

Quality Assurance Guidance Document

Revision 1.6

Quality Assurance Project Plan *for the Chemical Speciation Network*

OAQPS Category 2 QAPP

Prepared for:

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

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Prepared by:

Air Quality Research Center
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DOCUMENT HISTORY

Revision	Date Modified	Initials	Section/s Modified	Brief Description of Modifications
1.3	7/31/20	NJS	All	Title adjustment, cleaning list of acronyms and abbreviations, sentence restructuring, replacement and clarification of Figure 1 (org chart), update title changes and responsibilities for management personnel, added oven temperature criteria to Table 7 (QC criteria for TOA), added multiple point calibration criteria for Table 18 (UCD TOA calibrations), added clarification statements in Section 6.5 (Corrective Actions), and added new TIs to the Appendix.
1.4	6/30/21	NMH	4	Updated organization information
1.4	7/19/21	NJS	All	Adjusted for consistency between QAPP and SOPs/TIs. Made corrections and adjustments based on EPA feedback.
1.5	1/15/23	ML	All	Personnel and organization information, Document QA/QC Records, EDXRF replicate criteria minor, IC column back-pressure removed, Corrective Action Process, update SOP list, annual updates, and minor corrections
1.6	11/20/23	ML	All	Integrated RTI as subcontractor for sample handling and Ion Analysis. Organization updates. Added XRF replicate method. Updated HIPS verification filters to 14. Fixed table 19 formatting. Quartz filter pre-fire information. Various minor corrections.

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
CAPA	Corrective and Preventative Action
CAR	Corrective Action Report
CDMS	Chemical Speciation Network data management system
cm ²	square centimeter
COC	chain-of-custody
COV	coefficient of variation
cps	counts per second
CSN	Chemical Speciation Network
DART	data analysis and reporting tool
DDW	distilled-deionized water
DOPO	Delivery Order Project Officer
DQI	data quality indicator
DQO	data quality objective
EC	elemental carbon
EDXRF	energy dispersive X-ray fluorescence
EPA	U.S. Environmental Protection Agency
FID	flame ionization detector
HIPS	hybrid integrating plate/sphere analysis
IC	ion chromatography
IMPROVE	Interagency Monitoring of Protected Visual Environments
L	liters
L/min	liters per minute
LCOC	Laboratory chain of custody (Same as COC)
LAN	local area network
m	meter
m ³	cubic meter
mA	milliamp
MDL	method detection limit
ME-RM	multi-element reference material
µg	micrograms
µm	micrometers
min	minute
MQO	measurement quality objective
NAAQS	National Ambient Air Quality Standard
NIST	National Institute of Standards and Technology

NPS	United States of America National Park Service
NR	Nonconformance Report
OAQPS	EPA Office of Air Quality Planning and Standards
OC	organic carbon
PE	performance evaluation
PM	particulate matter
PM _{2.5}	particulate matter (with aerodynamic diameter less than 2.5 µm)
PM ₁₀	particulate matter (with aerodynamic diameter less than 10 µm)
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
RTI	Research Triangle Institute
SIP	state implementation plan
SLT	state, local, and tribal
STN	speciated trends network
SOP	standard operating procedure
SRM	standard reference material
SVOC	semi-volatile organic compound
TI	technical information document
TOA	thermal/optical analysis
TOR	thermal optical analysis by reflectance
TOT	thermal optical analysis by transmittance
TSA	technical systems audit
UCD	University of California at Davis
Urel	relative expanded uncertainty
XRF	X-ray fluorescence
z-score	standard score

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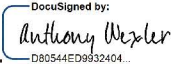

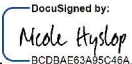

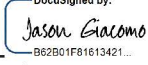

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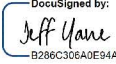


1. TITLE AND APPROVAL SHEET

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

UC Davis Air Quality Research Center

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<small>DocuSigned by:</small>  <small>D0129373D9FC4CF...</small> Melinda Beaver, EPA/OAQPS Program Manager	11/27/2023 <hr/> Date

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3. DISTRIBUTION LIST

UC Davis Air Quality Research Center (AQRC)

Anthony Wexler, AQRC Director
Nicole Hyslop, Associate Director of Quality Research
Harold Brunette, Program Manager
Sean Raffuse, Associate Director of Data & Software
Ann Dillner, Associate Director of Laboratory Research
Jason Giacomo, Laboratory Group Manager
Marcus Langston, AQRC QA Manager

Research Triangle Institute (RTI)

Keith Levine, RTI Director of Analytical Sciences
Tracy Dombek, Program Manager
Andrea McWilliams, RTI QA Manager

U.S. Environmental Protection Agency (EPA)

Joann Rice, EPA/OAQPS Technical Lead
Jeff Yane, EPA/OAQPS Project Officer
Doug Jager, EPA/OAQPS Quality Assurance Officer
Melinda Beaver, EPA/OAQPS Program Manager

4. PROJECT MANAGEMENT

4.1 Project/Task Organization

This QAPP is for contract number 68HERH23D0004 with the U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and

Standards (OAQPS). Work on this contract in support of the particulate matter (PM) Chemical Speciation Network (CSN) program is performed by the Air Quality Research Center (AQRC) at the University of California, Davis (UC Davis). UC Davis will perform energy dispersive X-ray fluorescence (EDXRF) analysis, hybrid integrating plate/sphere (HIPS) analysis, thermal/optical analysis (TOA), and will process, validate, and deliver the final concentration data. Research Triangle Institute (RTI), a subcontractor to UC Davis, will perform ion chromatography analysis as well as be responsible for the sample handling laboratory operations (e.g., shipping/handling filters and coordinating field activities).

Organizational charts for project personnel at UC Davis and RTI 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 AQRC organizational chart. Structure as it pertains to roles and responsibilities discussed in Section 4.1.1.

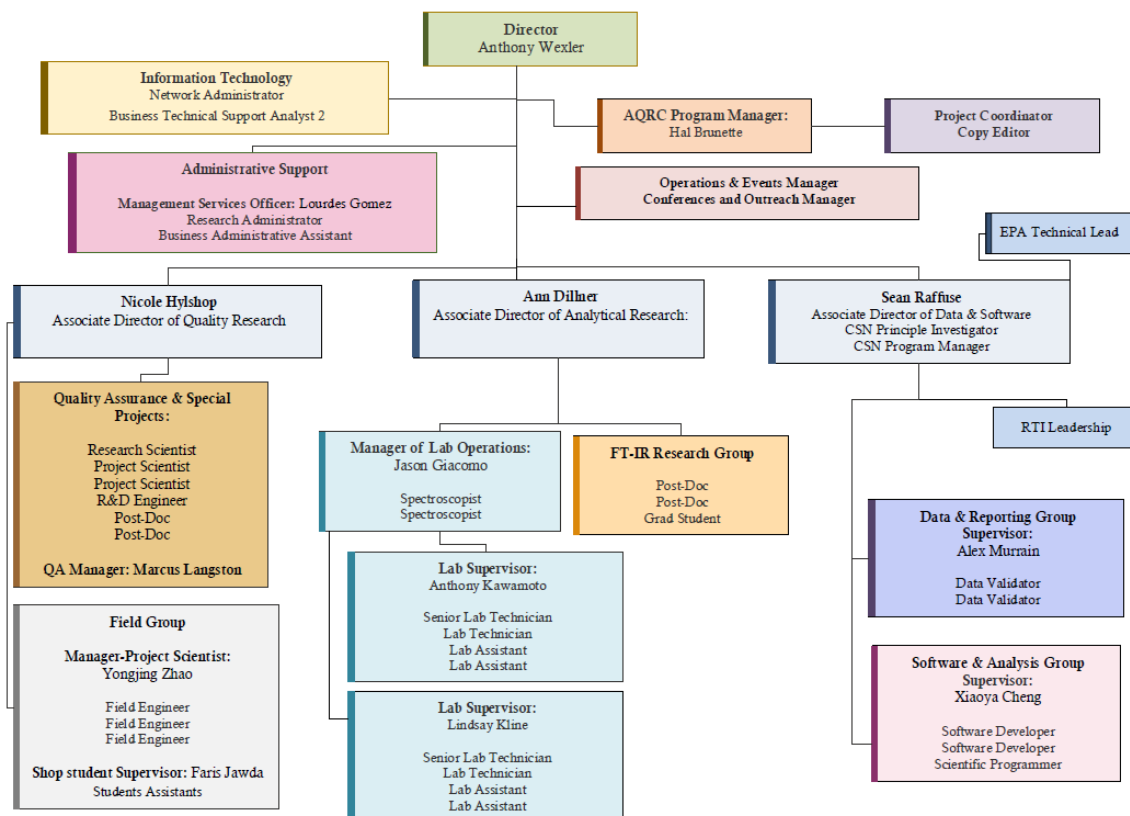
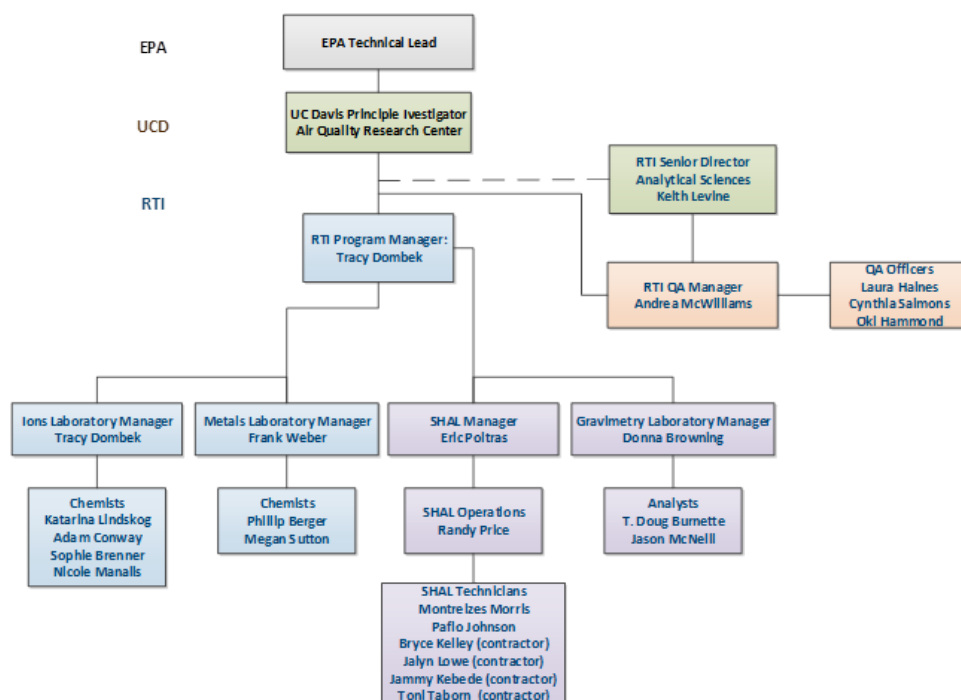


Figure 2. RTI organizational chart.



4.1.1 Position Responsibilities: UC Davis

4.1.1.1 AQRC Director, Anthony Wexler

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

1. Determining the research program adheres to its budget;
2. Facilitating interaction with other AQRC programs, as well as other programs on the UC Davis or other 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 over 34 years of experience in the field of atmospheric science with 22 years at UC Davis. Contact information: aswexler@ucdavis.edu and 530-754-6558.

4.1.1.2 Principal Investigator/CSN Program Manager, Sean Raffuse.

The CSN program at UC Davis is led by the Principal Investigator, who provides overall supervision to ensure that the technical program is performing in accordance with the EPA statement of work and according to this QAPP. Mr. Sean Raffuse holds that position for CSN. Responsibilities include:

1. Maintaining cooperative working relationships with the EPA Program Manager, Delivery Order Project Officers (DOPO), and AQRC 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. Overseeing subcontractor (RTI) deliverables through regular meetings, emails, and direction of staff to resolve issues;
3. Facilitating interaction among team personnel;
4. Ensuring that proper techniques and procedures are followed;
5. Ensuring the quality and timely delivery of data;
6. Ensuring that reporting requirements are satisfied;
7. Maintaining cost and schedule control;
8. Adjusting schedules to meet client needs; and
9. Reviewing and approving deliverables submitted to the client.

4.1.1.3 AQRC QA Manager, Marcus Langston

The AQRC QA Manager monitors quality assurance/quality control (QA/QC) for the CSN program at UC Davis. In this role, Mr. Langston is part of the Quality Assurance and Special Projects Group, reporting to the AQRC Associate Director of Quality Research, Dr. Hyslop.

For any project, such as CSN, the AQRC QA Manager can report issues to AQRC's highest level of management, regardless of the project structure. The QA Manager is independent of all data collection, and has the authority to report any findings or concerns directly to each project PI and the AQRC director. In practice, the AQRC QA Manager will work closely with the Principal Investigator with the expectation that most concerns can be solved without involvement from the AQRC Director.

Responsibilities include:

1. Reviewing the efforts of other AQRC staff to investigate problems identified during data review and to recommend corrective actions;

2. Reviewing control charts and other data quality reports from AQRC and RTI to assess the achievement of MQOs;
3. Overseeing subcontractor (RTI) data quality and ensuring compliance to main project QAPP.
4. Performing periodic in-lab and data review audits of data quality for the AQRC and RTI laboratories;
5. Conducting an annual review of the Standard Operating Procedures (SOPs), technical information documents (TIs), QAPP, and Quality Management Plan (QMP) for both AQRC and RTI;
6. Maintains officially approved QA Project Plan (QAPP)
7. Hosting external auditors; and
8. Distributing EPA-provided Performance Evaluation (PE) samples within AQRC and summarizing PE analysis results.
9. Hold current version of RTI SHAL and Ions QAPP, and assure compliance to main contract QAPP.

Mr. Langston is a quality professional with UC Davis AQRC. He holds several ASQ certifications including Certified Quality Auditor (CQA) and Certified Manager of Organizational Excellence (CQOME). He has a master's degree in Mechanical Engineering and has 10 years of quality and engineering experience in precision manufacturing, industrial equipment, and life sciences manufacturing. Contact information: mvlangston@ucdavis.edu and 530-754-2421.

4.1.1.4 AQRC Program Manager, Harold Brunette

Mr. Harold Brunette is the AQRC Program Manager. As internal Program Manager, his responsibilities include:

1. Preparing reports and program deliverables 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. Financial tracking, including preparation of budgets and submitting monthly budget summaries to the Principal Investigator;
5. Tracking the number of samples analyzed under each Delivery Order as input to the monthly invoices;
6. Coordinating subcontract activities for ion analysis with RTI;
7. Coordinating the purchasing of supplies and equipment;
8. Coordinating the recruitment and hiring of new staff, as needed; and

9. Scheduling and tracking the flow of data from the laboratories through DART and on to final submittal to ensure that schedules for each monthly submittal are met.

4.1.1.5 Associate Director of Analytical Research, Ann Dillner

Dr. Dillner, the Associate Director of Analytical Research, oversees laboratory operations and research. She has oversight over both UC Davis and RTI laboratory operations for CSN. Dr. Dillner is the lab manager for this CSN contract.

Dr. Dillner has been a researcher with the AQRC since 2005, has been PI of the Cooperative Agreement since 2015 and became the Associate Director of Analytical Research in 2020. Dr. Dillner has focused her research efforts on developing a method for non-destructive and cost-effective measurements of OC, EC, TC, inorganic ions and elements on PTFE filters for IMPROVE, CSN and FRM. She has developed methods to characterize the chemical composition of organic matter. She is applying these methods in two global networks, Surface Particulate Matter Network (SPARTAN) and Multi-Angle Imager of Aerosols (MAIA), both in support of composition retrieval from satellites and a new high-time resolution network in the US, Aerosol Science and Chemistry Network (ASCENT) funded by NSF.

4.1.1.6 Associate Director of Quality Research, Nicole Hyslop

Dr. Hyslop, the Associate Director of Quality Research, oversees two main groups. First is the quality assurance and special projects group. Second is field operations for the IMPROVE network.

The quality assurance and special projects group handles many of the non-routine data collection responsibilities. Whereas the lab group analyzes routine samples and records the data, Dr. Hyslop's group performs oversight and supporting functions. The quality assurance responsibilities include reviewing data, Standard Operating Procedures (SOPs), Technical Information (TIs), continuous improvement support, reporting issues, and addressing them through quality documents such as nonconformance reports, corrective action reports, and investigations. The Quality Manager for AQRC is part of this group and leads the effort. More details found later in this document.

The special projects responsibilities include troubleshooting issues in coordination with the lab and quality oversight, investigating new methods, new equipment, and performing smaller experiments or contracted work much smaller in scope than our main contracts for CSN and IMPROVE.

Dr. Hyslop is responsible for overseeing IMPROVE operations at UCD. Dr. Hyslop has BS and MS degrees in Chemical Engineering from the University of Wisconsin, Madison and University of Texas, Austin, respectively. She has 25 years of experience in the field of atmospheric science with 17 years at UC Davis. Contact information: nmhyslop@ucdavis.edu and 530-754-8979.

4.1.1.7 Associate Director of Software and Data, Sean Raffuse

The AQRC Associate Director of Software and Data oversees data management, validation, and the development of the CSN SQL database and software for laboratory operations, validation, and data analysis. The AQRC Associate Director of Software and Data oversees technical staff who share responsibilities for database management and programming.

Mr. Raffuse oversees technical staff who:

1. Maintain and upgrade 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. Work with staff to identify, map, design and implement improvements to the data management system;
3. Test, verify, and document modifications to the system; and
4. Design and maintain an archival system for all data and metadata records and source files.

As the AQRC Associate Director of Software and Data, 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 19 years of experience in the field of atmospheric science with eight at UC Davis. Contact information: sraffuse@ucdavis.edu and 530-752-4225.

4.1.1.8 AQRC Laboratory Group Manager, Jason Giacomo

The AQRC Laboratory Group Manager is responsible for overseeing all aspects of the laboratory, including sample handling, sample analysis by EDXRF, TOA, and HIPS, and analytical data quality. Responsibilities include:

1. Maintaining a smooth flow of filters through the laboratory;

2. 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;
3. 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;
4. Reviewing the SOPs, QAPP, and QMP;
5. Training and mentoring new staff; and
6. Managing tests comparing the AQRC laboratories with other 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 AQRC, analyzing the results, and working with the other laboratories to prepare reports and publications for external distribution.

Dr. Giacomo is assisted by several laboratory staff, including:

- Two Spectroscopists who oversee the technical details associated with analytical analyses and laboratory quality assurance. They are responsible for reviewing calibrations, reviewing quality control test data, reviewing XRF spectra, reviewing TOA thermograms, devising analysis protocols to meet study objectives, and diagnosing instrument problems and recommending solutions.
- Two laboratory technicians operate the XRF and HIPS instruments. They are responsible for routine changing of samples, maintaining analysis records, processing data, performing quality control tests, and performing routine instrument maintenance such as liquid nitrogen fills and automated detector calibrations.
- One laboratory technician operates the TOA instruments. They are responsible for routine analysis of samples, maintaining analysis records, preparation of standard solutions, and performing routine instrument maintenance.

As the Laboratory Group Manager, Dr. Giacomo is responsible for managing daily laboratory operations including sample preparation, gravimetric analysis, EDXRF analysis, TOA analysis, and optical absorption measurements. He has been the Laboratory Group Manager since 2020. Dr. Giacomo is also supporting the efforts to develop EDXRF calibration materials specifically for particulate matter analysis. He has 14 years of experience in the field of analytical chemistry with four years at UC Davis. Contact information: jagiacomo@ucdavis.edu and 530-752-2329.

4.1.1.9 Data and Reporting Group Supervisor, Sean Raffuse.

The Data & Reporting Group Manager role is being filled by Mr. Raffuse. In that role, Mr. Raffuse oversees data validation and delivery operations, including technical staff responsible for data validation and submission (see Section 7). Responsibilities include:

1. Coordinating project deliverables and documentation including tracking and coordinating tasks across multiple internal groups and external agencies to meet program deadlines;
2. Preparing and editing various project-related documents including contributing sections to the quality assurance reports, monthly reports, technical reports, and proposals;
3. Ensuring data validation documentation are maintained including designing, developing and implementing standard operating procedures for routine data processing, validation, and delivery;
4. Developing and maintaining internal and external communications with funding agencies and state validators;
5. Evaluating data characteristics and problems and guiding discussions regarding data validation practices and treatment of questionable data; and
6. Refining and developing tools necessary for effective data validation.

Mr. Raffuse supervises technical staff who:

1. Review the components of the measurements (flow rates, elemental concentration, etc.) in preparation for final data validation;
2. Work with laboratory staff to resolve problems or discrepancies encountered during data review;
3. Validate the final data set, with input as needed from data analysts;
4. Submit the data set to the DART system for SLT review;
5. Communicate with SLT data validators to resolve discrepancies;
6. Format the data to meet AQS standards; and
7. Submit the final data sets to AQS.

As the AQRC Data & Reporting Group Supervisor, Mr. Raffuse manages the data validation process, data deliverables, and documentation.

4.1.2 The Role of RTI in the Program

RTI is a subcontractor to UC Davis. RTI provides filter handling services including shipment to CSN sites, receiving from CSN sites, gravimetric analysis, shipment to other analytical labs, and ion analysis of nylon filters. As a subcontractor laboratory providing analytical services, RTI has contributed to this QAPP and provided their SOPs.

RTI has developed a QAPP to cover the requirements for sample handling and ions analysis. The RTI QAPP conforms to all the requirements of the main CSN project UC Davis QAPP as a subcontractor. The reason for a 2nd QAPP is to allow RTI the flexibility to maintain the document as requirements, procedures, or personnel change.

The data quality requirements specified in the UC Davis prime contract with EPA flow down contractually through the subcontract to RTI. RTI's ions data are also subject to data validation prior to submittal to AQS (see Section 7). UCD will arrange technical systems audits of the RTI facilities every two to three years.

RTI provides ion analysis for nylon filter samples collected in CSN. Each filter is extracted in distilled-deionized water (DDW) and analyzed for anions and cations by ion chromatography (IC). The sample extracts are archived for a period of six months. The reported anions are sulfate, nitrate, and chloride. The reported cations are ammonium, sodium, and potassium. Detailed description of RTI methods for ion analysis, along with references to the applicable SOP, can be found in Sections 5.4.2.

4.1.3 Position Responsibilities: RTI

4.1.3.1 RTI Senior Director of Analytical Sciences, Keith Levine

Dr. Keith Levine is responsible for the overall technical, administrative, and business development leadership for a large and diverse team of analytical scientists which includes the staff supporting this project. He manages strategically important projects and overall team budgets and operations. He develops technical staff at many professional levels and drives continuous improvement in operational efficiency and scientific stature. He manages an operation with atomic spectrometry, electron microscopy, X-ray spectrometry, mass spectrometry, and chromatographic instrumentation. Dr. Levine has an extensive track record in developing and applying novel analytical methods for determination of metals/metal species in a variety of media. Contact information: levine@rti.org, 919-541-8886.

4.1.3.2 RTI Program Manager, Tracy Dombek

Ms. Tracy Dombek is a Research Chemist in RTI International's Center for Analytical Sciences. In addition to this work, she manages the U.S. National Park Service (NPS) and the Ogawa project. In support of the NPS IMPROVE project and other related PM_{2.5} related tasks, Ms. Dombek serves as the Ion Laboratory Manager and oversees work that involves analyzing filters for inorganic anions and cations by ion chromatography. In this capacity, she is involved with day-to-day laboratory operations, ensuring proper maintenance and troubleshooting for

analyzers and other instrumentation and coordinating service needs for instrumentation through the equipment vendor. She trains staff on how to perform routine maintenance and troubleshooting of equipment. Ms. Dombek also coordinates work assignments that involve ions analysis for the National Toxicology Program. She is responsible for ensuring that completed work meets compliance and provides updates to the task leader for National Toxicology Program. Ms. Dombek reviews and analyzes data for Level 1 compliance. She is also responsible for developing maintenance plans and records of changes. She ensures that all RTI SOPs and QA documents are updated, as needed.

Ms. Dombek is responsible for the overall performance of RTI on this program and for technical communications with the client. She is ultimately responsible for ensuring that only fully qualified and trained staff members perform work under this contract. She also works closely with the RTI QA Manager to ensure implementation of the quality system, ensure that necessary resources are available for performing the required analyses, and ensure that effective corrective actions are taken when required. Contact information: tdombek@rti.org, 919-541-5934.

4.1.3.3 RTI Quality Assurance Manager, Andrea McWilliams

Ms. Andrea McWilliams is a Research Chemist in the Center for Analytical Sciences at RTI International. In this capacity, she applies and interprets standard analytical theories, concepts, and techniques. Applies a working knowledge of related disciplines and methodologies. Works on a wide range of analytical problems requiring the use of creative and imaginative thinking. Identifies, defines, and resolves problems without clear precedent. Investigates alternative analytical methods and approaches. Serves as a Program Manager for XRF measurements by using four laboratory-scale instruments (energy dispersive X-ray fluorescence [EDXRF] and wavelength dispersive X-ray fluorescence [WDXRF]) and assists with the X-ray diffraction laboratory, specifically for silica analysis. Trains staff on how to calibrate and operate instrumentation and manage data. For selected environmental analytical projects, serves as the QA Manager/Officer. Activities include conducting comprehensive audits of contract laboratories and performing data validations for inorganic, organic, and radiochemistry parameters. Prepares Standard Operating Procedures (SOPs), Laboratory Quality Manuals, Quality Management Plans, and Quality Assurance Project Plans. Ensures that the laboratory is in compliance with certification and accreditation requirements. Writes proposals, assists with technical sections of proposals, and prepares operational budgets for proposals. Serves as the Project Leader for various state and local XRF measurement projects. Leads internal and external presentations.

As QA Manager, she has primary responsibility for overseeing and coordinating all RTI QA activities. She has authority to declare any report, data, or analytical result as unacceptable and does not participate in laboratory activities over which she has QA responsibilities. Contact information: acm@rti.org, 919-485-5520.

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 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 trends and supplemental sites. Chemically speciated data are used to monitor air quality trends over time and also 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 four broad areas:

1. Preparing filters for shipment to field sites including lot acceptance of filters from suppliers, gravimetric measurements, packing logistics, shipping logistics, receiving filters from the field, storing and reporting data, and shipping the sampled filters to analytical labs.
2. Receiving field samples from the filter handling contractor (RTI) and analyzing the sample media for chemical constituents including elements, soluble anions and cations, and carbonaceous species as well as measuring filter optical absorption.
3. Validating laboratory results and assembling validated sets of data from the analyses, preparing data reports for EPA management and SLT, and entering data into the AQS.
4. Establishing and applying a comprehensive QA/QC system. UC Davis and RTI maintain their own: Quality Manual or QMPs, CSN QAPPs, and SOPs to provide the documentation for the quality system for this study.

UC Davis will provide 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 RTI through the subcontract that UC Davis has established with RTI.

4.3.1 Schedule

The current contract is active March 7, 2023 to March 6, 2028 (sample collection dates). After receipt of all filters and associated filter data, the analysis laboratories analyze the filters for elements, ions, carbon, and optical absorption. Levels 0 and 1 data validation is conducted prior to delivering the data to the Data Analysis and Reporting Tool (DART) site for review by state, local, and tribal (SLT) agencies. After the data has returned from DART, UC Davis reviews the DART output and data changes before uploading the data into AQS. Data is delivered to AQS within 160 days from the end of each sample month.

4.3.2 Sample Types and Quantities

Samples are received in monthly batches with > 1000 samples per batch; each sample contains three types of filters: 47mm polytetrafluoroethylene (PTFE), 47mm nylon, and 25mm quartz. PTFE and quartz filters (elements, absorption, and carbon) are shipped to UC Davis and the nylon filters (ions) stay at RTI (see Section 5.3). Approximately 13,400 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. Other standard sizes of filters may be used after consultation with EPA and a clear need due to supply chain or improved data quality.

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 Speciated Trends Network portion of CSN. The primary DQO, detection of trends in the chemical speciation data, was defined as follows:

“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)¹

The DQO study concluded that with sampling every third day for five years, trends greater than 5 % (or less than minus 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 ± 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. The DQOs described are only applicable to the portion of CSN that is a part of the Speciated Trends Network (STN).

4.5 Measurement Quality Objectives

Measurement Quality Objectives (MQOs) are performance requirements established to meet the DQOs for CSN. They are based on the coefficient of variation (COV) between collocated measurements of selected target species. Specifically, the COV of collocated measurement pairs must be less than or equal to the following requirements for each parameter category:

- Ions: 10 %

¹ https://www.epa.gov/sites/production/files/2017-01/documents/dqos_for_pm2.5_trends_and_speciation_monitoring_network_1998.pdf

- Total Carbon: 15 %
- Elements: 20 %

To meet the MQO requirements, data quality indicators (DQIs) are continuously monitored as part of routine laboratory procedures: precision, bias, representativeness, comparability, completeness, and detectability. The monthly data validation procedure compares CSN collocated measurements for all reported parameters. COV for each sampling year are calculated and reported in the annual QA reports and compared to the MQO listed above.

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. Precision is monitored by a combination of replicate analytical measurements and collocated samplers.

For calculating analytical precision of lab measurements, different equations are used to estimate analytical precision depending on the situation and the expected distribution. For example, standard deviations are used for distributions that are expected to be normal, whereas robust statistics (relative percent differences, percentiles) are used for distributions that are not expected to be normal. Each lab process will state their precision calculation method.

For MQO evaluation, collocated precision equations are used to compare the two filters sampled at the same site and time. These calculations are detailed in UC Davis *TI 801B Data Processing*.

Bias – is a measure of a systematic offset which skews data results in a single direction, either positive or negative, from an accepted value. Bias is assessed through various QC checks in the laboratory including calibration checks with different standard reference materials than used for the calibration or reanalysis of samples analyzed in the past to ensure stability. Limits placed on these checks ensure that biases are kept within acceptable limits.

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. Representativeness is outside the purview of the UC Davis contract and this QAPP. For more information, please refer to the field SOPs and Field QAPP on the EPA AMTIC website.

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. On a network-wide basis, comparability is assessed by comparison of co-incident measurements with either the IMPROVE network or state/local agency instruments; these analyses are performed ad-hoc and not incorporated into routine validation or reporting (Gorham et al., 2021).

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 58.16. Completeness is assessed in the annual QA report.

Detectability – is the lowest result value that a specific analytical method can reliably discern. This is expressed as the method detection limit, reported with each measurement record. Each month during data validation, the current calculated MDLs are compared against the proposed MDLs and the RFP MDLs for each parameter to ensure the MDL are stable and reasonable.

The DQIs that are used to support the MQOs for laboratory analyses are discussed in detail in Section 5.5 and shown in Tables 5 through 7. DQI criteria are summarized in Table 1. The existing CSN DQOs were based on IMPROVE data, and the MQOs for CSN are specified by the same DQIs as for IMPROVE.

Table 1. QC criteria summary.

QC Activity	Frequency
Gravimetric Analysis (PM 2.5)	
Laboratory Blank Filters	One (1) single use laboratory blank filter is weighed for every post weighing session.
Field Blank Filters	Unexposed filters from each shipment batch are designated as field blanks by the client.
Replicate Filter Weighing's	Minimum of every 10th filter is reweighed.
IC (Anions and Cations)	
Multipoint Calibration	Daily
Nylon Lab Blanks	Initially, then annually or after major instrument change (e.g., conductivity detector or column change)
Deionized Water Blank	Two at the beginning analysis before calibration
Method Blank and Laboratory Control Spikes	One for every 25 samples
QC Standards	Daily or every run
Check Standards	Every 10 samples
Replicates	Three per batch of 50 samples
EDXRF (Elements)	
Calibration Verification (SRM2783)	Following calibration
Calibration Verification (SRM2783)	Monthly
PTFE Lab Blanks	Daily
Multi-element RMs	Daily & weekly
Sample Replicates	Weekly
Reanalysis Samples	Monthly
TOA (Carbon)	
Laboratory Blank Check	Beginning of analysis day
System Leak Check	Before every analysis
Laser Performance Check	Beginning of analysis day
Calibration Peak Area Check	After every analysis
Sucrose Calibration Check	Beginning of analysis day
Instrument Blank Check	Beginning of analysis day

QC Activity	Frequency
Sample Replicates (on the same or a different analyzer)	Every 20 network sample analyses
Inter-instrument Comparison Check	Weekly
Multiple Point Calibrations	Every six months or after major instrument repair or change of calibration gas cylinder
Temperature Calibrations	Every six months, or after major instrument repair
Inter-laboratory comparisons	Once per year or as scheduled
External systems audits	Initiated by UC Davis once every two to three years
Oven Temperature Check	Every analysis
Carrier Gas Cylinder Leak Check	Every time after a gas cylinder is replaced
HIPS (optical absorption)	
Detector Verification Check	Beginning of analysis day
Registration Filter Check	After every 200 samples
Filter Reanalysis Check	Beginning and end of analysis day

4.6 Special Training and Certification

4.6.1 Purpose / Background

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

4.6.2 Training

The Laboratory Group Manager trains laboratory technicians in sample handling and analytical procedures. Physical records of training are maintained by the Laboratory Group Manager, who closely oversees all laboratory 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 EDXRF, IC, TOA, and/or optical absorption instruments.

Prior to training, analysts will read and understand the relevant SOP(s). Under the direction of the Laboratory Group Manager or designated technician, the analyst will follow the SOP to analyze samples and, if available, samples that have been analyzed previously by an experienced analyst. The Laboratory Group Manager 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 Group Manager through review of analytical data.

4.6.2.1 Experience and Training of Current Personnel

Permanent employees at UC Davis and RTI 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 the program. UC Davis utilizes 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 Group 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 Group 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 by the Laboratory Group Supervisors or Manager.

4.6.3 Certification

UC Davis regulations require that staff who operate EDXRF 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 2. 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, documentation will be retained as specified in the contract. Electronic records will be maintained on servers dedicated to the AQRC at UC Davis. Data records and QA documentation for the subcontract laboratory will be obtained from RTI as needed.

Some of the documents listed in Table 2 will be made available to UC Davis and RTI project staff for training and reference. These include this QAPP, the QMPs (UC Davis and RTI), SOPs and TIs, 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 TIs, and forms will be reviewed annually and revised as needed, as scheduled by the UC Davis Program Manager. Documents that are maintained and revised at RTI will be sent to UC Davis for review and archiving. Project staff will be notified when new/updated documents are available by the AQRC QA Manager. Document control and maintenance within each laboratory group is the responsibility of each group manager.

Document Amendment Practices

In the course of sample analysis and data validation, new information may become available that supports modifying operational practices. Any proposed changes will be discussed in detail with the EPA, clarifying the expected impacts on data results and historical trends. Proposed actions that have received support from the EPA will be documented in the monthly reports to the EPA, in a memo describing the actions to be taken, and in the CSN Annual Quality Report. All affected QA documents (e.g., QAPP, QMP, SOPs, and TIs) will be given a new revision number, distributed to the appropriate personnel, and notification will be sent to the EPA in a memo as well as the monthly and annual reports.

Document Management at RTI

Hardcopies of controlled project documents such as this QAPP and SOPs are limited and managed by the Principal Investigator. Current versions are available in both .pdf and .doc format, with the signed PDF version as the official one. To the extent possible, RTI 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 Principal Investigator 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 2.

Table 2. 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
CSN Annual Quality Report	Annual summary of data quality and analysis issues	Electronic; delivered to EPA	AQRC
Correspondence	Contractual correspondence with EPA & RTI	Electronic	AQRC
Purchase Requisitions	Copies of all approved purchase requisitions and purchase orders	Electronic	AQRC
Conference Call Notes	Notes made during conference calls and other project-related calls	Electronic	AQRC
E-mail	All project-related e-mail correspondence	Electronic	UCD server

4.7.2 QA/QC Records

A summary of QA/QC records that are maintained for this program is shown in Table 3.

Table 3. QA/QC records.

Document Name	Description	Format	Storage Location
Training Files	Records of training for lab analysts	Electronic; web-based records for online training	AQRC & RTI
Internal audits and questionnaires	Results of internal QA surveys & audits	Electronic	AQRC & RTI
External audits and questionnaires	Results of audits conducted by outside parties (ADQs, TSAs, audits of sample custody)	Electronic	AQRC & RTI
QAPP	Master version of QAPP, including pending revisions	Electronic & hardcopy	AQRC & RTI
QMPs	Master versions of UCD and RTI QMPs, including pending revisions	Electronic & hardcopy	AQRC & RTI
SOPs	Current versions of all SOPs	Electronic & hardcopy	AQRC & RTI
Intercomparison Study Results	Results of comparisons of two or more laboratories	Electronic	AQRC & RTI
Corrective Action Reports	Results of identified QA problems & their resolutions	Electronic	AQRC & RTI
Quality Forms	Various forms for documentation (Nonconformances, Deviations, Investigations, etc.)	Electronic	AQRC & RTI

4.7.3 Analytical Laboratories' Records

UC Davis and RTI analytical laboratories maintain the records listed in Table 4.

Table 4. Laboratory records.

Document Name	Description	Format	Storage Location
EDXRF Laboratory Records			
Laboratory Notebooks	Analysts' comments, instrument operations and maintenance logs	Electronic & hardcopy	EDXRF Lab
Calibration & Instrumentation Certificates & Records	Certificates of analysis, NIST traceability, and instrument testing & maintenance	Electronic & hardcopy	EDXRF Lab
Method Specific Application	Includes X-ray generation information and other information required to automate the EDXRF analyses	Computer files on each XRF instrument	EDXRF Lab
Instrument User's Manual and SOP	Information for setting up, using, and troubleshooting the EDXRF instrument	Electronic & hardcopy	EDXRF Lab
SOPs	Current copies of SOPs and TIs	Electronic & hardcopy	EDXRF Lab

Document Name	Description	Format	Storage Location
QAPP	Current copy of this QAPP	Electronic & hardcopy	EDXRF Lab
Analytical Results Database (Raw Data Records)	Results of EDXRF elemental analyses	Electronic (database)	EDXRF Lab
Analytical QC Records	Results of calibrations, SRM recoveries, QC checks, replicate analyses	Electronic	EDXRF Lab
Gravimetric Lab Records			
Filter Inventory and Inspection Form	Completed upon receipt of filter lots from the vendor; indicates the order to use filter boxes, date inspected, and number of filters rejected	Electronic	Gravimetry Laboratory
Filter Conditioning Information	Indicates the dates filters were conditioned and stability test results	Electronic	Gravimetry Laboratory
Calibration Certificates and Records	Includes certificates of NIST traceability and similar records	Electronic and Hard copy records	Gravimetry Laboratory
Gravimetric Filter Database	Includes filter ID, initial weighing information (including date, RH, temperature, cassette number), final weighing information (date, RH, temperature, and weight), and mass loading of the filter, and all QC information for each weighing session including standard weights, duplicates, field blanks, and laboratory blanks	Electronic (database)	Project data server (SQL server DB)
Weighing Room Environmental Data	Data logger is programmed to record "grab samples" at 5-minute intervals	Data logger spool file or spreadsheet	Project data server
Internal Tracking Forms	Forms used to track sample batches between the SHAL and RTI's internal laboratories	Hard copy	Internal Tracking Forms
Control Charts	QC information displayed in sequence to help diagnose problems with analytical	Electronic	Control Charts
IC Laboratory Records			
Laboratory Notebooks and Worksheets	Analysts' comments, instrument operations and maintenance logs	hardcopy	IC Lab & Project Managers Office, and Archive
Calibration & Instrumentation Certificates & Records	Certificates of analysis, NIST traceability, and instrument testing & maintenance (where applicable are available on vendor websites)	Electronic & hardcopy	IC Lab Computers & IC Prep Lab
Instrument User's Manuals & SOP	Information for setting up, using, and troubleshooting the instruments	Electronic & hardcopy	IC Lab & Vendor website
SOPs	Current copies of SOPs and TIs	Electronic & hardcopy	Project data server
QAPP	Current copy of this QAPP	Electronic & hardcopy	IC Lab

Document Name	Description	Format	Storage Location
Analytical Results Database (Raw Data Records)	Using the Chromeleon instrument software, to process results of ions analyses	Electronic (database)	Instrument PC
Analytical QC Records	Results of calibrations, QC recoveries, and replicate precision	Electronic	IC Lab Database and Archive
TOA Laboratory Records			
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 TIs	Electronic & hardcopy	Carbon Lab
QAPP	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
HIPS Laboratory Records			
Laboratory Notebooks and Files	Analysts' comments, instrument operations and maintenance logs	Electronic & hardcopy	HIPS Lab
Method Parameter Files	Information required to run the analysis	Electronic & hardcopy	HIPS Lab Database Hardcopies & Archive
Instrument User's Manuals	Information for setting up, using, and troubleshooting the instruments	Hardcopies	HIPS Lab
SOPs	Current copies of SOPs and TIs	Electronic & hardcopy	HIPS Lab
QAPP	Current copy of this QAPP	Electronic & hardcopy	HIPS Lab
Analytical Results Database (Raw Data Records)	Results of HIPS analyses	Electronic (database)	Instrument PC Computer Database
Analytical QC Records	Results of instrument blanks, verification, and reanalysis samples	Electronic and hardcopy	HIPS Lab Database

Electronic records at UCD and RTI are backed up according to the storage practices described in the QMP and the associated SOP/TIs.

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 website.

5.2 Sampling Methods Requirements

Collection of samples is conducted by the SLT agencies and is outside the purview of the UC Davis contract and this QAPP. For more information, please refer to the field SOPs on the EPA AMTIC website.

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 UC Davis Laboratories

The flowcharts for receiving and inventorying the PTFE (elements and optical absorption) and quartz (carbon) filter samples are shown in Figure 3 and 4. The filter samples are shipped in coolers from RTI to UC Davis, accompanied with chain-of-custody forms (COC).

The CSN project requires that the sampled filters be kept less than 4 °C when not being analyzed. This includes PTFE, Nylon, and Quartz filters.

RTI receives the sampled filters shipped from field operators in coolers with ice packs. RTI then organizes and ships the sampled filters to the research labs in large batches in multiple coolers. Each cooler has ice packs to maintain the temperature less than 4 °C and thermometers to report the temperature during shipment. When the analytical labs receive the coolers, they will document the temperature at receipt and then move the filters into refrigerators or freezers. If the temperature was found to be above 4 °C, the affected filters will be flagged by UC Davis with a temperature qualifier.

Upon receipt of the samples, the technician signs and dates the COC and stores the samples in a refrigerator.

The UCD CSN Data Management Site stores electronic data associated with all the sample types (quartz, nylon, and PTFE). Electronic records provided by RTI are ingested into the CSN database via the UCD 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 into the EDXRF, TOA, and HIPS instruments. Shipments from RTI 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. RTI is responsible for labeling the boxes and each Petri Tray with the set numbers. The samples are identified by the Lab Analysis ID barcode (A#####).

Additional details regarding filter receipt can be found at *UCD SOP #904: Receiving and Inventorying of CSN Samples*.

Figure 3. Flowchart of PTFE sample receiving and inventorying at UC Davis.

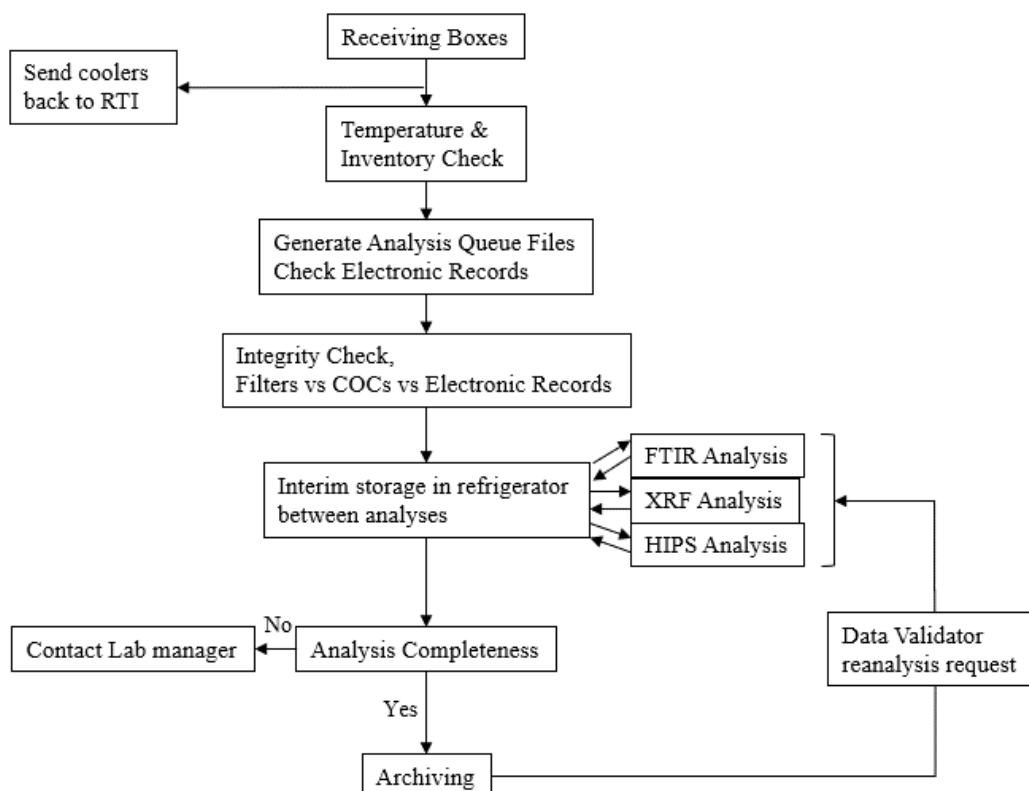
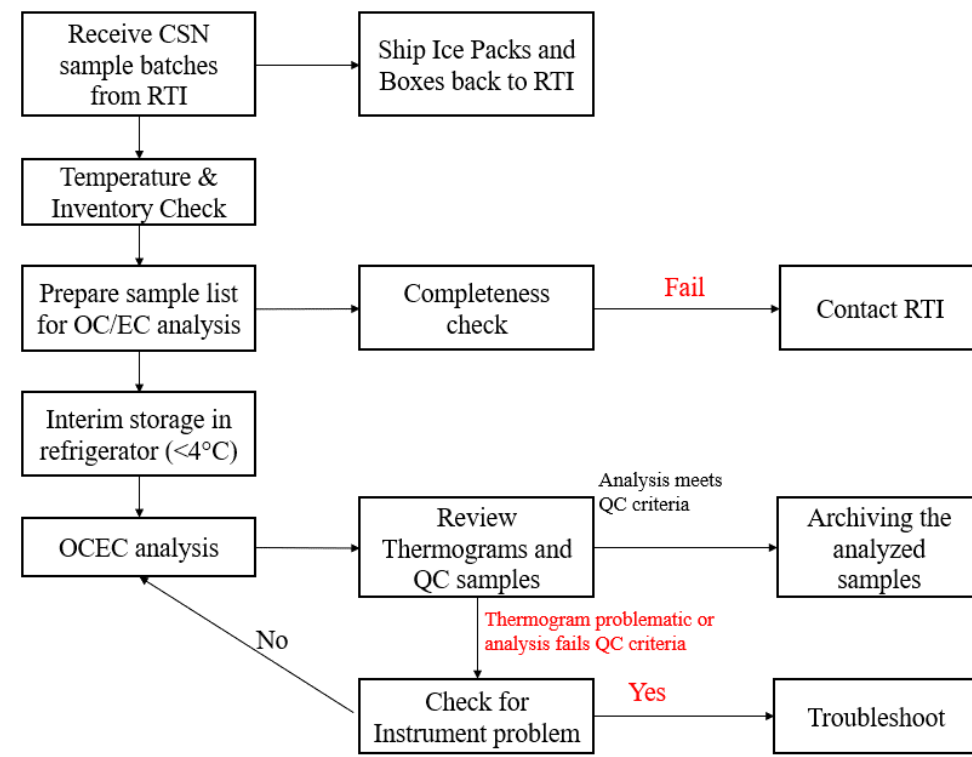


Figure 4. Flowchart of quartz sample receiving and inventorying at UC Davis.







COC forms originate from RTI. They are received at UCD by laboratory technicians, who are responsible for ensuring COC forms stay with the filters as they are transferred between laboratory rooms. Once the filters have completed analysis, both COCs and filters are archived by a laboratory technician.

The fields present on the COC form include: date and name of originator, a receipt date and recipient name, delivery order, and a barcode for analysis request ID (batch number). A table then follows containing barcodes of the filter analysis ID, filter type, and analysis requested.

The H-number in the upper left corner is the RTI internal batch number for each month. RTI will also provide the sampling month in YYYY-MM format for tracking and reporting. There are two identification numbers. The A- number is the filter analysis ID that matches the bar code. The number below is unique manufacturer number (PTFE only).

Figure 5. Example COC form from RTI for 47 mm PTFE samples.

 H44635N	Page 1 of 1 Training DB RTI PM 2.5 Laboratory Chain of Custody Form (LCOC) UC Davis XRF Analysis Lab		
Bar Code	Identification Number	Filter Type	Analysis Requested
Delivery Order: 001			
 A10157656 11923890	A10157656 11923890	Teflon Filter	XRF
 A1016350R 12254830	A1016350R 12254830	Teflon Filter	XRF
 A1018153W 11787136	A1018153W 11787136	Teflon Filter	XRF
Total Aliquot Count: 3			

5.3.1.2 Ion Analysis Laboratory (RTI)

Nylon filters are received by RTI from the field packaged in coolers. Using the COC, receipt of the filters is confirmed and any discrepancies are noted. The filter IDs are recorded in RTIs Sample Tracking and Extraction log. The nylon filters are then stored at or below 4° C until processing for analysis.

Refer to the RTI SOP for further details:

RTI SOP, Determination of Anions and Cations Extracted from Nylon® Filters by Ion Chromatography (IC)

5.3.2 Internal Tracking of Analytical Samples

The Teflon, carbon, and nylon filter samples will be received from the field and processed in the RTI SHAL. Shipments of the Teflon and carbon filters to UC Davis will be monthly. The transfer of Nylon filters to the RTI ions lab will also be monthly at the same timing as the shipments to UC Davis. See Section 4.3.1 for more details.

To keep pace, UC Davis sets an internal target of 47 days to finish lab analysis once received from the RTI SHAL in monthly shipments. This is tracked and displayed on a web application and regularly reviewed. This target can be adjusted based on workload and changing analysis requirements and does not contribute to overall requirements in section 4.3.1.

For EDXRF, TOA, and HIPS analysis at UC Davis, queue files are used in conjunction with barcode scanners to load sample information into each instrument. Filters are transferred from Petri slides into their respective sample holders for each analysis immediately after scanning the barcode associated with

each sample. For EDXRF, the sample holders (cups) are placed into 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 EDXRF instrument 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. For TOA, sample punches are taken from the quartz filters and immediately loaded into the instrument. The sample filter remains in the labeled Petri slide. For HIPS, samples are loaded into custom filter holders and loaded into analysis trays. After analysis is complete the filters are transferred back into their labeled Petri slides.

At RTI, 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.

CSN filters are designated as analytical filters, which have no requirements for maximum holding time or lab turnaround time before analysis for each process. UC Davis AQRC only analyzes analytical filters as part of their responsibility for the contract. However, the contract includes some regulatory PM 2.5 filters for 3 sites. These filters are handled and analyzed by RTI under this contract. The requirements and quality criteria can be found in the RTI QAPP.

5.3.3 Archiving of Filters and Extracts

Refer to the UC Davis SOP for details:

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

5.4 Analytical Methods Requirements

5.4.1 Gravimetric Analysis

Analysis of CSN PTFE filter samples is performed at RTI using the Measurement Technology Laboratories, LLC (MTL) robotic weighing system to measure PM filters before and after sampling, per the RTI SOP:

RTI CSN SOP #304-GEN-001: Standard Operating Procedure for Particulate Matter (PM) Gravimetric Analysis

5.4.2 EDXRF for Analysis of Elements

Analysis of CSN PTFE filter samples is performed at UC Davis using energy dispersive X-ray fluorescence (EDXRF) for analysis of elements, specifically using PANalytical Epsilon 5 systems, per the UC Davis SOP:

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

5.4.3 Extraction and IC for Analysis of Anions and Cations

Analysis of CSN nylon filter samples is performed at RTI using ion chromatography (IC) for analysis of water-soluble ions, specifically using Dionex 2000, 3000, and Aquion systems, per the RTI SOP:

RTI CSN SOP #Ions1: Determination of Anions and Cations Extracted from Nylon Filters by Ion Chromatography (IC)

5.4.4 TOA for Analysis of Carbon

Analysis of CSN quartz filter samples is performed at UC Davis using thermal optical analysis (TOA) for analysis of carbon, specifically using Sunset Laboratory thermal-optical OC/EC analyzers following the IMPROVE_A carbon analysis protocol, per the UC Davis SOP:

UCD CSN SOP #402: Thermal/Optical Reflectance (TOR) Carbon Analysis Using a Sunset Carbon Analyzer

5.4.5 HIPS for Optical Absorption Analysis

Analysis of CSN PTFE filter samples is performed at UC Davis using the AQRC custom hybrid integrating plate/sphere (HIPS) system for optical absorption, per the UC Davis SOP:

UCD CSN SOP #277: Optical Absorption Analysis of PM_{2.5} Samples

5.5 Quality Control Requirements

5.5.1 Quality Criteria for Gravimetric Analysis

The data quality objectives for the gravimetric mass determinations are outlined in:

- RTI SOP #304-GEN-001: *Standard Operating Procedure for Particulate Matter (PM) Gravimetric Analysis*, Section 13.0 and Tables 1-2.

- Section B.5.1 of the RTI Quality Assurance Project Plan (QAPP): *Filter Handling, Acceptance Testing, Gravimetric Analysis, and Ion Chromatography Analysis for Chemical Speciation Network*.

The steps taken when control limits are exceeded and effectiveness of controls are outlined in:

- RTI SOP #304-GEN-001: *Standard Operating Procedure for Particulate Matter (PM) Gravimetric Analysis*, Section 10.7.

5.5.2 Quality Criteria for Ion Analysis

The data quality objects for the ions are outlined in:

- RTI SOP: *Determination of Anions and Cations Extracted from Nylon® Filters by Ion Chromatography (IC)*, Section 8.0 and Tables 1-4.
- Section B.5.2 of the RTI QAPP: *Filter Handling, Acceptance Testing, Gravimetric Analysis, and Ion Chromatography Analysis for Chemical Speciation Network*.

The steps taken when control limits are exceeded and effectiveness of controls are outlined in:

- RTI SOP: *Determination of Anions and Cations Extracted from Nylon® Filters by Ion Chromatography (IC)*, Sections 10.0 and 14.0

5.5.3 Quality Criteria for Element Analysis

Quality control criteria for EDXRF analysis are shown in Table 6. QC failures are investigated as described in the SOP, and samples are not analyzed until the failure is resolved. After a QC failure is resolved, any samples analyzed between the last acceptable and the failed QC check are investigated. Due to time and resource-constraints, a subset may be re-run instead of the full set to determine if the results were significantly impacted. If the results were significantly different, the full set may be rerun. Depending on the severity, data may be flagged, commented, or documented in a report and the results delivered to AQS.

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} 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).

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

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

where, $c_{std,i}$ is the re-constructed loading ($\mu\text{g}/\text{cm}^2$) of calibration standard i (c_{std}) using the calibration factor (E , in $[(\mu\text{g}/\text{cm}^2)/(\text{cps}/\text{mA})]$) and I_{cor} is the blank subtracted intensity of X-rays emitted by the standard i (cps/mA). Although the uncertainty of c_{std} , $u(c_{std})$, is not a part of the $c_{std,i}$ calculation, it is added to the uncertainty equation for a conservative approach. The coverage factor, k , considers the distribution of uncertainties possible for a given measurement. 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).

- Relative percent difference (RPD): The ratio of the difference of two measures (M_1 and M_2) to the mean of their measures.

$$RPD = \frac{(M_2 - M_1)}{(M_1 + M_2)/2}$$

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

$$Bias = 100 * \frac{C_{E5} - C_{cer}}{C_{cer}} \quad \text{Eqn. 3}$$

where, C_{E5} and C_{cer} are the loadings by E5 and certified loadings of NIST SRM2783, respectively.

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

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

where, c_{E5} is the mass loading measured ($\mu\text{g}/\text{cm}^2$), c_{ref} is the reference mass loading, U_{cE5} and $U_{c_{ref}}$ are the uncertainties of measured (c_{E5}) and reference (c_{ref}) mass loadings.

- Acceptance limits:
 - PTFE blanks: Analyzed daily and determined as three times the standard deviation plus the median of a set of lab blanks.
 - Multi-element samples: Analyzed daily and weekly, and determined as $\pm 10\%$ or ± 3 standard deviations, whichever is larger, of the reference loadings. This was changed from previous years where only a $\pm 10\%$ criteria was used for two reasons. First, in previous years a different reference value was assigned to each ME-RM on a per-instrument basis. The lab now assigns a single reference mass loading to each element on a per-ME-RM basis. However, this requires larger acceptance ranges for elements which have higher inter-instrumental bias. Secondly, this was changed in order to accommodate the lower concentrations of some elements on the prepared ME-RM filters used for QC which approach the method detection limit.
 - SRM: Analyzed monthly, are element-specific and determined as root-mean-squared-relative-errors (RMSREs) plus three times standard deviations from a set of SRM measurements.

Table 5. UC Davis QC criteria for element analysis by EDXRF.

QC Activity	Inspection Frequency	Inspection Parameter	Acceptance criteria (MQO)	Corrective Action
Calibration Verification	Following calibration	<ul style="list-style-type: none"> - Correlation coefficient (r) - Bias from certified loadings of SRM 2783 for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb 	<ul style="list-style-type: none"> - $r \geq 0.98$ - Bias within element-specific acceptance limits 	<ul style="list-style-type: none"> - Check calibration line and spectra - Check standard(s) for damage/contamination - Exclude standard(s) from calibration line - Further cross-instrumental testing - Recalibration with current or new standards

QC Activity	Inspection Frequency	Inspection Parameter	Acceptance criteria (MQO)	Corrective Action
	Monthly	Bias from certified loadings of SRM 2783 for Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb	Bias within element-specific acceptance limits	
Instrument Stability/ Precision (repeatability)	Daily	PTFE Blank	\leq acceptance limits with exceedance of any element not to occur in more than two consecutive days	<ul style="list-style-type: none"> - Change/clean blank if contaminated/damaged - Clean the diaphragm, if necessary - Further cross-instrumental testing
	Daily & weekly	multi-element RMs (ME-RMs) for elements: Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb.	Larger of $\pm 10\%$ or 3 standard deviations of reference mass loadings with exceedance of any element not to occur in more than two consecutive days	<ul style="list-style-type: none"> - Check sample for damage/contamination - Further cross-instrumental testing - Replace filter sample as necessary
Replicate	Weekly	All elements reported* excluding Cl and Br (volatiles)	z-score within ± 3	<ul style="list-style-type: none"> - Repeat replicate to look for agreement. - Investigate Filter Integrity and visual quality - Investigate instrument
Reproducibility	Monthly	z-score based on reanalysis of 16 ME-RM samples for elements: Al, Si, S, K, Ca, Cr, Fe, Zn, As, Se, Rb, Sr, Cd, Sn, and Pb.	z-score within ± 1 for selected elements	Investigate and reanalyze set of samples as needed

*Meeting minimum number of pairs above 2x detection limit.

Control charts displaying z-scores for monitored elements as a function of analysis time are reviewed by the laboratory manager on a monthly basis. Measurements exceeding the acceptance criteria specified in Table 6 are investigated.

5.5.3.1 Elements Replicate Analysis

Due to resource limitations, replicate measurements are taken when the analyzers are not running routine samples. The only time available is on weekends after the last samples of the week have been run. The replicate runs receive QC analysis code 6 to distinguish them from routine analysis. Once finished with routine

analyses, the instrument will re-run as many samples loaded into the instrument as time allows. The replicate z-score will be calculated for these analysis pairs and should be within 3 standard deviations. With two major networks, replicate samples could be either CSN or IMPROVE; replicates are not run for each network on every weekend. However, the replicate analysis challenges the instrument's ability to replicate previous results, so is not necessarily related to one network or the other.

AQRC will be using the commonly used root mean square (RMS) of differences, also known as the standard deviation of a random variable. Mathematically:

$$RMS = \sqrt{\frac{1}{n} \sum_{i=1}^n D_i^2} \times 100 \% \quad \text{Eqn. 5}$$

where:

$$D_i = \frac{(C_{i1} - C_{i2})/\sqrt{2}}{\bar{C}_i} \quad \text{Eqn. 6}$$

The scaled relative difference, D_i , is the arithmetic difference of the routine and replicate measurements divided by the mean. The $\sqrt{2}$ term accounts for the propagated uncertainty in the two measurements. For more information about these metrics and their influences, please see (Hyslop and White, 2009).

The control limits for XRF replicates were determined by replicate data collected in sample years 2021 and 2022. A significant pool of past data is necessary to calculate limits with enough pairs above 2x MDL. Periodically, the data sets will be reviewed by the AQRC QA team in concert with program stakeholders to determine if they should be updated.

Control limits were calculated from the expanded uncertainty equation used to estimate uncertainty for both networks, namely

$$\sigma = \sqrt{(S_{LB})^2 + (fC)^2} \quad \text{Eqn. 7}$$

where S_{LB} is the analytical uncertainty calculated from laboratory blanks (only accounting for instrument uncertainty and media effects), f is a fractional uncertainty term that accounts for multiplicative effects, and C is the measurement result ($\mu\text{g}/\text{cm}^2$ in this case). We estimated f from the RMS for each element using 2021 and 2022 replicate results.

The results are plotted and reviewed the following business day after each set of replicate measurements were performed. The results must be within the ± 3 standard deviations for each element above 2x MDL. The 2x MDL requirement was set to eliminate evaluation of noise, but does reduce the number of pairs for some elements. All reported elements are reviewed and subject to the criteria with a few exceptions. Br and Cl are known to be volatile and are excluded from replicate analysis requirements.

If a replicate measurement falls outside of the control limits, the reason will be investigated. We will look for possible contamination, filter seating, or other outside factors. The corrective action will be to re-analyze the filter for a second replicate measurement.

- If the second replicate measurement passes, then the instrument remains in compliance.
- If the second replicate measurement value does not match the routine value but does match the first replicate value, then the check passes, we will invalidate the routine value and report the first replicate value.
- If the second replicate measurement fails and does not match the first replicate value, then the instrument/element pair fails. All sample analyses from this instrument/element are flagged with the QX AQS flag (Does not meet QC criteria) for the past week (since the last passing replicate QC check).
 - A discussion may determine if we re-run the filters, a subset, or just use the flag. In most cases it will be a single element, on a single replicate, from a single analyzer, that may not warrant a complete re-run.

5.5.4 Quality Criteria for Carbon Analysis

Quality control criteria for carbon analysis are shown in Table 7, assuming 12 hours per day, five days per week operation of the laboratory. QC failures are investigated as described in the SOP, and samples are not analyzed until the failure is resolved. After a QC failure is resolved, any samples analyzed between the last acceptable and the failed QC check are reanalyzed. Due to time and resource-constraints, a subset may be re-run instead of the full set to determine if the results were significantly impacted. If the results were significantly different, the full set may be rerun. Depending on the severity, data may be flagged, commented, or documented in a report and the results delivered to AQS.

Daily checks include an instrument blank analysis to check for system contamination and evaluate laser response and a single-point sucrose standard

check to evaluate FID response. Each is performed at the beginning of the analysis day. An instrument blank check uses a filter punch that has been previously analyzed to check for instrument contamination. If the measured TC level is outside $\pm 0.3 \mu\text{g C/cm}^2$, the instrument needs to be checked and possibly baked clean. If the reflected and/or transmitted laser reading is less than 5000 with a clean filter punch placed in the sample spoon, adjust laser position and examine oven and spoon for possible frosting. For the single-point sucrose calibration check, 10 μL of 1.0525 $\mu\text{g C/}\mu\text{L}$ sucrose solution (10.525 $\mu\text{g carbon}$) is injected onto a previously analyzed clean filter and analyzed for carbon content. If the resulting total carbon (TC) is over $\pm 7\%$ different from the calculated value, a second analysis is performed or a new sucrose solution is generated and analyzed before analyzing samples.

For every analysis, the oven pressure is checked for leaks and the calibration peak area is checked with an internal 5 % CH_4/He gas standard. If the leak check indicates that the oven pressure is below the pressure criteria determined for each instrument and does not stabilize, the cause of the leak is investigated, fixed, and must pass the leak check before samples can be analyzed. If the calibration peak area is over $\pm 10\%$ different from the daily average value for a specific analyzer, the analysis result is voided; the flowrates, FID ignition and sample oven pressure are checked; and the analysis is repeated using a second filter punch. If the second filter punch also fails, the instrument is taken offline and investigated for the root cause of the issue.

Sample replicate analysis is performed on every 20th network sample. The analyzer to perform the replicate analysis is randomly selected. If the acceptance criteria in Table 7 are not met, the analyzer and sample anomalies are investigated and another replicate is re-analyzed on a third analyzer. One 37 mm quartz sample collected on UC Davis campus is analyzed weekly on all six analyzers for inter-instrument comparison. If the acceptance criteria in Table 7 are not met, a second punch from the same sample is run on the failed analyzer to check for analyzer and sample anomalies. If the second filter punch also fails to meet the acceptance criteria in Table 7, the instrument is taken offline and investigated for the root cause of the issue.

A multi-point calibration is performed every six months, when the calibration gas (CH_4/He) cylinder or instrument main oven is replaced, or if a consistent one-sided bias is observed with the daily single-point sucrose standard check, whichever comes first. The calibrations use sucrose standards at seven different concentration levels that cover a wide range of TC concentrations typically seen on the CSN samples. The least-square correlation coefficient (r^2) of measured versus calculated mass of carbon, force-fit through the origin (0,0), should be higher than 0.995. The calibration constant for each analyzer is updated if the

measured and calculated sucrose concentrations deviate from the 1:1 line by more than 1 % (i.e., calibration slope > 1.01 or < 0.99).

A temperature calibration is performed every six months (usually along with a multi-point calibration) or after a major instrument repair (e.g., replacement of main oven or heating coils). The difference (i.e., offset) between the oven temperature and sample temperature at each IMPROVE_A protocol temperature set point is determined by using a manufacturer-provided temperature calibration device, inserted into the sample oven so that the external temperature probe sits where a sample punch would be during a routine analysis. The oven temperature cycles through the IMPROVE_A protocol temperature set points (from 140 °C to 840 °C). The differences in temperature readings by the calibration probe and the oven temperature probe (i.e., temperature offsets) are calculated and updated in the IMPROVE_A protocol parameter file. The system then goes through the IMPROVE_A protocol temperature cycle again to verify that the temperature readings from the two probes are within 10 °C at all temperature steps.

In addition, inter-laboratory comparisons are performed annually by participating in available inter-laboratory studies. The results are reviewed and procedures verified by the laboratory manager and the spectroscopist. External systems audits initiated by the EPA are typically performed once every two or three years. Actions are taken to correct any deficiencies noted in the audit report.

Table 6. UC Davis QC criteria for carbon analysis by TOA using the IMPROVE_A TOR/TOT carbon analysis method.

Type	Calibration Standards and Range	Frequency	Acceptance Criteria	Corrective Action
Laboratory Blank Check	NA	Beginning of analysis day	$\leq 1.0 \mu\text{g C/cm}^2$	Repeat analysis. If same result, check filter lot for possible contamination and perform pre-firing
Instrument Blank Check	NA	Beginning of analysis day	Between -0.3 and $0.3 \mu\text{g C/cm}^2$	Repeat analysis. If same result, check instrument and gas lines for possible contamination

Single-point Sucrose Standard Check	10 µL of 1.0525 µg C/ µL Sucrose solution	Beginning of analysis day	Within ± 7 % of the calculated value	Repeat analysis. If same result, run a different sucrose solution to determine if the problem is with the solution or instrument. If former, make new sucrose solution. If latter, perform multipoint calibration to determine new calibration constant.
Calibration Peak Area Check	5 % CH ₄ /He gas standard injected into a fix-volume loop; 20 µg equivalent carbon mass	Every analysis	Within ± 10 % of the daily average value for a specific instrument	Void analysis result; Repeat analysis with another filter punch. Up to three analyses can be performed.
System Leak Check	NA	Every analysis	Meet minimum oven pressure (criterion is instrument- specific)	Re-adjust the oven seal and check oven temperatures before analyzing samples
Laser Performance Check	NA	Beginning of analysis day	Laser Transmittance signal for Instrument blank > 5000	Adjust laser position and examine oven for frosting
Network Sample Replicates	NA	Every 20 th network sample analyses	Within ± 10 % RPD when TC > 10 µg C/cm ² within ± 20 % RPD when ECR > 2.5 µg C/cm ² or Within ± 1 µg/cm ² when TC ≤ 10 µg C/cm ² within ± 0.5 µg/cm ² when ECR ≤ 2.5 µg C/cm ²	Investigate instrument and sample anomalies; Analyze the third punch on a difference analyzer
Inter- instrument Comparison Check	NA	Once per week	Within ± 10 % RPD* when TC > 10 µg C/cm ² Within ± 20 % RPD when EC > 2.5 µg C/cm ² or	Analyze a second punch from the same sample on the failed analyzer. If same result, analyzer taken offline and investigated for the

			Within ± 1 $\mu\text{g}/\text{cm}^2$ when TC ≤ 10 $\mu\text{g C}/\text{cm}^2$ Within ± 0.5 $\mu\text{g}/\text{cm}^2$ when EC ≤ 2.5 $\mu\text{g C}/\text{cm}^2$ *RPD for each analyzer is calculated against the average measurement from all analyzers	root cause of the failure
Multi-point Sucrose Standard Check	10 μL of 0.211 - 21.050 $\mu\text{g C}/\mu\text{L}$ Sucrose solutions	Every six months or after major instrument repair or change of calibration gas cylinder	NA	Calculate new calibration constant based on calibration slope and update in the IMPROVE_A protocol parameter file
Temperature Calibrations	NA	Every six months or after major instrument repair	NA	Change the temperature offset values in the IMPROVE_A protocol parameter file accordingly
Carrier Gas Cylinder Leak Check	NA	Every time when a gas cylinder is replaced	Regulator pressure reading should not decrease overnight with tank valve closed	Correct for the leak in the gas line and/or fitting
Oven Temperature	NA	Every analysis	Back Oven: 870 ± 10 $^{\circ}\text{C}$ Methanator Oven: 500 ± 5 $^{\circ}\text{C}$	Check heating coils; replace the heating coils if needed

5.5.5 Quality Criteria for Filter Optical Absorption Analysis

Quality control criteria for HIPS optical absorption analysis are shown in Table 8. QC failures are investigated as described in the SOP, and samples are not analyzed until the failure is resolved. After a QC failure is resolved, any samples analyzed between the last acceptable and the failed QC check are investigated to determine the impact on the data. If there is an impact on the data the samples are reanalyzed; reanalysis results are reported to AQS.

Daily checks incorporate 14 verification filters and 22 reanalysis filters collected by the IMPROVE network, which span an order of magnitude in absorption values. The first tray includes a registration filter to which the detector response is normalized, thus establishing continuity with historical measurements. Both sets are analyzed at the beginning of each day of analysis. The results are plotted alongside previous measurements and with the expected linear relationship between transmittance and reflectance. The results of the verification and reanalysis filters must meet the acceptance criteria in Table 8 before samples are analyzed. If the verification or reanalysis filter results are out of bounds, the analytical system is investigated and the verification and reanalysis sets are reanalyzed. Sample analysis does not proceed until the QC process has completed successfully.

Table 7. UC Davis QC criteria for filter optical absorption analysis using the HIPS analysis method.

Type	Calibration Standards and Range	Frequency	Acceptance Criteria	Corrective Action
Verification Filter Check	Reference values of verification filter set	Beginning of analysis day	$\leq 3 \%$	Repeat analysis. If same result, investigate analysis system for error
Reanalysis Filter Check	Reference values of reanalysis filter set	Beginning of analysis day	Accuracy: within expanded uncertainty of reference Linearity: $R^2 > 0.95$ and slope within 0.95 to 1.0 Long-term stability: z-score ≤ 1	Check detector registration and repeat analysis. If same result, investigate analysis system for error
Replicate	Sample filters	Each Monthly Batch	TBD	Investigate and reanalyze set of samples as needed

5.5.6 Disaster Recovery Plan for Data

Refer to the UC Davis SOP for details:

UCD SOP #801: Processing and Validating Raw Data

5.5.7 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 to estimate uncertainties are: 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 20th, 2015) were based on bottom-up estimates of uncertainties in the measurement components (Flanagan et al., 2006). After November 20th, 2015, 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 uncertainty estimates include both an additive (analytical uncertainty) and multiplicative (fractional uncertainty) terms as shown in Equation 8: the additive term is dominant at low concentrations, and the fractional term is dominant at high concentrations.

$$\sigma(c) = \sqrt{(S_{FB})^2 + (fC)^2} \quad \text{Eqn. 8}$$

Where,

C = Ambient concentration (µg/m³)

f = Fractional uncertainty

S_{FB} = analytical uncertainty

Refer to the UC Davis SOP for details:

UCD SOP # 801B: CSN Data Processing

5.5.8 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.

Refer to the UC Davis SOP for details:

UCD SOP # 801B: CSN Data Processing

5.5.9 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_{2.5} PTFE samples for CSN have been collected 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 species present in large amounts.
- 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. CSN data are reported with artifact correction. The OC artifact for samples collected using the URG 3000N typically range between 0 and 1 µg/m³ based on field blank measurements.
- 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 EDXRF and TOA). 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 EDXRF instruments (Gutknecht et al., 2010). In the process, it was also ensured that the total uncertainties for the other CSN analytical techniques (gravimetry, ion chromatography, TOA, optical absorption) were comparable with those for EDXRF and were realistic, based on the collocation results.

5.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

5.6.1 Gravimetric Analysis Laboratory

The requirements for Gravimetric Analysis are outlined in:

- RTI SOP #304-GEN-001: *Standard Operating Procedure for Particulate Matter (PM) Gravimetric Analysis*
- Section B.6 Tables 10-11 of the RTI QAPP: *Filter Handling, Acceptance Testing, Gravimetric Analysis, and Ion Chromatography Analysis for Chemical Speciation Network*.

5.6.2 Ion Chromatography Laboratory

The requirements for Ions Analysis are outlined in:

RTI SOP #Ions1, Determination of Anions and Cations Extracted from Nylon® Filters by Ion Chromatography (IC)
Section B.6 and Tables 10-11 of the RTI QAPP, Filter Handling, Acceptance Testing, Gravimetric Analysis, and Ion Chromatography Analysis for Chemical Speciation Network

5.6.3 EDXRF 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 8. Inspection criteria for the UC Davis EDXRF Laboratory.

Item	Frequency	Parameter	Acceptance Criteria (MQO)	Action if Failed	Documentation
Detector Calibration	Weekly	Wavelength/energy alignment of the instrument	None	This is an automated process; manufacturer contacted if process fails	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 EDXRF database and in designated computer files
Ongoing Calibration Verification	Monthly	Loadings of SRM 2783	Absolute bias \leq 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 EDXRF database and in designated computer files

Item	Frequency	Parameter	Acceptance Criteria (MQO)	Action if Failed	Documentation
Long-term Reproducibility	Monthly	z-score based on reanalysis of a set of 16 ME-RM samples.	z-score within ± 1 for selected elements	Investigate, correct, and possibly reanalyze affected samples	Results are stored in the EDXRF database and in designated computer files

Table 9. UC Davis EDXRF Laboratory maintenance schedule and responsibility.

Item	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

5.6.4 TOA Laboratory

Refer to UCD SOP for details:

UCD CSN SOP #402: Thermal/Optical Reflectance (TOR) Carbon Analysis Using a Sunset Carbon Analyzer

Table 10. Inspection criteria for the UC Davis TOA Laboratory.

Item	Frequency	Parameter	Action if Failed	Documentation
Laser Performance	Daily	Initial laser transmittance reading for a clean filter	1) Check for frosted spoon and/or oven 2) Adjust laser or photodetector position to maximize signal	Results are stored in the carbon database and in designated computer files
Instrument Blank	Daily	Compare total carbon (TC) against criteria	1) Check baseline 2) Check oven seal 3) Check gas lines for possible contamination. Contact supervisor or call Sunset tech support if necessary	Results are stored in the carbon database and in designated computer files
Single-point Sucrose Standard	Daily	Compare TC against calculated value	1) Check for system leak or contamination 2) Make new sucrose standard and rerun	Results are stored in the carbon database and in designated computer files
Inter-instrument comparison	Weekly	Compare network replicate pairs and weekly QC PC sample results	1) Check sample for inhomogeneity 2) Rerun a sample punch on a different analyzer 3) Check oven for frosting sign	Results are stored in the carbon database and in designated computer files

Table 11. UC Davis TOA Laboratory maintenance schedule and responsibility.

Item	Frequency	Responsible Party
Carbon analyzer	As needed (daily checks are performed on key components)	Carbon lab supervisor and/or manufacturer (Sunset)
Sucrose standard	semi-annually or as needed	Carbon lab supervisor
Muffle furnace	As needed	Carbon lab supervisor
Sample oven	As needed	Carbon lab supervisor and/or Sunset tech support

5.6.5 HIPS Laboratory

Refer to UCD SOP for details:

UCD CSN SOP #277: Optical Absorption Analysis of PM_{2.5} Samples

Table 12. Inspection criteria for the UC Davis HIPS Laboratory.

Item	Frequency	Parameter	Action if Failed	Documentation
Laser and detector verification	Daily	Transmittance and reflectance detector response to verification set of filters	1) check physical condition of verification filters. 2) Repeat detector registration and reanalyze verification filter set.	Results are stored in the database and in designated computer files
Calibration verification	Daily	Optical absorption depth of reanalysis filter set	1) Repeat detector registration and verification set test. Then reanalyze the reanalysis set filters. 2) Stop analysis, notify lab supervisor and troubleshoot system.	Results are stored in the database and in designated computer files
Long-term reproducibility	Daily	Z-score from reanalysis filter set	1) Repeat detector registration and verification set test. Then reanalyze the reanalysis set filters. 2) Stop analysis, notify lab supervisor and troubleshoot system.	Results are stored in the database and in designated computer files

Table 13. UC Davis HIPS Laboratory maintenance schedule and responsibility.

Item	Frequency	Responsible Party
Instrument maintenance	As needed (daily checks are performed for laser and detectors)	Lab supervisor
State mandated radiation safety checks	Yearly	UC Davis Environmental Health & Safety Department

5.7 Instrument Calibration and Frequency

Instrument calibrations are the responsibility of the respective laboratory supervisors. Calibration results and comments are stored digitally and are accessible by QA personnel. Deficiencies in calibration result are investigated for root causes and communicated to EPA during the regularly scheduled phone calls, monthly reports, and with a corrective action report.

5.7.1 Gravimetric Analysis Laboratory

Instrument calibration and frequency is detailed in the RTI SOP #304-GEN-001: *Standard Operating Procedure for Particulate Matter (PM) Gravimetric Analysis* and included in Section B.7.1 of the RTI Quality Assurance Project Plan (QAPP): *Filter Handling, Acceptance Testing, Gravimetric Analysis, and Ion Chromatography Analysis for Chemical Speciation Network*.

5.7.2 Ion Chromatography Laboratory

Instrument calibration and frequency is detailed in the RTI SOP #Ions1: *Determination of Anions and Cations Extracted from Nylon® Filters by Ion Chromatography (IC)* and included in Section B.7.2 of the RTI QAPP: *Filter Handling, Acceptance Testing, Gravimetric Analysis, and Ion Chromatography Analysis for Chemical Speciation Network*.

5.7.3 EDXRF Laboratory

The PANalytical 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 analyzers.

1. 47 mm MicroMatter thin film foils on Nuclepore membranes, prepared by vacuum deposition.
2. UC Davis generated single-compound standards on 25 and 47 mm PTFE membranes (sulfur, sodium, potassium, chlorine, aluminum, silicon, titanium, vanadium, calcium, chromium, iron, copper, zinc, lead, and cerium).
3. UC Davis generated multi-element standards on 47 mm PTFE membranes.
4. NIST Standard Reference Material (SRM) 2783 air particulate on polycarbonate filter membranes.

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)

Calibration of the Epsilon 5 EDXRF 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 0.98 for elements with stoichiometric standards and reference materials used for calibration. 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 17). The calibration factors (linear regression slope) are stored in the application specific calibration file on the EDXRF computer.

Table 14. Concentration ranges for EDXRF 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	0.088-19.4	Mg	0.025-7.1	Al	0.053-49.5
Si	0.151-32.6	P	0.013-14.5	S	0.105-18.1
Cl	0.5-29.9	K	0.053-26.3	Ca	0.053-7.2
Ti	0.005-50.2	V	0.005-41.5	Cr	0.009-52.8
Mn	0.009-47.6	Fe	0.053-19.6	Co	0.001-50.9
Ni	0.005-20.3	Cu	0.005-42.7	Zn	0.005-17.8
As	0.002-25.2	Se	0.009-48	Br	5.6-19
Rb	0.002-18.3	Sr	0.005-37	Zr	0.005-28.6
Ag	0.009-52	Cd	0.005-28.3	In	15.2-48
Sn	17-50	Sb	0.007-54	Cs	9.4-31.6
Ba	0.013-43.8	Ce	3.41-35.9	Pb	0.018-54

5.7.4 TOA Laboratory

Four types of calibration procedures are required for the TOA instruments (Table 18):

1. End-of-run calibration peak.
2. Daily single-point sucrose calibration check before analysis of network samples.
3. Full instrument calibration, performed every six months or after major instrument repair or after replacement of calibration gas (CH₄/He) cylinder, using sucrose solution at seven different concentration levels.
4. Temperature calibrations performed every six months or after major instrument repair using the manufacturer (Sunset) temperature calibration device.

Table 15. UC Davis TOA laboratory instrument calibrations and frequencies.

Calibration	Calibration Standard and Range	Calibration Frequency	Acceptance Criteria (MQO)	Corrective Action
End-of-Run Internal Calibration Peak Area Check	5 % CH ₄ /He gas standard injected into a fix-volume loop; 20 µg equivalent carbon mass	Every analysis	90-110 % of average calibration peak area of the previous two weeks	Void analysis result; check for system leak; repeat analysis with second filter punch
Single-point Sucrose Calibration Check	10 µL of 1.0525 µg C/ µL Sucrose solution	Daily	Within ± 7 % of the calculated value	Repeat analysis. If same result, run a different sucrose solution to determine if the problem is with the solution or instrument. If former, make new sucrose solution. If latter, perform full 5-point calibration to determine new calibration constant.
Multiple Point Calibrations	10 µL of 0.211 - 10.525 µg C/ µL Sucrose solutions	Every six months or after major instrument repair or change of calibration gas cylinder	R ² ≥ 0.995 linear least-squares fit forced through the origin	Calculate new calibration constant based on calibration slope and update in the parameter file
Temperature Calibrations	Sunset temperature calibration device	Every six months or after major instrument repair	NA	Change the temperature offset values in IMPROVE_A.par files accordingly

5.7.5 HIPS Laboratory

There are no traceable standards for the calibration of optical absorption of aerosols collected on filters. Instead, calibration of the HIPS instrument is performed on the premise that blank PTFE filters have no absorption. Therefore, HIPS can be calibrated by scaling the response of the transmittance and reflectance detectors such that blank filters read zero absorption.

Refer to UC Davis SOP for details:

UCD CSN SOP # 377: CSN Standard Operating Procedure for the Optical Absorption Analysis of PM_{2.5} Samples

To properly scale the raw transmittance (T) and reflectance (R) values so the field blanks have zero absorption, a linear regression must be performed on the field blanks and the coefficients, a_0 (y-intercept) and a_1 (slope), must be determined. This is performed by measuring at least 80 field blanks from the same PTFE filter lot as the samples which are being analyzed. Next, a linear regression of T to R is performed and the coefficients are calculated, which are used for field blank correction of measured samples.

There are many factors which can change the field blank correction coefficients. These include changes to the HIPS system (e.g. replacement of a detector, laser, or optical component, adjusting the alignment of the optics) or changes in the PTFE filter lot or manufacturer. Anytime a change occurs, a set of field blanks of matching PTFE filter material must be analyzed on HIPS and new regression coefficients determined and uploaded to the database.

5.8 Inspection/Acceptance of Supplies and Consumables

5.8.1 Filters

Filters are purchased and inspected by RTI as the filter handling subcontractor. The shipping and handling QAPPs and SOPs can be found at <https://www.epa.gov/amtic/chemical-speciation-network-quality-assurance>.

Quartz filters will be inspected for acceptance, then pre-fired and sent to UC Davis for contamination testing of each pre-fire batch. RTI will review and approve or reject the pre-fire test data. The acceptance criteria for pre-fire contamination is found in RTI document *SHAL3 Standard Operating Procedure for Procurement and Acceptance Testing of Teflon, Nylon, and Quartz Filters*

5.8.2 Reference Materials and Standards

The laboratory manager is responsible for sourcing of critical supplies such as reference materials and standards. Supply sources are governed by University of California acquisition rules and regulations.

5.8.3 Criteria for Other Materials

Deionized water for sucrose generation used in TOA Carbon analysis is purchased from a vendor that arrives with purity certification and expiration date. The water will be used until expiration, when another bottle is procured. Upon receipt of a bottle, a filter is spiked with the deionized water and tested in a

carbon analyzer to verify the results of the certification on our equipment. Section 10 of TI 402H Sucrose Generation has the steps and acceptance criteria.

For other materials, refer to UC Davis and RTI SOPs. The laboratory manager is responsible for ensuring all equipment receives testing, inspection, and maintenance. Spare parts are kept in cabinets alongside their respective instruments. Specific locations are shown to laboratory personnel during training. The laboratory manager is responsible for ensuring spare parts are available when needed.

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 has obtained historical CSN data from AQS for comparison to current data and observed trends. This data has undergone limited inspection to ensure compatibility with software applications.

5.10 Data Management

To manage data flow from sample collection, laboratory analysis, concentration processing, validation, delivery and return from DART, 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 UCD 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 for DART

UCD CSN TI #801E: CSN Data for AQS Delivery

For the electronic records associated with sample archive:

UCD CSN TI #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 (see Section 8 in *UCD CSN TI #801A: CSN Data Ingest* for more information). 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 (see Section 8.4 in *UCD CSN TI #801C: CSN Data Validation* for more information). The comments are marked with the user's ID and a time stamp.

In some cases, it may be necessary to change records during 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 (RTI), the sample date would be changed. This is not enabled through the CSN web application and only the Data & Reporting Manager can authorize these 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, lab blank, or other irregular filter. Filter purposes are assigned by RTI.
2. AQS Null and Informational Flags: 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 flag and up to ten informational or quality assurance qualifier flags.
3. Analysis QC Codes: distinguish 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. Some parameters are provided to DART for informational purposes even though they are not ultimately delivered to AQS.

Additional AQS null and informational flags are automatically applied during data processing and validation based on criteria for specific operational parameters. The following table documents acceptable value ranges for the CSN for operational parameters as well as the acceptable value ranges for data to be successfully submitted to AQS. Outside of these value ranges, an appropriate AQS null or informational flag is applied. Note that the flag application is both flag and case specific; a flag may be applied to a specific parameter(s) from a specific filter or sampling event, multiple parameters, or all parameters. See Section 8.2 in *UCD CSN TI #801C: CSN Data Validation* for more information.

Table 16. List of parameters automatically flagged by UC Davis validation software according to EPA guidelines.

Parameter	URG 3000N	Met One SASS/Super SASS	AQS Flag	Flag Type	URG 3000N	Met One SASS/Super SASS	AQS Flag [†]	Flag Type
	Acceptable Range for CSN				Acceptable Range for AQS			
Average Ambient Temperature	-20 to 45 °C	-30 to 50 °C	QT	Qualifier	-40 to 55 °C	-40 to 55 °C	AN	Null Code
Average Ambient Pressure	600 to 810 mmHg	600 to 810 mmHg	QP	Qualifier	450 to 1000 mmHg	450 to 850 mmHg	AN	Null Code
Sample Flow Rate*	19.8 to 24.2 LPM	6.0 to 7.4 LPM	AH	Null Code	N/A	N/A	N/A	N/A
Sample Flow Rate CV	0 to 2 %	0 to 5 %	AH	Null Code	0 to 20 %	0 to 20 %	AN	Null Code
Sample Volume	28.5 to 34.9 m³	8.6 to 10.6 m³	SV	Null Code	0 to 35 m³	0 to 25 m³	AN	Null Code
Sample Time*	1380 to 1500 minutes	1380 to 1500 minutes	AG	Null Code	N/A	N/A	N/A	N/A

* Specific parameter not reported to DART or AQS.

For more information regarding the data flagging and validation process, please see *UCD CSN SOP #801: Processing & Validating Raw Data*.

5.10.3 Validation of the CDMS

Validation of the CDMS 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 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.

For further details, refer to UCD SOP:

UCD CSN SOP #801: Processing & Validating Raw Data, see Section 10.

5.10.4 Facility Recovery

Refer to UCD SOP for details:

UCD CSN SOP #801: Processing & Validating Raw Data, see Section 9.1.1.

5.10.5 Hardware Recovery

Refer to UCD SOP for details:

UCD CSN SOP #801: Processing & Validating Raw Data, see Section 9.1.2.

5.10.6 Software and Data Recovery

Refer to UCD SOP for details:

UCD CSN SOP #801: Processing & Validating Raw Data, see Section 9.1.3.

5.10.7 Data Security

Refer to UCD SOP for details:

UCD CSN SOP #801: Processing & Validating Raw Data, see Section 9.1.4.

6. ASSESSMENTS AND RESPONSE ACTIONS

UC Davis and RTI 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 AQRC QA Manager will perform periodic technical systems audits (TSA) of the UC Davis activities on a biannual basis. The RTI QA Manager will perform audits at RTI. Every two to three years, the AQRC QA Manager will initiate and participate in external audits of RTI to ensure RTI is meeting the quality system flow down requirements of the prime contract.

External audits of UC Davis and/or RTI activities will also be performed by the EPA – or designated contractor – as determined and communicated by the EPA Program Manager and EPA Quality Assurance Officer.

Audits will cover all aspects of the CSN work, including quality management system, sample receipt, custody, sample analysis, and data reduction and reporting. The audits will include a review of all applicable documentation (QAPP, QMP, and SOPs/TIs) along with verification that the SOPs and TIs 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 20.

Table 17. Types of audits of data quality.

Type of Audit	
UC Davis	RTI
Quality Management System	Quality Management System
Sample receipt & chain of custody	Sample receipt & chain of custody
Elemental analysis (EDXRF)	Ions analysis (IC)
Carbon analysis (TOA)	Data processing, validation, & submittal
Filter Optical Absorption (HIPS)	Sample archiving
Data processing, validation, & submittal	Gravimetry analysis
Sample archiving	

Prior to each audit, a checklist will be prepared, based on this QAPP, the QMP, the SOPs/TIs, and applicable guidance documents. After each audit has been completed, the following post-audit activities will be conducted to document the audit findings and corrective actions following details documented in Section 15.3.3 and Section 15.3.4 of the *EPA Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II* (https://www3.epa.gov/ttn/amtic/files/ambient/pm25/qa/Final%20Handbook%20Document%201_17.pdf):

- A TSA report will be prepared and delivered to the UC Davis Program Manager and UC Davis Principal Investigator (in the case of an audit of UC

Davis) or the RTI Program Manager (in the case of an audit of RTI) within 30 days. The report will include:

- Audit title, number, and any other identifying information;
 - Audit team leaders, audit team participants, and audited participants;
 - Background information about the project, purpose of the audit, dates of the audit, particular measurement phase or parameters that were audited, and a brief description of the audit process;
 - Summary and conclusions of the audit and corrective action requirements; and
 - Attachments or appendices that include all audit evaluations and audit finding forms.
- The organization being audited will have 30 days to respond to the TSA report with comments and/or questions, following which the audit team lead will have 30 days to finalize the TSA report.
 - The organization being audited will respond to the findings documented in the final TSA report within 30 days, providing a corrective action report in official report format (see Section 6.5, Figures 6 and 7) for each finding that documents actions taken, timeline, responsibility, and status.

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 Principal Investigator, the Associate Director of Quality Research, and the AQRC 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 the CSN Annual Quality Report.

6.3 External Quality Assurance Assessments

The UC Davis laboratories will participate in external QA assessments as requested by EPA. The AQRC QA Manager will coordinate and oversee external QA assessments of the RTI laboratories every two to three 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). This is prepared by the data analysis group.

UC Davis will also supply an additional monthly report that summarizes delivery status, corrective actions, and issues identified during the laboratory, validation, or DART review processes. This is prepared by the AQRC Program Manager with help from all departments.
- Quarterly Metadata Reports. UC Davis will prepare quarterly metadata reports to address laboratory changes and any other information that may affect the data reported to AQS. Suspect data points are identified in the UC Davis SQL database, and database queries are used to assess flagged or compromised data. 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. This is prepared by the AQRC Program Manager with help from all departments.
- 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 resultant values along with the associated uncertainties, method detection limits, and sampling metadata. This is done by the data validation team.
- CSN Annual 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. This is prepared by the AQRC Quality Manager with help from all departments.
- Data Archival. All laboratory data records associated with each analysis will be stored and archived for a period of five years following sample analyses. This is done by the sample handling team.

6.5 Corrective Actions

AQRC uses the Nonconformance Report (NR) and Corrective Action Report (CAR) to identify, document, and track the resolution of problems or deviations that impact laboratory processes and/or quality of data. The non-conformance report is used to document routine issues and includes a root-cause and Corrective and Preventative Actions (CAPA) summary. Audit findings are documented in a Non-conformance and escalated to CAR for documentation of the effectiveness check. Both forms work together to document the corrective action process, although not all issues are escalated to CAR status. Besides audit findings, the Quality Manager in discussion with staff decide if an issue needs to be escalated to CAR status, which adds an effectiveness check.

All AQRC staff are aware of the corrective action process through reading of this document and can initiate the process at any time by informing the Quality Manager and relevant Manager of the issue and filling out the documentation. The same forms are used for documenting and responding to Technical System Audit corrective action findings as described in Section 6.1. Any issues that affect data quality will be discussed with the EPA as part of the process.

The Nonconformance and Corrective Action Reports document the name of the initiator, open date, description of finding, cause of the problem, action taken or planned for correction, and effectiveness check (when required). The Quality Manager maintains digital copies of all active and resolved forms. Active/unresolved corrective actions from audits are listed in a table included in the CSN Monthly Report prepared for the EPA by UC Davis. The AQRC QA Manager is included on distribution of the CSN Monthly Report and informs the Program Manager of any changes or updates to status of corrective actions. Corrective actions will be handled in a timely manner per the timeline documented on each Corrective Action Report.

In addition to tracking active/unresolved corrective actions using the Corrective Action Report and CSN Monthly Report, a summary of the past years' corrective actions is documented in the CSN Annual Quality Report prepared for the EPA by UC Davis.

The Principal Investigator, Program Manager, and AQRC QA Manager have the authority to issue stop work orders at any time when deemed necessary to preserve data fidelity. The EPA is informed of corrective actions and status via the Corrective Action Report, CSN Monthly Report, CSN Annual Quality Report, as well as further discussion as needed during regularly scheduled teleconferences between UC Davis and EPA. Any actions that impact delivered data are accompanied by a public data advisory describing the issue, the actions taken, and

the anticipated impacts on the measurement data. Data advisories are posted on the AQRC website.

Figure 6. Nonconformance Report (NR).

AIR QUALITY RESEARCH CENTER		Nonconformance Report		UC Davis AQMT 1560 Drew Ave. Davis, CA 95618	
NR#	Ref #	Open Date			
Status	Audit Finding <input type="checkbox"/>	Review Date			
Severity	Group	Close Date			
Initiated By	Location	Escalations: - -			
Category	Process	Related QC Criteria SOP/TI			
Project <input type="checkbox"/> Improve <input type="checkbox"/> CSN <input type="checkbox"/> Other	Equipment				
	Area Manager				
Affected Item(s) and Time Period			Short Summary		
<Select Project>			<Select Project>		
Batches & QTY					
Sample Dates					
Analysis Dates					
Detailed Description of Findings		Passed Daily QC: <input type="radio"/> Yes <input type="radio"/> No <input type="radio"/> N/A			
Root Cause Summary		Category:			
Impact to Data, Method, & Justification		Impact Category:			
Corrective and Preventative Actions Taken					
SOP(s), TI(s) Updates:					
Selected Disposition(s): Describe the actions taken on flagged filters/data.					
Re-run Analysis	Comparison Study	Invalidate Data	Flag Data	Completion Date:	
-	-	-	-		
Summary and Task List		Approvers		Date	
Extent of Issue: <input type="radio"/> Isolated <input type="radio"/> Systematic		Submitter:			
Elevate to CAR <input type="radio"/> No <input type="radio"/> Yes		Area Manager:			
CAR ID:		Quality:			
Reported Data Impacted <input type="radio"/> No <input type="radio"/> Yes		Funding Agency			
Communicate to Agency <input type="radio"/> No <input type="radio"/> Yes		(if required):			
Method					
Date Sent					
Supplemental Data on Server <input type="checkbox"/> Yes					
Form # F01		Form Revision A04		Date Generated: 8/8/2022	

Figure 7. Corrective Action Report (Escalation of NR).

AIR QUALITY RESEARCH CENTER		Corrective Action Report		UC Davis AQMT 1560 Drew Ave. Davis, CA 95618					
CAR #	Ref #	Open Date							
Status	Audit Finding <input type="checkbox"/>	Review Date							
Severity	Group	Close Date							
Initiated By	Location	Escalations: - -							
Category	Process	Related QC Criteria SOP/TI							
Project <input type="checkbox"/> Improve <input type="checkbox"/> CSN	Equipment								
<input type="checkbox"/> Other		Area Manager							
Affected Item(s) and Time Period			Short Summary						
	<Select Project>	<Select Project>							
Batches & QTY									
Sample Dates									
Analysis Dates									
Please refer to the Reference Document (usually a Nonconformance Report) for documentation of findings, root causes, and corrective and preventative actions.									
Effectiveness Check. Describe what will be done and when.									
Responsible Staff:			Planned Date:						
Result of Effectiveness Check. If unsatisfactory, note results and next steps.									
Effectiveness Check Verified by									
Name:		Position:		Date:					
Result:		SOP Update(s) Verified:							
						Approvers		Date	
						Submitter:			
						Area Manager:			
						Quality:			
Funding Agency (if required):									
<div style="display: flex; justify-content: space-between; font-size: x-small;"> Form # F02 Form Revision A05 Date Printed: 8/8/2022 </div>									

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 exceedances may also trigger a corrective action investigation by the Data & Reporting Manager or AQRC 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, 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 UC Davis 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 UC Davis 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 reanalysis. After all identified issues have been resolved, the data are delivered to DART for review and validation by the SLT validators. Data returned from DART are reviewed for accuracy and consistency, then reformatted for delivery to AQS. For additional detail refer to:

UCD CSN SOP # 801: Processing and Validating the Raw Data

7.1 Validation

Analytical sample results must meet the QC criteria defined in Section 5.5. Analytical sample results that do not initially meet or cannot be brought into control through reanalysis to meet, the QC analytical criteria defined in Section 5.5 are invalidated. UCD is currently developing QC criteria for replicate analysis. For elemental XRF analyses, Cl and Br results for reanalyzed filters will be invalidated. AQS null data qualifier codes are used for qualifying the null analysis results submitted to AQS.

Refer to UCD SOP for details:

UCD CSN TI #801C: CSN Data Validation

7.2 Data Corrections

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

7.2.1 Element Analysis by EDXRF

EDXRF 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 EDXRF 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 Analysis by IC

Artifacts and interferences in the analysis of PM_{2.5} 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 Carbon Analysis by TOA

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

Carbonates and bicarbonates present in some filter samples may cause interference in the TOA 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 CO₂) 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_{2.5} 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*).

7.2.4 Filter Optical Absorption by HIPS

Quality control test samples such as verification and reanalysis filters will be used to detect the existence of abnormalities in the HIPS system. In the event that they occur the most likely remedy will be reanalysis of the affected samples. The primary source of inconsistency in filter optical absorption is due to the scattering properties of PTFE filters during manufacturing. Differences in the reflectance measurement are observable between filter lots. To reduce these inconsistencies, filter lot specific calibrations are 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 RTI will work closely with the EPA to ensure that all required performance characteristics are met.

There will be regular communication between the UC Davis Principal Investigator, UC Davis Program Manager, the EPA Program Manager, the EPA technical leader, and the filter handling contractor (RTI). Communications will include conference calls scheduled monthly 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 UC Davis Principal Investigator. Allowable exceptions include technical discussions with EPA personnel (e.g., to define data delivery formats for AQS) and with RTI personnel for the purpose of coordinating the transfer of samples and data. No one at UC Davis other than the Principal Investigator 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 Principal Investigator.

8. REFERENCES

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9. APPENDIX

9.1 Appendix A: List of RTI SOPs

1. QAPP: Filter Handling, Acceptance Testing, Gravimetric Analysis, and Ion Chromatography Analysis for Chemical Speciation Network
2. SHAL1: Standard Operating Procedure for Sampling Handling and Archiving Laboratory (SHAL) Activities
3. SHAL2: Standard Operating Procedure for Database Operations
4. SHAL3: Standard Operating Procedure for Procurement and Acceptance Testing of Teflon, Nylon, and Quartz Filters
5. SHAL4: Standard Operating Procedure for Honeycomb Denuder Cleaning and Coating
6. SHAL5: Standard Operating Procedures for Data Entry and Monthly Datafile Report Transfers for Sample Handling and Archiving Laboratory (SHAL)
7. SHAL6: Standard Operating Procedure for Leak Testing of Met One Sampling Modules and URG 3000N Sampling Cartridges
8. Ions1: Determination of Anions and Cations Extracted from Nylon® Filters by Ion Chromatography
9. Ions3: Filter Extraction via SimPRep Autodilution System
10. 203-EQP-008: Operation and Maintenance of Dionex Ion Chromatography Systems
11. 100-EQP-004: Calibration, Use and Maintenance of Balances
12. 100-EQP-009: Calibration of Temperature Measuring Devices
13. 100-EQP-007: Refrigerator and Freezer Monitoring, Maintenance and Operation with Storage Condition Definitions
14. 100-EQP-020: Receipt, Storage and Tracking of Analysis Samples for Trace Inorganics Metals Gravimetric Calibration Verification and Maintenance of Liquid Dispensing Devices
15. 304-GEN-001: Standard Operating Procedure for Particulate Matter (PM) Gravimetric Analysis

9.2 Appendix B: List of UC Davis SOPs

1. UCD SOP #277: Optical Absorption Analysis of PM_{2.5} Samples
 - UCD TI #277A: Preparation of HIPS Analysis
 - UCD TI #277B: Performing HIPS Analysis
 - UCD TI #277C: Quality Assurance/Quality Check of Analysis of PM_{2.5} Loaded Filters Using Hybrid Integrating Plate/Sphere (HIPS) Method for Measuring Light Absorption
 - UCD TI #277si: Hardware Specifications of the HIPS System
2. 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 #302C: Sample Changes for 8-Position Trays
 - UCD TI #302D: Quality Assurance/Quality Checks (QA/QC) of XRF Performance
3. UCD SOP #402: Thermal/Optical Reflectance (TOR) Carbon Analysis Using a Sunset Carbon Analyzer
 - UCD TI #402B: Carbon Analysis Daily Operation
 - UCD TI #402C: Gas Cylinder Change
 - UCD TI #402D: Troubleshooting
 - UCD TI #402E: Instrument Startup and Shutdown
 - UCD TI #402F: Main Oven Temperature Calibration
 - UCD TI #402G: Punch Certification
 - UCD TI #402H: Sucrose Generation
 - UCD TI #402I: Flow Sensor Calibration
 - UCD TI #402J: Quartz Filter Pre-Fire Acceptance Testing
 - UCD TI #402K: Sunset Autoloader
4. 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 for DART
 - UCD TI #801E: CSN Data for AQS Delivery

- 5. UCD SOP #901: Long-Term Archiving of Filters
 - UCD TI #901A: Long-Term Archiving of Filters
- 7. UCD SOP #903: Sample Tracking and Storage
- 8. UCD SOP #904: Receiving and Inventorying of CSN Samples
 - UCD TI #904A: Receiving and Inventorying of CSN Quartz Samples
 - UCD TI #904B: Receiving and Inventorying of CSN Teflon Samples