instrument PC Analyst PC Database
Analytical QC Records	Results of calibrations, SRM recoveries, and replicate precision	Electronic	IC Lab Database
<b>Carbon Laboratory Records</b>			
Laboratory Notebooks and Files	Analysts' comments, instrument operations and maintenance logs	Electronic & hardcopy	Carbon Lab
Calibration & Instrumentation Certificates & Records	Certificates of analysis, NIST traceability, and instrument testing & maintenance	Electronic & hardcopy	Carbon Lab Network project files
Method Parameter Files	Information required to run the analysis	Electronic & hardcopy	Carbon Lab Database Hardcopies & Archive
Instrument User's Manuals	Information for setting up, using, and troubleshooting the instruments	Hardcopies	Carbon Lab
SOPs	Current copies of SOPs and associated TI documents	Electronic & hardcopy	Carbon Lab
QAPP	A current copy of this QAPP	Electronic & hardcopy	Carbon Lab
Analytical Results Database (Raw Data Records)	Results of carbon analyses	Electronic (database)	Instrument PC Computer Database
Analytical QC Records	Results of instrument blanks, calibrations, standard recoveries and replicate precision	Electronic and hardcopy	Carbon Lab Database

## 5. DATA GENERATION AND ACQUISITION

### 5.1 Sampling Process Design (Experimental Design)

The experimental design, including design of the sampling network and sampling locations, is outside the scope of this QAPP. Refer to EPA planning documents available on the EPA AMTIC Web site.

### 5.2 Sampling Methods Requirements

Collection of samples is conducted by representatives from state and local agencies, outside the purview of the UC Davis contract and this QAPP.

### **5.3 Sample Handling and Custody**

This section describes the procedures for sample handling, chain of custody, and archiving of the filters.

#### 5.3.1 Sample Handling and Chain of Custody

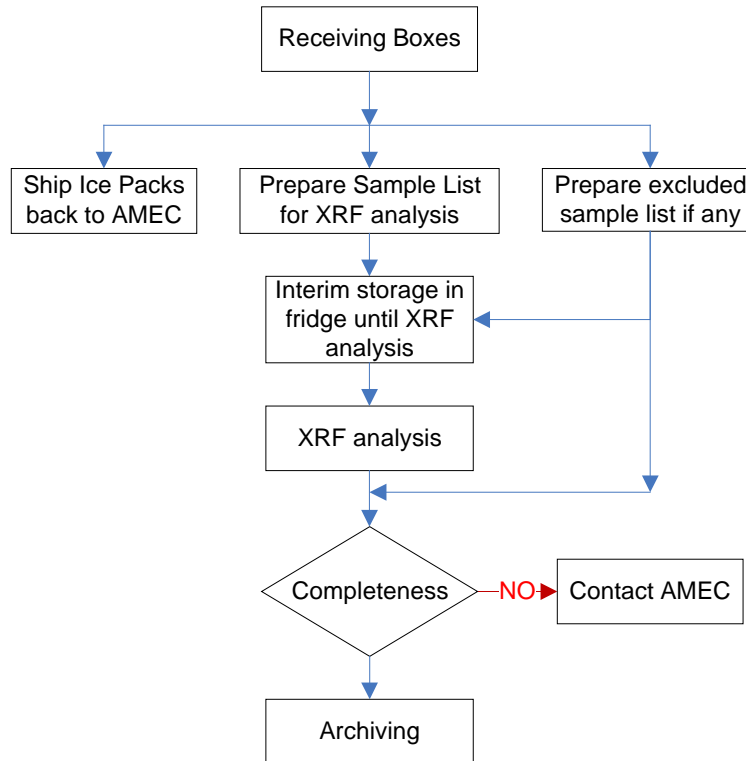
##### 5.3.1.1 Elemental Analysis Laboratory (UC Davis)

The flowchart for receiving and inventorying the PTFE filter samples is shown in Figure 6. The PTFE filter samples are shipped in coolers from Amec Foster Wheeler to UC Davis, accompanied with chain-of-custody (COC). Upon receipt of the samples the operator signs and dates the COC, and stores the samples in a refrigerator.

The CSN Data Management Site at UC Davis stores electronic data associated with all the sample types (Quartz, Nylon, and PTFE). Electronic records provided by Amec Foster Wheeler are ingested into the CSN database via the CSN Data Management Site.

An integrity check is performed by verifying the filter count and the number of samples on the COC and in the queue file, and a detailed inventory is done when loading samples to the XRF instruments. Shipments from Amec Foster Wheeler are assigned batch numbers, with each batch containing multiple boxes of Petri trays. Each Petri box can hold two Petri trays, and each tray contains 50 Petri slides. The samples are organized in numerical order based on the COC. Amec Foster Wheeler is responsible for labeling the boxes and each Petri Tray with the set numbers. The samples are identified by the Lab Analysis ID barcode (F#####) on the bottom of the Petri slide.

Figure 6. Flowchart of sample receiving and inventorying at UC Davis.



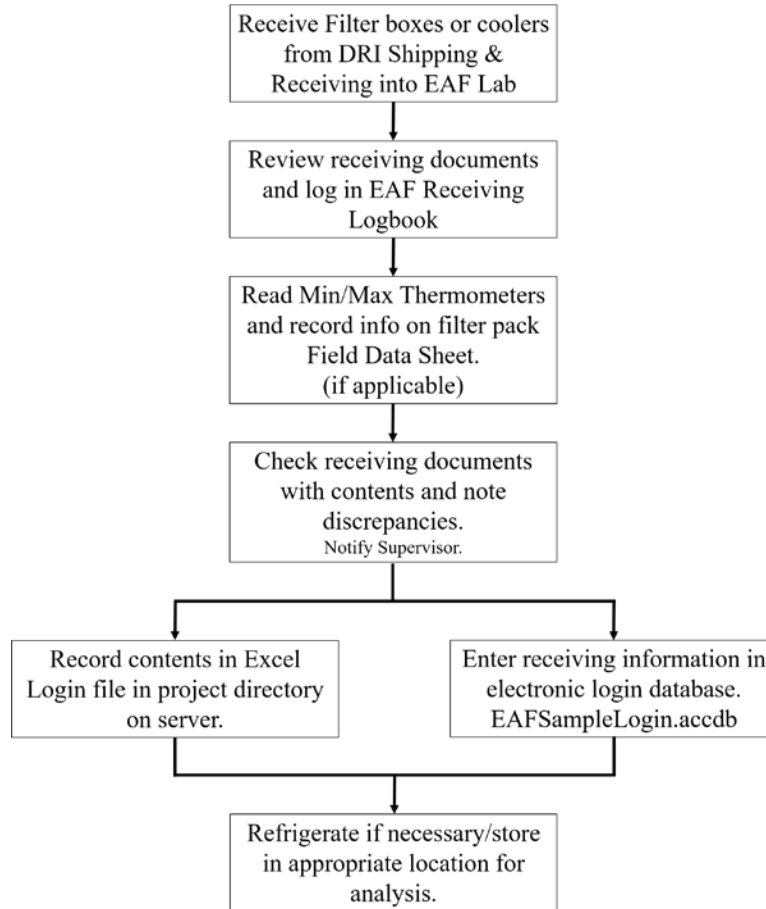
### 5.3.1.2 Ion and Carbon Analysis Laboratory (DRI)

The flowchart for receiving filters at DRI is shown in Figure 7. Nylon (47 mm Whatman Nylasorb) and quartz-fiber (25 mm Pall TissuQuartz) filters, along with COC forms, packaged in coolers are received from Amec Foster Wheeler. Using the COC, receipt of the filters is confirmed and any discrepancies are noted. The filter IDs are recorded in DRI's current batch login file and the receiving logbook. Nylon and quartz filters are separated and the filters are assigned a DRI sub-batch number. The nylon and quartz-fiber filters are then stored in separate refrigerators until ready to be processed for analysis.

Refer to the DRI SOP for further details:

*DRI SOP #2-117, Filter Pack Sample Shipping, Receiving and Chain-of-Custody*

Figure 7. DRI sample flow diagram.



### 5.3.2 Internal Tracking of Analytical Samples

For XRF analysis at UC Davis, queue files are used in conjunction with the barcode scanning capabilities of the PANalytical software to load sample information into the instrument. Filters are transferred from Petri slides into cups immediately after scanning the barcode associated with each sample. The cups are placed into one of six 8-position trays (as assigned at the time of scanning). The instrument name and assigned tray and position number are written on the COC. The trays are placed into the Epsilon 5 sample changer compartment, then the samples are queued in the software. After analysis is complete, trays are removed and filters are transferred back into labeled Petri slides.

At DRI samples are tracked internally by batch or sub-batch. Analysis lists are prepared, and barcode labels are used to program and track Petri slides and extract vials through the analysis process.

### 5.3.3 Archiving of Filters and Extracts

Refer to the UC Davis SOP for details:

*UCD CSN SOP# 901, Archiving.*

## 5.4 Analytical Methods Requirements

### 5.4.1 XRF Analysis for Elements

Analysis of CSN PTFE filter samples is performed at UC Davis using energy dispersive X-ray fluorescence (EDXRF) systems, specifically PANalytical Epsilon 5 XRF analyzers operating under vacuum. The basis of the method is the interaction of X-ray photons from the analyzer's excitation source with atoms of the elements present in the filter deposit.

Refer to the UC Davis SOP for details:

*UCD CSN SOP # 302: CSN Standard Operating Procedure for the X-Ray Fluorescence Analysis of Aerosol Deposits on PTFE Filters (with PANalytical Epsilon 5)*

### 5.4.2 Extraction and Analysis of Anions and Cations

Analysis of CSN nylon filter samples is performed at DRI using ion chromatography (IC) for analysis of water soluble ions, specifically using a Dionex ICS-5000<sup>+</sup> system. Prior to analysis nylon filters are extracted per the DRI SOP:

*DRI SOP #2-109: Extraction of Ionic Species from Filter Samples*

Separate analysis for anions (e.g., Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>=</sup>) and cations (e.g., NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) is performed, each utilizing approximately 2 ml of the filter extract. Refer to the DRI SOPs for details:

*DRI SOP #2-228, Anion Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography Using the Dionex ICS-5000<sup>+</sup> System*

*DRI SOP #2-229, Cation Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography Using the Dionex ICS-5000<sup>+</sup> System*

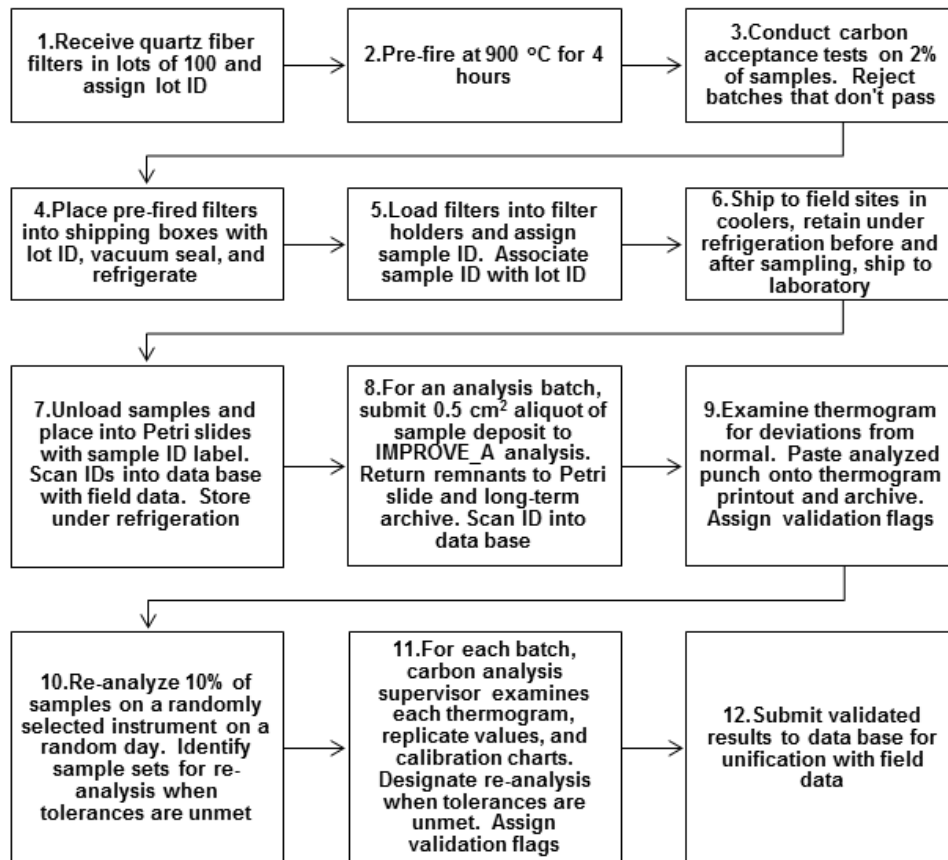
### 5.4.3 Carbon Analysis

Analysis of CSN quartz-fiber filter samples is performed at DRI using thermal optical carbon analysis, specifically using the DRI Model 2015 multi-wavelength

analyzer using the IMPROVE\_A carbon analysis method. The steps involved in preparation and analysis of CSN quartz-fiber filters are summarized in Figure 8, and analysis details are available in the DRI SOP:

*DRI SOP #2-226, DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples – Method IMPROVE\_A*

Figure 8. General flow diagram for CSN quartz-fiber IMPROVE\_A carbon analysis.



## 5.5 Quality Control Requirements

### 5.5.1 Quality Criteria for Ion Analysis

Quality control criteria for analysis of ions is listed in Table 6. The multipoint calibration is discussed in detail in Section 5.7.1.

Chromatogram background for each filter batch is established by analyzing distilled deionized water (DDW). DDW blanks are analyzed initially then one is analyzed after every 10 samples to verify the instrument response to DDW

without extraction. The DDW blanks should be within three standard deviations of the MDL (see Section 5.5.5); if not, the quality of the DDW and the instrument response are checked. In addition, a method blank (reagent blank) is analyzed once every 40 samples to verify the chromatogram baseline. The method blank concentration should be within three standard deviations of the MDL; if not, the quality of the DDW, extraction process, and instrument response are checked. Failure to meet the DDW and method blank criteria may result in samples being voided or flagged.

QC standards (NIST-certified multi-component solutions) are used daily or every run to ensure instrument accuracy. If the measured value is not within  $\pm 10\%$  of its listed value, samples and standards before the QC standard are reanalyzed. In addition, a NIST-certified check standard (from a different source than the QC standard) is analyzed after every 10 samples in order to verify instrument accuracy. If the measured value is not within  $\pm 10\%$  of its listed value, samples and standards before the check standard are reanalyzed. For each group of 40 samples analyzed on a given instrument, four are chosen randomly to be analyzed on alternate instruments. The replicates are used to check instrument precision. If the initial and replicate values do not have a RPD within  $\pm 10\%$ , when the average value is greater than ten times the MDL, then the sample is reanalyzed on a different instrument, and samples and standards before the replicate are reanalyzed.

After analysis, each chromatogram is reviewed for the following: 1) proper operational settings, 2) correct peak shapes and integration windows, 3) peak overlaps, 4) correct background subtraction, and 5) QC sample comparisons. Individual samples with unusual peak shapes, overlapping peaks, background subtractions, or deviations from standard operating parameters are designated for reanalysis.

Table 6. DRI QC criteria for ion chromatography (anions and cations).

QC Activity	Purpose	Frequency	Standard	Acceptance Criteria (MQO)	Response/ Action
Multipoint Calibration	Establish instrument response curves to known concentrations	Daily or every batch of ~100 samples, whichever comes first	NIST Certified ERA	$\pm 10\%$ of certified value	Recalibrate

MDL	Ensure cleanliness of filter lots and establish minimum concentration measurable for each instrument	Initially, then annually or after major instrument change (e.g., conductivity detector or column change)	Nylon lab blanks (7 or more)	Within $\pm 10\%$ of previous instrument limit	Troubleshoot instrument and check filter lots
DDW	Establish chromatogram background of filter batch	Four initially to establish background, followed by one every 10 samples	DDW with resistance $\geq 18 \text{ M}\Omega$	Within three standard deviations of MDL	Verify instrument response to DDW without extraction
Method Blank <sup>a</sup>	Reagent blank to verify chromatogram baseline of filter batch	One for every 40 samples	DDW with resistance $\geq 18 \text{ M}\Omega$	Within three standard deviations of MDLs	Check instrument response for DDW with extraction
QC Standards <sup>b</sup>	Ensure instrument accuracy	Daily or every run	Multi-component solution	$\pm 10\%$ of listed value	Samples before QC standard and previous standards reanalyzed
Check Standards <sup>c</sup>	Verify instrument accuracy	Every 10 samples	Multi-component solution	$\pm 10\%$ of listed value	Samples before check standard and previous standard reanalyzed
Replicates	Check instrument precision	10% of samples	N/A <sup>a</sup>	$\pm 10\%$ when value $> 10 \times$ MDL	Reanalysis of previous samples
Level 1 Data Validation	Inspect chromatograms for abnormalities	Every sample	N/A <sup>a</sup>	See note <sup>d</sup>	Sample reanalysis or flagging per SOP

<sup>a</sup> 15 mL DDW solution that follows the same extraction procedure as the sample extraction.

<sup>b</sup> NIST-certified standard from Thermo Scientific.

<sup>c</sup> NIST-certified standard from ERA.

<sup>d</sup> Per Section 5.1 in *DRI SOP #2-228* and *DRI SOP #2-229*. Non-quantitative criteria such as baseline position and noise, identification of peaks, shape of peak and integration with respect to baseline.



### 5.5.2 Quality Criteria for XRF

Quality criteria for XRF analysis are shown in Table 7. The inspection parameters selected for the criteria are defined as:

- Correlation coefficient (r; Equation 1): a measure of the relative mutual dependence of two variables, equal to the ratio of their covariances to the positive square root of the product of their variances.

$$r = \frac{\sum_{i=1}^n (c_{std,i} - \bar{c}_{std,i})(I_{cor,i} - \bar{I}_{cor,i})}{\sqrt{\sum_{i=1}^n (c_{std,i} - \bar{c}_{std,i})^2} \sqrt{\sum_{i=1}^n (I_{cor,i} - \bar{I}_{cor,i})^2}} \quad \text{Eqn. 1}$$

where,  $c_{std,i}$  is the loading ( $\mu\text{g}/\text{cm}^2$ ) of calibration standard  $i$  ( $\mu\text{g}/\text{cm}^2$ ) for any given element,  $I_{cor,i}$  is the blank subtracted intensity of X-rays emitted by the standard  $i$  (cps/mA),  $\bar{c}$  and  $\bar{I}$  denote the mean; and  $n$  is the number of the standards included in the calibration.

- Relative Expanded Uncertainty ( $U_{rel}$ ; Equation 2): The ratio of uncertainty estimated by the summation of contributions of each factor effective on the measurement to the result of measurement (%).  $U_{rel}$  of calibration function is estimated following an international method as detailed in the *Evaluation of Measurement Data - Guide to the Expression of Uncertainty in Measurement* published by the Joint Committee for Guides in Metrology (JCGM, 2008).

$$c_{cons,i} = \frac{I_{cor,i}}{b} \rightarrow U_{rel\ c_{std,i}} = k \frac{u(c_{cons,i})}{c_{std,i}} = k \frac{\sqrt{\sum \left(\frac{\partial c_{cons,i}}{\partial x}\right)^2 u_x^2}}{c_{std,i}} = \quad \text{Eqn. 2}$$

$$k \sqrt{\frac{u^2(I_{cor,i})}{b^2} + \left(\frac{I_{cor,i}}{b^2}\right)^2 u^2(b_i) + u^2(c_{std,i})}$$

$c_{std,i}$

where,  $c_{cons,i}$  is the re-constructed loading ( $\mu\text{g}/\text{cm}^2$ ) of calibration standard  $i$  using the calibration factor ( $b$ , in [(cps/mA)/( $\mu\text{g}/\text{cm}^2$ )]). Although uncertainty of  $c_{std,i}$ ,  $u(c_{std,i})$ , is not a part of  $c_{cons,i}$  calculation, it is added to the uncertainty equation for a conservative approach. The coverage factor,  $k$ , takes into account the distribution of uncertainties possible for a given measurement and in this work, a coverage factor of 2 is used to give approximately the 95% confidence interval on the uncertainty value ( $k=1.96$  at 95% confidence level for a normal distribution).

- Absolute bias (Equation 3): The ratio of difference between measured and certified loading of NIST SRM2783 to certified loading (%).

$$Absolute\ bias = 100 * \frac{|c_{E5} - c_{cer}|}{c_{cer}} \quad Eqn. 3$$

where,  $c_{E5}$  and  $c_{cer}$  is loadings by E5 and certified loadings of NIST SRM2783, respectively.

- Z-score (Equation 4): The ratio of absolute difference between each result from monthly reanalysis and reference value to accompanying uncertainty.

$$z = \frac{|c_{E5} - c_{ref}|}{\sqrt{U_{c_{E5}}^2 + U_{c_{ref}}^2}} \quad Eqn. 4$$

where,  $c_{E5}$  is the mass loading measured ( $\mu\text{g}/\text{cm}^2$ ),  $c_{ref}$  is the reference mass loading,  $U_{c_{E5}}$  and  $U_{c_{ref}}$  are the expanded uncertainties of measured ( $c_{E5}$ ) and reference ( $c_{ref}$ ) mass loadings. The expanded uncertainties are estimated following an international method, defined above.

- Acceptance limits:
  - PTFE blanks: Analyzed daily, and determined as three times MDLs;
  - Multi-element samples: Analyzed daily and weekly, and determined as  $\pm 10\%$  of the reference loadings (calculated as the mean of five measurements after calibration).
  - Micromatter made multi-element samples: Analyzed weekly, and determined as  $\pm 10\%$  of the reference loadings (calculated as the mean of five measurements after calibration).
  - SRM: Analyzed monthly, are element-specific and determined as root-mean-squared-relative-errors (RMSREs) plus three times standard deviations from 44 measurements, January 2013 through July 2016.

Table 7. UC Davis QC criteria for XRF (elements).

QC Activity	Inspection Frequency	Inspection Parameter	Acceptance criteria (MQO)	Corrective Action
Calibration Verification	Following calibration	<ul style="list-style-type: none"> <li>- Correlation coefficient (r)</li> <li>- Urel</li> <li>- Absolute bias from certified loadings of SRM 2783 for Al, Si, S, K, Ca, Ti, Cr,</li> </ul>	<ul style="list-style-type: none"> <li>- <math>r &gt; 0.99</math></li> <li>- <math>U_{rel} \leq 10\%</math> for stoichiometric standards, with loadings <math>\geq 3x</math> MDL.</li> <li>- Absolute bias <math>\leq</math> element-specific acceptance limit</li> </ul>	<ul style="list-style-type: none"> <li>- Check calibration line and spectra</li> <li>- Check standard(s) for damage/contamination</li> <li>- Exclude standard(s) from calibration line</li> <li>- Further cross-instrumental testing</li> </ul>

		Mn, Fe, Ni, Cu, Zn and Pb		- Recalibration with current or new standards
	Monthly	Absolute bias from certified loadings of SRM 2783 for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	Absolute bias $\leq$ element-specific acceptance limit	
Instrument Stability/ Precision (repeatability)	Daily	PTFE Blank	$\leq$ acceptance limits	- Change/clean blank if contaminated/damaged - Clean the diaphragm, if necessary - Further cross-instrumental testing
	Daily & weekly	multi-element RMs (ME-RMs)	$\leq$ acceptance limits	- Check sample for damage/contamination - Further cross-instrumental testing - Replace filter sample as necessary
Reproducibility	Monthly	Z-score based on reanalysis of SRM 2783, ME-RM and 16 selected samples	Z-score $\leq$ 1 for selected elements	Investigate and reanalyze set of samples as needed

Control charts displaying Z-scores for aluminum, silicon, sulfur, potassium, calcium, titanium, manganese, iron, zinc, selenium, and strontium as a function of analysis time are reviewed by the laboratory manager on a monthly basis. Measurements exceeding the acceptance criteria specified in Table 7 are investigated.

### 5.5.3 Quality Criteria for OC/EC Analysis

Quality criteria for OC/EC analysis are shown in Table 7, assuming 24/7 operation of the laboratory.

Daily checks include a leak check to detect leakage in the sample oven and a laboratory blank analysis to check for system contamination and evaluate laser response. Each is performed at the beginning of the analysis day. If the leak check

indicates that the oven pressure drops at a rate of 0.1 psi per second or more and does not stabilize, then the cause of the leak is identified and the leak is fixed. A laboratory blank check uses a filter punch that has been previously analyzed to check for instrument contamination. If the measured TC level is not less than 0.2  $\mu\text{g C}/\text{cm}^2$ , then the instrument needs to be checked and possibly baked clean. If the transmittance in the laser performance check using the 635 nm laser is not between 100-300 mv, the reflectance is not between 350-550 mv, and/or there is laser saturation, then the light pipes and filter holder position are checked and adjusted as needed, including the reflectance or transmittance trim pot. If the transmittance and/or reflectance value of the 635 nm laser drifts greater than 5% from the laser baselines, then the punch is replaced with a blank punch and baked, and/or the alignment of the thermocouple pushrod and the tilt of the boat relative to the lasers are checked and corrected. For every analysis a calibration peak area check is performed using a NIST 5%  $\text{CH}_4/\text{He}$  gas standard. If the calibration peak area is not greater than 17,000 and between 95% and 105% of the average calibration peak area for the day, then the analysis result is voided; the flowrates, sample oven pressure, and the 6-port valve temperature are checked; an auto-calibration is performed; and the analysis is repeated using a second filter punch. An auto-calibration check using a NIST 5%  $\text{CH}_4/\text{He}$  gas standard is performed daily, alternating at the beginning or end of each analysis day. If the recovery is not between 95-105% and the calibration peak area is not between 90-110% of the weekly average, then the system is checked and corrected before analyzing samples.

A manual injection calibration using a NIST 5%  $\text{CH}_4/\text{He}$  or a NIST 5%  $\text{CO}_2/\text{He}$  gas standard is performed four times a week (Sunday, Tuesday, Thursday and Saturday). If the recovery is not between 95-105% and the calibration peak area is not between 90-110% of the weekly average, then the system is checked and corrected before analyzing samples. A sucrose calibration check, using a 1800 ppm C sucrose standard (18  $\mu\text{g C}$ ), is performed three times a week (Monday, Wednesday, Friday). If the results are not between 17.1-18.9  $\mu\text{gC}/\text{filter}$ , then the system is checked and corrected before analyzing samples. A potassium hydrogen phthalate (KHP) calibration check, using a 1800 ppm C KHP standard (18  $\mu\text{g C}$ ) is performed twice per week (Tuesday and Thursday). If the results are not between 17.1-18.9  $\mu\text{gC}/\text{filter}$ , then the system is checked and corrected before analyzing samples. A system blank check, in which no filter punch is used, is performed once per week (Sunday). If the measured TC level is not less than 0.2  $\mu\text{g C}/\text{cm}^2$ , then the instrument needs to be checked and possibly baked clean. Sample replicates are performed on randomly selected filters and assigned randomly to the same or different analyzer at a frequency of one for every ten analyses. If the acceptance criteria in Table 8 are not met, then the instrument and

sample anomalies are investigated and another replicate is rerun when the difference is greater than  $\pm 10\%$ .

A multi-point calibration is performed every six months or after a major instrument repair. The calibrations use KHP, sucrose, NIST 5% CH<sub>4</sub>/He and NIST 5% CO<sub>2</sub>/He standards at different concentration levels. All slopes must be within  $\pm 5\%$  of the average. If not, the instrument is checked and the calibration repeated until the results are within the stated tolerances. A temperature calibration is performed every six months (usually along with a multi-point calibration) or whenever the thermocouple is replaced. The sample oven temperature is set to various temperatures ranging from 40 °C to 840 °C. A NIST certified thermocouple probe is used to measure the temperature at the sample punch. The readings measured by the NIST thermocouple are plotted against the readings measured by the pushrod thermocouple at the corresponding temperatures. A linear regression is done separately for the lower temperatures and the higher temperatures, separated with a toggle point (the temperature at which the two regressions are equal to one another or intersect) typically around 200-300 °C. Once the regressions and the toggle point have been inputted into the oven calibration configurations, temperature steps are verified and calibration is repeated until results are within tolerances. Every six months or whenever a leak is detected, the oxygen level in the helium atmosphere is checked with a GC/MS instrument utilizing a certified gas-tight syringe in the 0-100 ppmv range. The oxygen level should be less than the certified amount of the helium cylinder. If not, the He cylinder and/or the O<sub>2</sub> scrubber is replaced.

In addition, inter-laboratory comparisons are performed once a year. The results are reviewed and procedures verified. External systems audits initiated by UC Davis are typically performed once every two or three years. Actions are taken to correct any deficiencies noted in the audit report.

Table 8. DRI QC criteria for OC/EC analysis using the IMPROVE\_A TOR/TOT carbon analysis method.

Requirement	Calibration Standard and Range	Calibration Frequency <sup>a</sup>	Acceptance Criteria (MQO)	Corrective Action
Laboratory Blank Check	NA	Beginning of analysis day	<0.2 µg C/cm <sup>2</sup>	Check instrument and filter lots
Leak Check	NA	Beginning of analysis day	Oven pressure drops less than 0.1 psi per second	Locate leaks and fix

Laser Performance Check	NA	Beginning of analysis day	635 nm laser transmittance 100-300; Reflectance 350-550; No saturation at EC stage	Check light pipes and filter holder position; adjust reflectance or transmittance trim pot
Calibration Peak Area Check	NIST 5% CH <sub>4</sub> /He gas standard; 20 µg C (6-port valve injection loop, 1000 µl)	Every analysis	Counts >17,000 and 95-105% of average calibration peak area of the day	Void analysis result; check flowrates, leak, and 6-port valve temperature; conduct an auto-calibration; and repeat analysis with second filter punch
Auto-Calibration Check	NIST 5% CH <sub>4</sub> /He gas standard; 20 µg C (Carle valve injection loop, 1000 µl)	Alternating beginning or end of each analysis day	95-105% recovery and calibration peak area 90-110% of weekly average	Troubleshoot and correct system before analyzing samples
Manual Injection Calibration	NIST 5% CH <sub>4</sub> /He or NIST 5% CO <sub>2</sub> /He gas standards; 20 µg C (Certified gas-tight syringe, 1000 µl)	Four times a week (Sun, Tue, Thu, and Sat)	95-105% recovery and calibration peak area 90-110% of weekly average	Troubleshoot and correct system before analyzing samples
Sucrose Calibration Check	10µL of 1800 ppm C sucrose standard; 18 µg C	Thrice per week (began March, 2009)	17.1-18.9 ug C/filter	Troubleshoot and correct system before analyzing samples
KHP Calibration Check	10µL of 1800 ppm C KHP standard; 18 µg C	Twice per week (Tue and Thu)	17.1-18.9 ug C/filter	Troubleshoot and correct system before analyzing samples
System Blank Check	NA	Once per week	<0.2 µg C/cm <sup>2</sup>	Check instrument
Sample Replicates (on the same or a different analyzer)	NA	Every 10 analyses	±10% when OC and TC ≥10 µg C/cm <sup>2</sup> ±20% when EC > 10µg C/cm <sup>2</sup> or <±1 µg/cm <sup>2</sup> when OC and TC <10 µg C/cm <sup>2</sup> <±2 µg/cm <sup>2</sup> when EC <10µg C/cm <sup>2</sup>	Investigate instrument and sample anomalies and rerun replicate when difference is > ±10%

Multiple Point Calibrations	1800 ppm C KHP and sucrose; NIST 5% CH <sub>4</sub> /He, and NIST 5% CO <sub>2</sub> /He gas standards; 9-36 µg C for KHP and sucrose; 2-30 µg C for CH <sub>4</sub> and CO <sub>2</sub> .	Every six months or after major instrument repair	All slopes ±5% of average	Troubleshoot instrument and repeat calibration until results are within stated tolerances
Temperature Calibrations	NIST certified thermocouple, 20 set points from 40 to 840 degrees C	Every six months, or whenever the thermocouple is replaced	Linear relationship between thermocouple and NIST thermocouple for both low and high temperature values with R <sup>2</sup> >0.99	Troubleshoot instrument and repeat calibration until results are within stated tolerances
Oxygen Level in Helium Atmosphere (using GC/MS)	Certified gas-tight syringe; 0-100 ppmv	Every six months, or whenever leak is detected	Less than the certified amount of He cylinder	Replace the He cylinder and/or O <sub>2</sub> scrubber
Inter-laboratory comparisons	NA	Once per year.	NA	Review and verify procedures.
External systems audits	NA	Once every two to three years.	NA	Take action to correct any deficiencies noted in audit report.

<sup>a</sup> Calibration performed by carbon analyst, except for inter-laboratory comparisons and external systems audits, which are conducted by the U.S. Environmental Protection Agency (EPA) National Air and Radiation Environmental Laboratory (NAREL). Audits of the DRI facilities will be initiated/conducted by UC Davis.

#### 5.5.4 Disaster Recovery Plan for Data

Refer to the UC Davis SOP for details:

*UCD SOP # 903, Data Processing Disaster Recovery Plan*

#### 5.5.5 Uncertainty Determination

There are no absolute standards by which to develop uncertainty estimates for particulate matter measurements. Therefore, uncertainties must be estimated from either theoretical or empirical approaches. Three options exist to estimate the uncertainties: 1) a bottom-up method which involves identifying and combining the uncertainty estimates from individual measurement components, 2) a top-down

empirical method using duplicate measurements, or 3) a combination of 1) and 2). The previous uncertainty estimates (reported through November 20<sup>th</sup>, 2015) were based on bottom-up estimates of uncertainties in the measurement components (Flanagan et al., 2006). The new uncertainties are based on a combination of the two approaches by utilizing the collocated measurements in the CSN network and the uncertainty in the blank measurements to estimate an overall uncertainty. These reported uncertainties only capture the variability in the measurements themselves and do not reference any outside or absolute measurement standards. These estimates are limited by the fact that collocated measurements are only available at a small fraction of the CSN sites, and these sites may not be representative of the entire network. The CSN and IMPROVE uncertainty estimates align, which is valuable for analysts using data from both networks. The uncertainty estimates include both an additive and multiplicative terms as shown in Equation 5: the additive term is dominant at low concentrations, and the multiplicative term is dominant at high concentrations.

$$Uncertainty = \sqrt{(Unc_{Additive})^2 + (Unc_{Multiplicative} * Conc.)^2}, \quad \text{Eqn. 5}$$

The additive uncertainty term is one-third of the detection limit; this provides an estimate of one standard deviation for low concentration measurements because the detection limit is three times the standard deviation of blanks (lab blanks for XRF and field blanks for ions and carbon). The multiplicative uncertainty term is estimated using a robust approach involving percentiles, as shown in Equations 6 and 7; the technique is described in detail in Hyslop and White, 2009. The multiplicative uncertainty is an estimate of one standard deviation in the measurements. Only values greater than three times the detection limit were used in Equations 6 and 7.

$$Unc_{Multiplicative} = \frac{1}{2}(P_{84}(D_i) - P_{16}(D_i)) * 100\%, \quad \text{Eqn. 6}$$

$$\text{where } D_i = \frac{(C_{i1} - C_{i2})/\sqrt{2}}{C_i} \quad \text{Eqn. 7}$$

$P_{84}(D_i)$  and  $P_{16}(D_i)$  = the 84<sup>th</sup> and 16<sup>th</sup> percentiles in the distribution of measurement differences ( $D_i$ )

$C_{i1}$  and  $C_{i2}$  = concentrations measured by the routine and collocated samplers, respectively

Table 9 lists the multiplicative uncertainty values used starting November 20<sup>th</sup>, 2015 along with the number of collocated pairs that were used to develop the



estimates. Only concentration values greater than three times the MDL were used to calculate the proportional uncertainties, and the values were capped at 25%. A cap is set based on replicate measurements at higher concentrations present on calibration standards; the small selection of collocated sites do not represent the range of concentrations at every site in the CSN. The multiplicative uncertainties will be evaluated on an annual basis and updated as necessary.

Table 9. Average MDL and proportional uncertainty estimates along with the number of collocated data pairs that were included in the uncertainty estimation for each reported parameter.

Parameter	Average MDL ( $\mu\text{g}/\text{m}^3$ )	Number of Collocated Pairs	Proportional Uncertainty
<b>Elements</b>			
Ag	0.018	1	25%
Al	0.035	1209	25%
As	0.002	155	19%
Ba	0.082	123	17%
Br	0.004	1610	15%
Ca	0.029	4067	17%
Cd	0.023	0	25%
Ce	0.122	21	25%
Cl	0.004	1740	34%
Co	0.003	10	25%
Cr	0.004	83	39%
Cs	0.077	7	25%
Cu	0.008	2313	27%
Fe	0.022	5520	17%
In	0.029	0	25%
K	0.016	4825	11%
Mg	0.056	365	25%
Mn	0.006	623	15%
Na	0.068	1270	16%
Ni	0.002	400	18%
P	0.002	93	18%
Pb	0.015	381	19%
Rb	0.008	0	25%
S	0.009	5530	6%
Sb	0.045	0	25%
Se	0.006	43	25%
Si	0.017	3897	15%
Sn	0.046	0	25%

Sr	0.006	58	25%
Ti	0.004	697	17%
V	0.002	499	13%
Zn	0.004	3144	12%
Zr	0.036	3	25%
<b>Carbon</b>			
EC1	0.014	1606	13%
EC2	0.012	1948	37%
EC3	0.002	992	25%
ECTR	0.018	4	16%
ECTT	0.014	4	13%
OC1	0.024	1774	33%
OC2	0.059	1039	14%
OC3	0.196	1877	18%
OC4	0.051	1860	16%
OCTR	0.297	1487	12%
OCTT	0.299	1487	7%
OPTR	0.014	1557	25%
OPTT	0.017	1557	17%
TCTC	0.063	1557	25%
<b>Ions</b>			
Ammonium	0.015	5466	7%
Chloride	0.132	0	25%
Nitrate	0.072	5767	8%
Potassium Ion	0.006	2072	13%
Sodium Ion	0.048	3562	25%
Sulfate	0.117	5680	5%

#### 5.5.6 Method Detection Limits

The method detection limits (MDLs) for the CSN analytes are reported with each concentration measurement. The MDLs are calculated on a monthly basis using field blank filters collected during the respective month when possible; if an adequate number of blanks weren't collected in the respective month, blanks from the prior month/s are included.

The MDLs are calculated monthly for all reported species using a harmonized calculation for all analysis pathways: 95<sup>th</sup> percentile minus mean.

Table 9 (Section 5.5.5) lists the average MDLs reported for each species from April 1, 2016, through July 1, 2016.

#### 5.5.7 Programmatic Uncertainty

Effort during prior CSN contracts helped to identify additional quality issues that were incorporated into the program as they were recognized:

- Shipping/handling components of uncertainty – The laboratory component of random error is typically much smaller than the total random error observed with paired field samples. Thus, improving the precision of laboratory measurements beyond a certain point (e.g., better than +/- 5% for most species) does not appreciably help overall uncertainty.
- Sensitivity issues – The majority of the PM<sub>2.5</sub> sampling for the CSN has been performed using the MetOne SASS sampler, which operates at a flow rate of 6.7 liters per minute and uses 46.2 mm filters. Compared with the IMPROVE program, this relatively low flow rate and large filter size results in a sensitivity deficit of up to 11- fold. This sensitivity difference is immaterial for gravimetric mass and species present in large amounts, such as sulfate, nitrate, and OC. Many trace elements analyzed by XRF are usually detectable at high levels, including iron, sulfur, and silicon.
- OC artifact – The OC artifact is thought to be the result of adsorbed SVOCs from the gas phase and represents a non-particulate source of carbon. With the MetOne sampler, the OC artifact can amount to 2 µg/m<sup>3</sup> or more, which can bias the results by 20%–30% on a typical sample. Methods for correcting for the artifact are available but can never be perfect. Because of the relatively higher flow and smaller surface area, the OC artifact for samples taken with the URG 3000N or the IMPROVE samplers are much smaller than for those taken with the MetOne SASS. Samples taken with higher flow samplers, such as the PM<sub>2.5</sub> FRM sampler, will have intermediate magnitude of OC artifact.
- Uncertainty definitions – Work with receptor modelers during prior CSN contracts highlighted the importance of consistent definitions of uncertainty to be reported to the AQS database. The original formulation of uncertainty was based on the IMPROVE program’s propagation of errors approach and relied on uncertainty values provided by the analytical instruments’ software (for XRF and OC/EC). To meet the needs of receptor modeling, it was important that the uncertainties be calculated in a consistent way across all analyzers. An approach was developed for harmonizing the uncertainties reported between different XRF instruments. In the process, it was also ensured that the total uncertainties

for the other CSN analytical techniques (gravimetry, ion chromatography, OC/EC) were comparable with those for XRF and were realistic, based on the collocation results.

## 5.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

### 5.6.1 Ion Chromatography Laboratory

Refer to DRI SOPs for details:

*DRI SOP #2-228, Anion Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography Using the Dionex ICS-5000<sup>+</sup> System*

*DRI SOP #2-229, Cation Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography Using the Dionex ICS-5000<sup>+</sup> System*

Table 10. Inspection criteria for DRI ion chromatography laboratory.

Item	Frequency	Parameter	Action if Item Fails Inspection	Documentation
IC column back pressure	Daily	Column specific (Dionex)	1) Check for blockage 2) Replace column if necessary	Record pressure in instrument log and log book
IC background conductivity	Daily	Eluent specific (within control limits)	1) Check eluent flow 2) Check suppressor 3) Contact supervisor or call Dionex tech support if necessary	Record conductivity in instrument log and log book
Baseline	Daily	Steady – no pulsing	1) Check for leaks 2) Check for air bubbles in conductivity cell 3) Contact supervisor or call Dionex tech support if necessary	Record corrective action in instrument log book

Table 11. DRI ion chromatography maintenance schedule.

Item	Frequency	Parameter	Responsible Party
IC system preventive maintenance	Yearly	Check all valves, fittings, flows and replace as needed; replace piston seals, gaskets and check valves on pump head	IC Lab supervisor or Dionex service representative
Check for leaks at valves and column fittings	Daily	Check for leaks	IC analyst
Ultrasonic bath	Monthly	Check that power produces noticeable agitation	IC analyst

### 5.6.2 XRF Laboratory

Refer to UC Davis SOP for details:

*UCD CSN SOP # 302: CSN Standard Operating Procedure for the X-Ray Fluorescence Analysis of Aerosol Deposits on PTFE Filters (with PANalytical Epsilon 5)*

Table 12. Inspection criteria for the XRF laboratory.

Item	Inspection Frequency	Inspection Parameter	Acceptance Criteria (MQO)	Action if Failed	Documentation Required
Energy Calibration	Weekly	Wavelength/energy alignment of the instrument	Instrument resolution < 140 keV	This is an automated process; manufacturer contacted if failed	Documented in instrument's run log book and computer files
Instrument Stability/Precision	Daily and weekly	Loadings of blank and ME-RMs	Acceptance limits	Investigate, correct, and possibly recalibrate	Results are stored in the XRF database and in designated computer files
Ongoing Calibration Verification	Monthly	Loadings of SRM 2783	Absolute bias ≤ limits for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	Investigate and recalibrate if needed	Results are stored in the XRF database and in designated computer files
Long-term Reproducibility	Monthly	Z-score based on reanalysis of SRM 2783, a ME-RM and 16 selected samples.	z-score ≤ 1 for selected elements	Investigate, correct, and possibly reanalyze affected samples	Results are stored in the XRF database and in designated computer files

Table 13. XRF laboratory maintenance schedule & responsibility.

Item	Maintenance Frequency	Responsible Party
Instrument maintenance including vacuum pump maintenance and oil change	Every 6 months	Manufacturer (PANalytical)
State-mandated radiation safety checks	Yearly	UC Davis Environmental Health & Safety Department

### 5.6.3 OC/EC Laboratory

Refer to DRI SOP for details:

*DRI SOP #2-226, DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analysis (TORTOT) of Aerosol Filter Samples – Method IMPROVE\_A*

Table 14. DRI carbon analysis laboratory maintenance schedule.

Item	Frequency	Responsible Party
Carbon analyzer	As needed (daily checks are performed on key components)	Carbon analyst

Analytical balance and check weights	Yearly or as needed	Quality Control Services (routine) or Mettler Toledo, Inc. service representative (as needed)
Muffle furnace	As needed	Carbon analyst

## 5.7 Instrument Calibration and Frequency

### 5.7.1 DRI Ion Chromatography Laboratory

Multipoint calibration using seven different concentrations ranging from 0.02 to 3.0 ppm (0.02, 0.05, 0.1, 0.2, 0.5, 1.0 and 3.0 ppm) is performed daily or after every 100 samples, whichever comes first. For all ions except ammonium, a linear fit forced through the origin is used. For ammonium, a quadratic fit forced through the origin is used. Acceptance criteria is  $r^2 < 0.98$  for both cases.

Calibration is followed by analysis of QA/QC samples, including:

1. QC samples containing anions/cations at concentrations typical of those found in the middle range of actual filter extract concentrations
2. QC sample containing anions/cations at concentrations typical of those found in the lower end of actual filter extract concentrations
3. A commercially prepared NIST-traceable QA sample containing known concentrations of anions/cations

All field sample ion concentrations that exceed 3.0 ppm are reanalyzed after dilution.

### 5.7.2 XRF Laboratory

The Epsilon 5 has been shown to be a stable analyzer that does not need frequent calibrations. Calibrations are performed upon first installation, approximately yearly or when the analyzer fails verification tests, and whenever an analysis-critical component (e.g., x-ray source or detector) of the analyzer is maintained or replaced.

Four types of standard reference materials are used for calibrating the Epsilon 5 analyzers.

1. 47 mm Micromatter thin film foils on Nuclepore membranes, prepared by vacuum deposition (Table 15a).
2. UC Davis generated single-compound standards on 25 and 47 mm PTFE membranes (sulfur, sodium, potassium, chlorine, aluminum, silicon, titanium, vanadium, chromium, iron, copper, zinc, lead, and cerium).
3. UC Davis generated multi-element standards on 47 mm PTFE membranes (Table 15b).

4. NIST Standard Reference Material (SRM) 2783 air particulate on polycarbonate filter membranes (Table 15b).

Table 15. Standard reference materials used for calibration of Epsilon 5.

a) Standards on Nuclepore from micromatter.

Analyte/Code	Analyte/Code	Analyte/Code	Analyte/Code	Analyte/Code	Analyte/Code
Ag 32554	CeF3 37493	Fe 32524	Mn 32521	Sb 32561	SrF2 32543
AgHg 32569	CeF3 37494	Fe 35141	Mn 32522	Sb 32562	SrF2 32544
AgHg 32570	CeF3 37495	Fe 35142	MoO3 32551	ScF3 32513	SrF2 33055
Al 32501	Co 32525	GaAs 32535	MoO3 32552	ScF3 32514	SrF2 33056
Al 32502	Co 32526	GaAs 32536	NaCl 32498_R	Se 32537	Te 32563
Al 33044	Cr 32519	GaP 32505	Nb2O3 32549	Se 32538	Te 32564
Al 35136	Cr 32520	GaP 32506	Nb2O3 32550	Se 33057	Ti 32515
Al 35137	CsBr 32539	GaP 33059	Ni 32527	Se 33058	Ti 32516
Al 35138	CsBr 32540	GaP 33060	Ni 32528	SiO 32503	V 32517
Al 35164	CsBr 32565	Ge 32533	Ni 33047	SiO 32504	V 32518
Al 35165	CsBr 32566	Ge 32534	Ni 33048	SiO 33045	WO3 37730
Al 35166	Cu 32529	In 32557	Pb 32571	SiO 33046	WO3 37731
BaF2 32567	Cu 32530	In 32558	Pb 32572	SiO 33053	YF3 32545
BaF2 32568	Cu 33049	KCl 32509	Pb 35146	SiO 33054	ZnTe 32532
CaF2 32511	Cu 33050	KCl 32510_R	Pb 35163	SiO 35139	ZnTe 34875
CaF2 32512	Cu 35143	MgF2 32499	RbI 32541	SiO 35140	ZnTe 34876
CdSe 32555	CuSx 32507	MgF2 32500	RbI 32542	SiO 35160	ZnTe 35162
CdSe 32556	CuSx 32508	MgF2 33041	RbI 33051	Sn 32559	ZrF4 32547
CeF3 37492	Fe 32523	MgF2 33042	RbI 33052	Sn 32560	ZrF4 32548

b) Standards produced by UC Davis and NIST. The letters after “25” or “47” of UC Davis standards refer to certified element(s).

Code	Code	Code	Code
UCD-47-Al&Ce-003	UCD-47-Si-001	AWIM1 CRM S 246	UCD-25-Fe-002
UCD-47-Al&Ce-012	UCD-47-Si-005	AWIM1 CRM S 250	UCD-25-K&Cl-004
UCD-47-Cr-002	UCD-47-Si-043	AWIM1 CRM S 253	UCD-25-S-001
UCD-47-Cr-006	UCD-47-Ti-003	AWIM1 CRM S 257	UCD-25-S-002
UCD-47-Cu&K-001	UCD-47-ZnO-020	AWIM1 CRM S 263	UCD-25-S-003
UCD-47-Cu&S-002	UCD-47-ZnO-010	AWIM1 CRM S 265	UCD-25-S-004
UCD-47-CuO-005	UCD-47-ME-133	AWIM1 CRM S 268	UCD-25-Ti-002
UCD-47-Fe-008	UCD-47-ME-148	AWIM1 CRM S 280	UCD-25-Ti-004
UCD-47-K&Cl-014	UCD-47-ME-155	AWIM1 CRM S 288	UCD-25-V-002

UCD-47-Na&Cl-007	UCD-47-ME-156	AWIM1 CRM S 291	UCD-25-V-003
UCD-47-Na&Cl-008	UCD-47-MTL-ME-007	AWIM1 CRM S 293	UCD-25-V-006
UCD-47-Na&Cl-011	UCD-47-MTL-ME-013	AWIM1 CRM S 299	UCD-25-ZnO-001
UCD-47-Pb-004	AWIM1 CRM NaCl 189	UCD-25-Al&Ce-003	SRM2783 1617
UCD-47-Pb-058	AWIM1 CRM NaCl 194	UCD-25-CaZr-002	SRM2783 1618
UCD-47-Pb-074	AWIM1 CRM NaCl 196	UCD-25-CaZr-007	SRM2783 1719
UCD-47-S-006	AWIM1 CRM NaCl 198	UCD-25-CaZr-009	SRM2783 1720
UCD-47-S-023	AWIM1 CRM NaCl 204	UCD-25-Cr-015	
UCD-47-S-086	AWIM1 CRM NaCl 205	UCD-25-Fe-001	

Calibration of the Epsilon 5 XRF analyzers is performed using the standards described above. First, the standards are selected in the application, and the software calculates the theoretical relative intensities of the standards listed in the standards file using the operating and deconvolution parameters in the selected application; this calculation will be most accurate when the full composition of the standards is entered, including elements that are not of interest. Next, the standards are analyzed. The software performs a least-squares regression with the theoretical and measured intensities forcing the intercept to zero for each element.

Correlation coefficient of calibration line is required to be over 0.99 for elements with stoichiometric standards and reference materials used for calibration. The relative uncertainty of each stoichiometric standard (including standard uncertainty from manufacturer, linear fitting, and instrument repeatability) is required to be less than 10%. Each type of standard sample media has corresponding blank sample media that is analyzed and utilized for blank subtraction. The number of calibration standards varies from two to 30, depending on the element and the range of mass loadings. At least two standards (low and high) are required for each element, and preferably spanning the range of concentrations expected in the CSN samples (Table 16). The calibration factors (linear regression slope) are stored in the application specific calibration file on the XRF computer.

Table 16: Concentration ranges for XRF element standards.

Element	Range, $\mu\text{g}/\text{cm}^2$	Element	Range, $\mu\text{g}/\text{cm}^2$	Element	Range, $\mu\text{g}/\text{cm}^2$
Na	0.187-19.9	Mg	0.118-19.9	Al	0.36-49.5
Si	0.7-32.6	P	0.06-14.5	S	0.105-21.4
Cl	1.78-30.6	K	0.35-7.3	Ca	0.36-22.1
Ti	0.02-50.2	V	0.005-54.4	Cr	0.014-52.8
Mn	0.03-47.6	Fe	0.36-48.5	Co	0.02-50.9
Ni	0.007-56.6	Cu	0.04-45.2	Zn	0.17-17.8
As	0.002-25.2	Se	0.06-48	Br	5.6-19



Rb	0.002-18.3	Sr	0.024-37	Zr	8.9-28.6
Ag	0.2-52	Cd	0.024-28.3	In	15.2-48
Sn	17-50	Sb	15-54	Cs	9.4-31.6
Ba	0.03-43.8	Ce	3.42-35.9	Pb	0.032-54

### 5.7.3 OC/EC Laboratory

Four types of calibration procedures are required for the OC/EC analyzers (Table 17):

1. End-of-run calibration peak.
2. Routine beginning and end-of-day calibration injections of CH<sub>4</sub>/He (or the auto calibration check using the *AutoCalib* protocol) and CO<sub>2</sub>/He.
3. Full instrument calibration, performed every six months or after major instrument repair, using KHP, sucrose, and calibration gases.
4. Temperature calibrations performed every six months or after replacing the thermocouple using temperature-sensitive indicating liquids with different melting points.

Table 17. DRI carbon laboratory instrument calibrations and frequencies.

Calibration	Calibration Standard and Range	Calibration Frequency	Acceptance Criteria (MQO)	Corrective Action
Calibration Peak Area Check	NIST 5% CH <sub>4</sub> /He gas standard; 20 µg C (6-port valve injection loop, 1000 µl)	Every analysis	Counts >17,000 and 95-105% of average calibration peak area of the day	Void analysis result; check flowrates, leak, and 6-port valve temperature; conduct an auto-calibration; and repeat analysis with second filter punch
Auto-Calibration Check	NIST 5% CH <sub>4</sub> /He gas standard; 20 µg C (Carle valve injection loop, 1000 µl)	Alternating beginning or end of each analysis day	95-105% recovery and calibration peak area 90-110% of weekly average	Troubleshoot and correct system before analyzing samples
Manual Injection Calibration	NIST 5% CH <sub>4</sub> /He or NIST 5% CO <sub>2</sub> /He gas standards; 20 µg C (Certified gas-tight syringe, 1000 µl)	Four times per week (Sun, Tue, Thu, and Sat)	95-105% recovery and calibration peak area 90-110% of weekly average	Troubleshoot and correct system before analyzing samples
Multiple Point Calibrations	1800 ppm C KHP and sucrose; NIST 5% CH <sub>4</sub> /He, and NIST 5% CO <sub>2</sub> /He gas standards; 9-36 µg C for KHP and	Every six months or after major instrument repair	All slopes ±5% of average	Troubleshoot instrument and repeat calibration until results are within stated tolerances

	sucrose; 2-30 $\mu\text{g C}$ for $\text{CH}_4$ and $\text{CO}_2$			
Temperature Calibrations	NIST certified thermocouple, 20 set points from 40 to 840 degrees C	Every six months, or whenever the thermocouple is replaced	Linear relationship between thermocouple and NIST thermocouple for both low and high values with $R^2 > 0.99$	Troubleshoot instrument and repeat calibration until results are within stated tolerances

## 5.8 Inspection/Acceptance of Supplies and Consumables

### 5.8.1 Filters

Filters are purchased and inspected by Amec Foster Wheeler, outside the purview of the UC Davis contract and this QAPP.

### 5.8.2 Criteria for Other Materials

Refer to UC Davis and DRI SOPs.

## 5.9 Data Acquisition Requirements (Non-direct Measurements)

This work does not directly involve the use of any historical databases, literature files, etc. Any supplemental, non-direct measurement data supplied by the monitoring organizations or subcontractors for inclusion in the database will be subject to limited validation to ensure that data have been correctly entered and identified.

UC Davis expects to obtain historical CSN data from AQS for comparison to current data and observed trends.

## 5.10 Data Management

To manage data flow from sample collection, laboratory analysis, concentration processing, validation, and delivery to AQS, UC Davis has developed a custom database and connected applications, referred to collectively as the CSN data management system (CDMS). As data management is an area of constant improvement, the specifics of the CDMS and its individual components are discussed in the relevant SOPs and their associated TI documents.

For additional detail refer to UC D SOP and TIs:

*UCD CSN SOP # 801: Standard Operating Procedure for Processing and Validating the Raw Data*

*UCD CSN TI #801A: CSN Data Ingest*

*UCD CSN TI #801B: CSN Data Processing*

*UCD CSN TI #801C: CSN Data Validation*

*UCD CSN TI #801D: CSN Data Delivery*

For the electronic records associated with sample archive:

*UCD CSN SOP # 901: Long-Term Archiving of Filters*

5.10.1 Data Integrity

The primary goal of the CDMS design is to preserve data integrity, as detailed in the following sections.

5.10.1.1 Relational Database Structure

All CSN sample operational data, site metadata, laboratory analysis results, and final concentrations are contained within a structured relational database. The database structure is normalized, such that each data element is stored in only one location. Tables are joined by primary and foreign keys that disallow duplicates. Referential integrity is enforced to ensure that dependent (child) records cannot be created without first creating parent records, and parent records cannot be deleted creating orphaned child records.

5.10.1.2 Data Entry and Input Validation

All CSN data are ingested to the database through a data upload application. This eliminates the need for manual data entry at UC Davis, which is a common source of data errors. The upload applications perform validation on all inputs, catching errors in input data before they are loaded and preventing duplicate records.

5.10.1.3 Data Editing Restrictions

Data editing is strictly controlled. The UC Davis CSN laboratory staff have access to the web application for applying flags to sample records. The application requires that any flag changes are accompanied by a comment that is also stored in the database. The comments are marked with the user's ID and a time stamp.

In some cases, it may be necessary to change records in the data validation process, typically during Level 0 validation. For example, if a transcription error on the sample date is discovered and confirmed with the operator or sample handling lab, the sample date would be changed. This is not enabled through the CSN web application and only the Data & Reporting Manager has authority to make those changes.

#### 5.10.2 Data Flagging

The CSN database uses extensive flagging to ensure all samples, blanks, and metadata are properly accounted for, calculated, and routed. The most important flag categories are:

1. Filter Purpose: distinguishes a filter as a routine sample, field blank, trip blank, lab blank, or other irregular filter.
2. AQS Null and Qualifier Codes: the UC Davis CSN internal data flagging system for null and informational flags employs the same list of flags as is available in AQS. The database structure allows for up to one null code and any number of informational or quality assurance qualifiers.
3. Analysis QC Codes: distinguishes analysis results as either valid, reanalysis or repetition, or test data.
4. Reporting flags: determine whether specific parameters are to be delivered to DART and/or to AQS.

#### 5.10.3 Validation of the CDMS

While the CDMS is largely new code, it borrows extensively from the IMPROVE data management system. Validation of the system is an ongoing process, as new features are added over time and must be tested. The steps for testing and validating new functionality for the CDMS are:

1. Software Testing: new and changed features are tested offline by end users by following a test plan designed to exercise all functions of the affected software. Core calculations are covered by unit and regression tests, which are executed whenever code is added or changed to ensure that the new code does not break existing functionality or change data values unexpectedly.
2. Data Validation Testing: new code that impacts data values is tested by a thorough comparison between records produced by old and new records to ensure either equivalence or changes as expected.
3. Hand Calculation: in the case where no existing vetted analogous calculation is available, results will be confirmed via manual or spreadsheet calculations.

4. **Data Completeness and Duplicate Checks:** when updates involve new database queries, completeness and duplicate checks are run to ensure that queries are returning all of the intended results.

#### 5.10.4 Facility Recovery

The UC Davis police department patrols buildings on a regular basis (including nights, weekends, and holidays). In addition, campus facilities and maintenance staff are on call at all times.

In the event of damage to the Jungerman Hall data facilities, the UC Davis police will notify the Information Technology (IT) Administrator. The IT Administrator will assess the damage to determine the scope of recovery operations. If the building can be safely entered, surviving equipment will be relocated to another building. All buildings on the UC Davis campus are connected to internal Ethernet, and a relocated server could be immediately operable.

#### 5.10.5 Hardware Recovery

**Database and file servers:** The campus network of IT Administrator staff allow for rapid response to server failure and recovery issues.

**Bar-code scanners:** Bar-code scanners are used to record sample information. In an emergency, a keyboard could be used for data entry rather than a bar-code scanner. Bar-code scanner replacements are available on short notice.

**XRF system computers:** Each XRF instrument has an associated computer. Instrument service contracts with PANalytical for each instrument guarantee service within 48 hours, enabling quick replacement of XRF computers with little disruption to the flow of samples.

#### 5.10.6 Software and Data Recovery

##### 5.10.6.1 UC Davis XRF

Raw and processed spectra are saved and available for use at any time on the Epsilon 5 computers. Data safety and security are ensured by frequent transfer of computerized raw data from the Epsilon 5 PCs in the CNL XRF Laboratory (Jungerman Hall) to two different servers located in the CNL and LAWR buildings on campus. Differential backups are performed daily and full backups are performed weekly.

#### 5.10.6.2 DRI Ions and Carbon

Raw data files are 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 has no windows, no drop ceilings, and is buried in a 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.

Newer analytical instruments typically have frequent software modifications to provide enhanced data processing and review capabilities. The DRI EAF archives major software modifications for analytical instruments and maintains computers to run them in order have the ability to reprocess or review older data. Similar archiving applies to legacy systems and software for analytical systems no longer being used.

#### 5.10.7 Data Security

**UC Davis and DRI access policies:** Access to database and computers associated with this project is limited to authorized project personnel by use of access control lists for files, programs, and database access. Access to laboratory and office space is controlled by keycards.

**Password policies:** Unique passwords are issued to each employee by the UC Davis campus system administrator. Password integrity is monitored by the UC Davis campus system administrator.

**Termination policies:** System access is revoked for terminated personnel. The IT Administrator disables domain accounts and passwords upon termination of employment.

**Virus protection:** Microsoft Endpoint Protection is used for virus scanning and protection. All staff are required to complete annual cyber security awareness training.

## 6. ASSESSMENTS AND RESPONSE ACTIONS

UC Davis and DRI will participate in laboratory assessment or proficiency programs established by EPA, and will maintain analyst or laboratory certifications required for the program. The assessments that are planned are described in this section.

### 6.1 Audits of Data Quality

The UC Davis QA Manager will perform periodic technical systems audits of the UC Davis activities. The EAF QA Manager will perform audits at DRI. The UC Davis QA Manager will initiate and participate in external audits of DRI to ensure DRI is meeting the quality system flow down requirements of the prime contract. An external audit of DRI will occur every two to three years.

These audits will cover all aspects of the CSN work, including sample receipt, custody, sample analysis, data reduction and reporting. The audits will include a review of all applicable documentation (QAPP, QMP, SOPs) along with verification that the SOPs are being followed by the project staff. The audits will also include verification of calculated values by manually calculating a few selected derived values and comparing them to the values produced by the project software. The types of audits to be conducted are listed in Table 18.

Table 18. Types of audits of data quality.

Type of Audit	
UC Davis	DRI
Sample receipt & chain of custody	Sample receipt & chain of custody
Elemental analysis (XRF)	Ions analysis
Data processing, validation, & submittal	Carbon analysis
Sample archiving	Sample archiving

Prior to each audit, a checklist will be prepared, based on this QAPP, the QMP, the SOPs, and applicable guidance documents. When each audit has been completed the following string of reports will document the audit results and subsequent corrective actions:

- After each audit, the UC Davis QA Manager will summarize the results in a memorandum to the Services Program Manager within two weeks. The memoranda for DRI will also be provided to the EAF Director. These memoranda will clearly spell out any areas in which corrective action is necessary. If any serious problems are identified that require immediate action, such as a large, systematic analytical bias, the UC Davis QA Manager

will convey these to the Services Program Manager and EAF Director verbally and through electronic mail the day that such problems are identified.

- Corrective actions are the responsibility of the Services Program Manager and EAF Director. For problems requiring action, a memorandum describing the action will be provided to all relevant project staff, including the UC Davis QA Manager, and be archived in the project files.
- Once each problem has been resolved, the UC Davis QA Manager will verify the effectiveness of any formal corrective actions and summarize these in a memorandum, indicating the results of any identified problems and their resolutions.

Since these memoranda constitute the corrective action system for this project, all memoranda will be retained in the UC Davis QA Manager's files, where they will be available for internal or external review. The memoranda will also be provided to the EPA CSN Program Manager and UC Davis QA Manager.

## **6.2 Data Quality Assessments**

Data quality is continually assessed through the tracking of data quality indices and through the data validation process. In addition, a formal data quality assessment will be conducted once a year, led by the Services Program Manager, the Data & Reporting Manager, and the UC Davis QA Manager. The data quality assessment is a statistical and scientific evaluation of the data sets to determine the validity and performance of the data and to determine the adequacy of the data set for its intended use. The reliability of each type of data to satisfy its MQOs will be assessed. If any type of data consistently falls short then recommendations for corrective action will be provided. The results of the data quality assessment will be provided in each year's Annual Data Quality Report.

## **6.3 External Quality Assurance Assessments**

The UC Davis laboratories will participate in external QA assessments as requested by EPA. The UC Davis QA Manager will coordinate and oversee external QA assessments of the DRI laboratories every two years.

## **6.4 Reports to Management**

The following regularly scheduled technical and quality-related reports will be provided to EPA:

- Monthly Data Reports. Each month UC Davis will provide the latest month of CSN data to EPA (or its designated contractor) in a format suitable for uploading to the Data Analysis and Reporting Tool (DART). DART is a tool



that allows the SLT agencies to review and validate data for their sites. UC Davis will also supply an additional monthly report that summarizes the samples that the analysis laboratories identified as suspect or invalid.

- Quarterly Metadata Reports. UC Davis will prepare quarterly metadata reports to address laboratory changes, flagged or compromised data, and any other information that may affect the data reported to AQS. Suspect data points will be identified in the UC Davis SQL database, so database queries will be used to assemble complete and accurate reports. Because CSN is a long-term trends network, changes will be made to laboratory procedures only when necessary. Some events, however, are unavoidable, such as instrument calibrations and routine maintenance, and these events will be documented in the quarterly reports.
- Reporting of Data to AQS. After the SLT agencies have reviewed their data using DART, UC Davis will resolve any remaining data validation issues prior to submitting data to AQS. Submittals will be made on a monthly basis, with each submittal comprising a calendar month of data. The data submittal will consist of final ambient air concentrations in  $\mu\text{g}/\text{m}^3$  along with the associated uncertainties, method detection limits, and sampling metadata.
- Annual Data Quality Report. This report will be prepared as required by the EPA, generally following the example outline for the analysis laboratory presented in Appendix A of the solicitation for this contract. UC Davis will conduct ongoing data validation and review of the data each month throughout the year. The annual report will summarize the validation findings and provide recommendations where changes could improve data quality.
- Data Archival. All laboratory data records associated with each analysis will be stored and archived for a period of five years following sample analyses.

## **7. DATA REVIEW AND VALIDATION**

The following describes the UC Davis approach to data review, validation, and verification. The QC criteria given elsewhere in this QAPP will be used as the data validation requirements. Any data that fail routine validation checks will be flagged for review by the monitoring agencies. Large or systematic exceedance criteria may also trigger a corrective action investigation by the Data & Reporting Manager or UC Davis QA Manager.

Data validation begins with the site operator, who may flag or invalidate samples based on sampling conditions or instrumental errors. Next, the sample handling laboratory examines sample integrity and monitors COC forms for irregularities. The analytical laboratories will again examine sample integrity upon receipt and note any damage that may have occurred during transport.

Analytical data are validated using data from laboratory blanks, calibration checks, standard spikes, and laboratory duplicates. Based on QC verification data, a filter or other sample may be invalidated or specific results flagged prior to submitting results to the central database. Reasons for invalidation may include, but are not limited to, damaged filter, contamination, and invalid holding times.

Once all data have been ingested in the central database, the data validation analyst will review analytical pathways individually as well as perform a series of cross-comparisons between analytical methods. Resultant data are compared to any applicable notes recorded by the site operators and questionable data are reported back to the analytical laboratories for re-analysis. After all issues have been resolved, the data is delivered to DART for review and validation by the SLT validators. Data returned from DART is reviewed for accuracy and consistency, then reformatted for delivery to AQS. For additional detail refer to *UCD CSN SOP # 801: Standard Operating Procedure for Processing and Validating the Raw Data* and *UCD CSN TI #351C: CSN Data Validation*.

## **7.1 Validation**

UC Davis and DRI are each responsible for validating analytical data produced in their individual laboratories. Each laboratory will apply Level 0 and Level 1 screening to data produced in their laboratories. UC Davis is responsible for overall data review, validation, and verification and for data reporting.

### **7.1.1 Level 0 Validation**

Level 0 data sets contain all available analytical data and may contain non-analytical data in the form of QC checks and/or flags indicating missing or invalid data. Any missing data will be retrieved, if available, and any problems related to chain of custody, shipping integrity, sample identifications, and inspections will be rectified to the extent possible. The initial identification of these problems will be the responsibility of the Laboratory Manager, who works closely with the Data & Reporting Manager and other personnel to document systematic problems and to take or recommend corrective actions. Data will be flagged or invalidated if problems are identified during Level 0 validation but cannot be rectified.

Examples of data at Level 0 validity in CSN are:

- 24-hour averaged pressure, temperature, and flow data recorded from sampler user interface during sample change procedures
- XRF raw spectra
- Sample date and sampling time before consistency checks
- Overall sample counts

Sources for the information used to screen data for Level 0 validation include the analyst's notes (logbooks and data forms), sample labels, COC forms, package shipping labels, and inspection results for filters and other sample media.

### 7.1.2 Level 1 Validation

Prior to delivery to DART, UC Davis performs Level 1 validation of the filter records provided by the sample handling lab and the processed analysis results provided by the analytical labs. The Level 1 data validation process consists of the automated screening checks followed by thorough manual review by a trained data validation analyst.

Comments from all upstream validators (site operator, sample handling lab, analytical lab) are reviewed to verify consistency between records and correct for typographical error.

#### 7.1.2.1 Screening checks

Several automated range checks are applied and investigated, including:

- Ratio of sulfur by XRF to sulfate by IC;
- Ratio of potassium by XRF to potassium ion by IC;
- Ratio of gravimetric mass (where available) or collocated mass to reconstructed mass;
- Ratio of anions to cations from IC;
- Z-score of OC/EC ratios.

Values outside of a screening criterion is flagged with a qualifier code. The data validation analyst reviews flagged samples during further data validation. No samples are invalidated as a result of the screening process.

#### 7.1.2.2 Manual Validation

The data validation analyst reviews sample data in a variety of ways to ensure integrity of the data set, including single-site, single-parameter time series; ratio time series; and comparisons to site-specific historical values.

Anomalous data (e.g., sulfur/sulfate ratio outside site norms or a single element much higher than the historical range) are further scrutinized. Investigations and corrective actions may include the following:

- Investigating the specific conditions that contributed to anomalous results for a single laboratory sample or related group of samples;
- Contacting the site operator or monitoring agency (potentially indirectly through the sample handling lab) to determine if there were any environmental conditions that might lead to anomalous results;

- Repeating analyses for the affected samples;
- Reviewing logs and other records for transcription errors and evidence of operational problems or equipment malfunction.

Based on the results of the investigation, entire filter samples or single parameters may be invalidated or flagged with additional non-terminal qualifiers. Any new qualifiers are accompanied by comments, which are stored in the database and readily accessible to both the internal and SLT data validators. Data validation flags generated during screening are reviewed by the UC Davis QA Manager; however, the UC Davis QA Manager often requires input from laboratory staff to address any problems. Data problems that originate outside the scope of UC Davis operations are reported to EPA.

Once Level 1 data validation is complete, the data are exported from the UC Davis database for delivery to DART.

#### 7.1.3 DART Validation

The SLTs will perform Level 2 validation, incorporating historical data, local conditions and events, and operator knowledge. The changed flags and comments resulting from Level 2 validation will be returned to UC Davis for final review for consistency and accuracy. Anomalous changes will be resolved between UC Davis and the appropriate SLT validator. Level 2 data will incorporate all AQS codes generated during the data validation process, including all changes requested by the DOPOs during their review. UC Davis will take any necessary corrective actions on problems identified during all levels of data review prior to delivery to AQS.

#### 7.1.4 Validation of Subcontractor Data

Although DRI will conduct their own validation of ions and carbon data, UC Davis must further validate results at Level 0 to ensure a consistent data set. In doing so, UC Davis will ensure that the sample identifications and COC information from DRI are consistent with the sampling records. This process will consist primarily of comparing the original sample numbers, dates, types, and so on, with the data received from DRI. UC Davis validation of DRI ions and carbon data includes assignment checks based on date, site, and the various ID numbers assigned to filters and analysis runs. Data from DRI are also scanned for unusually high blank values and possible filter swaps between routinely sampled filters and blanks. Discrepancies in sample attribution uncovered during Level 0 screening will be investigated and rectified before the data are reported.

## 7.2 Data Corrections

The following paragraphs briefly discuss the types of data corrections that are typically encountered in this work.

### 7.2.1 Elemental Analysis

XRF is subject to interferences and artifacts that are corrected for as follows:

- Spectral interferences with the analyte line intensity determination include elemental peak overlap, escape peak, and sum peak interferences. These interferences are automatically corrected within the specific application. No action is required by the XRF operator once these interferences have been addressed within the application.
- No attenuation corrections for light elements (sodium through sulfur) will be applied.
- Filter lot-specific background corrections will be applied during data processing (*UCD CSN TI 801B – CSN Data Processing*).
- Occasional Zn contamination due to mechanical malfunction of the instrument gripper are investigated and corrected.

### 7.2.2 Ions

Artifacts and interferences in the analysis of PM<sub>2.5</sub> ions using state-of-the-art IC systems are rare but they can occur. Quality control test samples such as blanks, replicates, and calibration standards will be used to detect the existence of artifacts or interferences. In the event that they occur the most likely remedy will be reanalysis of the affected samples. Month specific background corrections will be applied during data processing (*UCD CSN TI 801B – CSN Data Processing*).

### 7.2.3 OC/EC

This method is subject to a number of potential interferences. DRI uses best judgment in applying corrections, fully documents any such corrections, and will discuss them with UC Davis and EPA before the data are submitted to AQS.

Carbonates and bicarbonates present in some filter samples may cause interference in the OC/EC analysis. Two alternative procedures may be used to measure carbonate carbon. The first approach includes analysis of a second portion of the filter sample after it has been acidified (i.e., exposed to hydrochloric acid vapor, which removes carbonate as CO<sub>2</sub>) and takes carbonate carbon as the difference between the pre- and post-acidification results. The second approach estimates carbonate carbon by integrating separately the

carbonate peak in the thermogram and using the instrument's software to calculate the mass of carbonate carbon volatilized. Carbonate carbon is not generally present in PM<sub>2.5</sub> on quartz filters at loadings above the absolute error of the measurement; therefore, carbonate carbon was not included in the list of analytes for the current contract. Month specific background corrections will be applied during data processing (*UCD CSN TI 801B – CSN Data Processing*).

### **7.3 Reconciliation with User Requirements**

UC Davis will ensure that measurement data meet requirements as expressed in this QAPP and associated SOPs. UC Davis and DRI will work closely with EPA to ensure that all required performance characteristics are met.

Regular communications between the UC Davis Services Program Manager and the EPA Project Officer, the EPA technical leader, and the filter handling contractor (Amec Foster Wheeler). Communications will include conference calls scheduled biweekly or as needed, e-mail and written correspondence, and meetings with EPA/OAQPS personnel in the Research Triangle Park, NC, area.

Most programmatic communications with outside participants including EPA/OAQPS, the DOPOs, and the state agencies flow through the Services Program Manager. Exceptions are allowable for technical discussions with EPA personnel (e.g., to define data delivery formats for AQS) and with Amec Foster Wheeler personnel for the purpose of coordinating the transfer of samples and data. No one at UC Davis other than the Services Program Manager is authorized to alter analysis schedules, increase or decrease the number of samples to be analyzed, or change the delivery schedule. All such requests must go through the UC Davis Services Program Manager.

## **8. REFERENCES**

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## 9. APPENDIX

### 9.1 Appendix A: List of DRI SOPs

1. DRI SOP # 2-106: Pre-firing and Acceptance Testing of Quartz Fiber Filters for Aerosol and Carbonaceous Material Sampling
2. DRI SOP #2-109: Extraction of Ionic Species from Filter Samples
3. DRI SOP #2-117: Filter Pack Sample Shipping, Receiving and Chain-of-Custody
4. DRI SOP #2-228: Anion Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography, using the DIONEX ICS-5000+ System for the Chemical Speciation Network
5. DRI SOP #2-229: Cation Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography, using the DIONEX ICS-5000+ System for the Chemical Speciation Network (CSN)
6. DRI SOP #2-231: DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples – Method IMPROVE\_A for the Chemical Speciation Network (CSN)

## **9.2 Appendix B: List of UC Davis SOPs**

1. UCD SOP #302: X-Ray Fluorescence Analysis of Aerosol Deposits on PTFE Filters (with PANalytical Epsilon 5)
  - UCD TI #302A: LN2 Fills and Detector Calibrations
  - UCD TI #302B: Receiving and Inventorying of CSN Samples
  - UCD TI #302C: Sample Changes for 8-Position Trays
  - UCD TI #302D: Quality Assurance/Quality Checks (QA/QC) of XRF Performance
2. UCD SOP #801: Processing and Validating Raw Data
  - UCD TI #801A: CSN Data Ingest
  - UCD TI #801B: CSN Data Processing
  - UCD TI #801C: CSN Data Validation
  - UCD TI #801D: CSN Data Delivery
3. UCD SOP #901: Long-Term Archiving of Filters
4. UCD SOP #902: Document Control
5. UCD SOP #903: Data Processing Disaster Recovery Plan
6. UCD SOP #904: Training for Laboratory Staff Working on CSN