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Quality Assurance Project Plan
Chemical Speciation of $PM_{2.5}$ Filter Samples

Prepared for:

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

EPA Contract No. EP-D-09-010

Prepared by:

RTI International*
P.O. Box 12194
3040 Cornwallis Road
Research Triangle Park, NC 27709

* *RTI International is a trade name of Research Triangle Institute.*

A.1 QA Project Plan Identification and Approval

Quality Assurance Project Plan

Chemical Speciation of PM Filter Samples

Prepared for:

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

Approvals:

Margaret Dougherty — 3/12/2014

EPA/OAQPS
Project Officer
Margaret Dougherty

Date

Dennis W. Crumpler — 3/12/2014

EPA/OAQPS
Quality Assurance Officer
Dennis Crumpler

Date

R. K. M. Jayanty — 1-27-2014

Research Triangle Institute
Program Manager
R. K. M. Jayanty

Date

1/27/2014

Research Triangle Institute
Quality Assurance Manager
Prakash Doraiswamy

Date

A.2 Table of Contents

Section **Page**

A.1 QA Project Plan Identification and Approval....2
A.2 Table of Contents....3
A.3 Distribution....7
A.4 Project/Task Organization....7
A.4.1 Key Personnel....9
A.4.1.1 Program Manager and Administrative Program Coordinator....9
A.4.1.2 QA Manager....10
A.4.2 Analytical Subcontractors....10
A.4.2.1 CHESTER LabNet....10
A.4.2.2 Desert Research Institute....11
A.5 Problem Definition/Background....12
A.6 Project/Task Description....14
A.6.1 Schedule....14
A.6.2 Sample Types and Quantities....14
A.7 Quality Objectives and Criteria for Measurement Data....15
A.7.1 Data Quality Objectives Process....15
A.7.2 Quality Objectives for Total Measurement Error....16
A.7.3 Measurement Quality Objectives....18
A.7.4 References....19
A.8 Special Training Requirements/Certification....20
A.8.1 Current Personnel....21
A.8.2 Summary of Experience and Training....24
A.8.3 New Personnel....26
A.9 Documentation and Records....27
A.9.1 QA/QC Records....27
A.9.2 SHAL Records....28
A.9.3 Analytical Laboratories' Records....29
A.9.4 Gravimetric Mass Laboratory Records....29
A.9.5 XRF Laboratory Records....30
A.9.6 IC Laboratory Records....31
A.9.7 OC/EC Laboratory Records....31
A.9.8 Denuder Refurbishment Laboratory Records....32
B.1 Sampling Process Design (Experimental Design)....33
B.2 Sampling Methods Requirements....33
B.3 Sample Handling and Custody Requirements....33
B.3.1 Sample Handling Delivery Order Process....33
B.3.2 Chain of Custody....35
B.3.3 Processing System for PM Chemical Speciation Modules....35
B.3.3.1 Assembly of Sampling Modules....39
B.3.3.2 Shipping to and from the Field....39
B.3.3.3 Disassembly of Sampling Modules....41
B.3.3.4 Internal Tracking of Analytical Samples....41
B.3.3.5 Archiving of Filters and Extracts....41
B.3.3.6 Denuder Preparation....43

B.4 Analytical Methods Requirements 44
B.4.1 Gravimetric Mass Determination 44
B.4.2 EDXRF Analysis for Elements 44
B.4.3 Extraction and Analysis of Anions and Cations 45
B.4.4 Carbon Analysis 45
B.4.5 Semivolatile Organic Compounds 46
B.4.6 Characterization of Particles by Electron and Optical Microscopy 46
B.4.6.1 Scanning Electron Microscopy 46
B.4.6.2 Optical Microscopy 47

B.5 Quality Control Requirements 48
B.5.1 Quality Criteria for Gravimetric Analyses 48
B.5.1.1 Gravimetric Disaster Recovery Plan 49
B.5.2 Quality Criteria for Ion Analysis 49
B.5.2.1 Ion Disaster Recovery Plan for Data 50
B.5.3 Quality Criteria for EDXRF 50
B.5.3.1 RTI 50
B.5.3.2 CHESTER LabNet 51
B.5.4 Quality Criteria for RTI OC/EC Analysis 52
B.5.4.1 RTI OC/EC Lab Disaster Recovery Plan for Data 55
B.5.5 Quality Criteria for Denuder Refurbishments 55
B.5.6 Uncertainty Determination 56
B.5.7 Method Detection Limits 57

B.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements 57
B.6.1 Gravimetric Mass Laboratory 57
B.6.2 Ion Chromatographic Laboratory 58
B.6.3 EDXRF Laboratory 59
B.6.3.1 RTI 59
B.6.3.2 CHESTER LabNet 60
B.6.4 ICP/MS Laboratory 60
B.6.5 Organic/Elemental Carbon (OC/EC) Laboratory 62
B.6.5.1 RTI OC/EC Laboratory 62
B.6.5.2 DRI OC/EC Laboratory 62

B.7 Instrument Calibration and Frequency 63
B.7.1 Gravimetric Mass Laboratory 63
B.7.2 Ion Chromatography Laboratory 63
B.7.3 EDXRF Laboratory 63
B.7.3.1 RTI 64
B.7.3.2 CHESTER LabNet 65
B.7.4 OC/EC Laboratories 65
B.7.4.1 RTI OC/EC Laboratory 65
B.7.4.2 DRI OC/EC Laboratory 66

B.8 Inspection/Acceptance Requirements for Supplies and Consumables 67
B.8.1 Filters 67
B.8.1.1 Teflon Filters 68
B.8.1.2 Nylon Filters 68
B.8.1.3 Quartz Filters 68
B.8.2 Criteria for Other Materials 69

B.9 Data Acquisition Requirements (Non-direct Measurements) 69

B.10 Data Management 69
B.10.1 Overview 70
B.10.2 DMS Design Features 70
B.10.2.1 Sample Identifiers 70

B.10.2.2 Barcode Scanners 71
B.10.2.3 Relational Integrity 71
B.10.2.4 Double Entry of Field Data 71
B.10.2.5 Direct Transfer of Laboratory Data 71
B.10.2.6 Training and Development Databases 72
B.10.2.7 Database Backup and Recovery 72
B.10.3 Automated and Semi-Automated QC Limit Checks for Outlier Detection 72
B.10.4 Report Preparation and QA Screening 74
B.10.4.1 Data Set Completeness and Integrity 74
B.10.4.2 Entry and Verification of Data Changes from the States 75
B.10.5 AQS Data Entry 75
B.10.6 Data Management in the Laboratories 80
B.10.7 Management and Reporting of Field Audit Data 80
C.1 Assessments and Response Actions 81
C.1.1 External Quality Assurance Assessments 81
C.2 Reports to Management 83
D.1 Data Review, Validation, and Verification Requirements 85
D.2 Validation and Verification 85
D.2.1 Level 0 Validation 85
D.2.2 Level 1 Validation 86
D.2.3 Screening of Subcontractor Data 86
D.2.4 Data Corrections 87
D.2.4.1 Mass 87
D.2.4.2 Elemental Analysis 87
D.2.4.3 Ions 87
D.2.4.4 OC/EC 87
D.2.4.5 SVOCs 87
D.3 Reconciliation With User REquirements 85
Appendix 1 Uncertainty Calculations 90
Appendix 2 Method Detection Limits 94

List of Tables

Table **Page**

Table A.3.1. QAPP Distribution List 7
Table A.4.1. Personnel Responsibilities and Lines of Communication 8
Table A.6.1. Families of SVOCs to be Quantitated by GC/MS Methodologies 12
Table A.6.2. Sample Quantities for Base Period January 8, 2009 through January 7, 2010 15
Table A.7.3. Recommended MQOs for Total Measurement Error 16
Table A.7.4. Laboratory MQOs 18
Table A.9.1. Management Records 27
Table A.9.2. QA/QC Records 27
Table A.9.3. SHAL's Records 28
Table A.9.4. Analytical Laboratories' Records 29
Table A.9.5. Gravimetric Mass Laboratory Records 29
Table A.9.6. XRF Laboratory Records 31
Table A.9.7. IC Laboratory Records 31
Table A.9.8. OC/EC Laboratory Records 32
Table B.3.1. Sampler Component and Laboratory Speciation Analysis Matrix 40
Table B.4.1. Carbon Fractions Reported 47
Table B.5.1. QC Criteria for Ion Chromatography (Anions and Cations) 50

Table B.5.2. RTI QC Procedures to Analyze EDXRF Elements....51
Table B.5.3. CHESTER LabNet's QC Procedures Used to Analyze EDXRF Elements....51
Table B.5.4a. QC Criteria for OC/EC Analysis by CSN/TOT and IMPROVE_A/TOR-TOT Methods in RTI's OC/EC Laboratory....52
Table B.5.4b. QC Criteria for OC/EC Analysis by IMPROVE_A/TOR-TOT Methods in DRI's OC/EC Laboratory....54
Table B.5.5. QC Criteria for Denuder Refurbishments....56
Table B.6.1. Inspection Criteria for Gravimetric Mass Laboratory....57
Table B.6.2. Gravimetric Mass Laboratory Maintenance Schedule and Responsibility....58
Table B.6.3. Inspection Criteria for Ion Analysis Laboratory....58
Table B.6.4. Ion Analysis Laboratory Maintenance Schedule and Responsibility....59
Table B.6.5. Inspection Criteria for RTI EDXRF Laboratory....59
Table B.6.6. RTI EDXRF Laboratory Maintenance Schedule and Responsibility....60
Table B.6.7. Inspection Criteria for CHESTER LabNet EDXRF Laboratory....60
Table B.6.8. CHESTER LabNet XRF Laboratory Maintenance Schedule and Responsibility....60
Table B.6.9. Elements to be Analyzed by ICP/MS....61
Table B.6.10. Quality Control Activities for ICP/MS Analysis Sequences....62
Table B.6.11. OC/EC Laboratory Maintenance Schedule and Responsibility....62
Table B.6.12. OC/EC Laboratory Maintenance Schedule and Responsibility....63
Table B.7.1. Elements Present on Micromatter, Co. Standard....64
Table B.7.2. Certified Values of Elements Present on NIST Standard Reference Material No. 1832....65
Table B.7.3. RTI OC/EC Instrument Calibration and Frequency....66
Table B.7.4. DRI OC/EC Instrument Calibration and Frequency....67
Table B.10.1. Label Identifiers for Tracking CSN Records and Equipment....71
Table B.10.2. Statistical Validation Limits for Routine Data....73
Table B.10.3. Statistical Validation Limits for Blanks....73
Table B.10.4. Mapping of Outlier Flags onto AQS Codes....74
Table B.10.5. Automated Checks Based on Fixed Criteria....74
Table B.10.6. Analytes and AQS Parameter Codes ($PM_{2.5}$ Only)....76
Table B.10.7. Field Data and AQS Parameter Codes....78
Table B.10.8. AQS Validity Status Codes....78
Table B.10.9. AQS Null Value Codes....79

List of Figures

Figure **Page**

A.4.1. Schematic of RTI's team members and organization for the chemical speciation of $PM_{2.5}$ filter samples....8
B.3.1. Overview of sample handling and custody system.....34
B.3.2. Diagram of RTI filter processing and analysis activities by filter type (arrangement may vary by sampler model)....37
B.3.3. Movement of filters and extracts through RTI and subcontractor laboratories.....38
B.3.4. RTI Laboratory COC form used in tracking.....42

A.3 Distribution

Upon finalization, controlled copies of this Quality Assurance Project Plan (QAPP) will be distributed in hard copy to the individuals listed in **Table A.3.1.** The latest version of each Standard Operating Procedure (SOP) will also be available at the laboratory where it is used. The Quality Assurance (QA) Manager will oversee control and update of the QAPP and SOPs.

Table A.3.1. QAPP Distribution List

Copy Number	Recipient Name	Position	Organization
1	M. Dougherty	Project Officer	U.S. EPA/OAQPS
2	E. Landis	Technical Project Manager	U.S. EPA/OAQPS
3	D. Crumpler	Quality Assurance Officer	U.S. EPA/OAQPS
4	P. Schraufnagel	Delivery Order Project Officer	U.S. EPA/Region 5
5	J. Rickard	Delivery Order Project Officer	U.S. EPA/Region 8
6	L. Hyden	Delivery Order Project Officer	U.S. EPA/Region 3
7	J. Elkins	EPA Quality Assurance Laboratory Director	U.S. EPA
8	R.K.M. Jayanty	Program Manager	RTI/TIE
9	D.M. Haas	Administrative Coordinator	RTI/TIE
10	P. Doraiswamy	Quality Assurance Manager	RTI/TIE
11	J.A. O'Rourke*	SHAL Technical Area Supervisor	RTI/TIE
13	P. Presler-Jur*	Gravimetric Mass Technical Area Supervisor	RTI/TIE
14	E.D. Hardison*	Ions Analysis Technical Area Supervisor	RTI/TIE
15	E.E. Rickman*	Data Management Technical Area Supervisor	RTI/TIE
16	A.C. McWilliams*	Elemental Analysis Technical Area Supervisor	RTI/TIE
17	J. Nichol*	Carbon Analysis Technical Area Supervisor	RTI/TIE
18	F.X. Weber*	ICP-MS Technical Area Supervisor	RTI/TIE
19	R. Tropp*	DRI Quality Assurance Manager	DRI
20	P. Duda*	CHESTER LabNet Quality Assurance Manager	CHESTER LabNet

* Individuals responsible for maintaining current SOPs at laboratory stations where procedures are performed.

A.4 Project/Task Organization

This QAPP describes quality planning for contract number EP-D-09-010 with the U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS). Work on this contract in support of the PM Chemical Speciation Network (CSN) program is performed by staff from RTI International's Environmental and Industrial Sciences Division (EISD), which is a component of the Discovery and Analytical Sciences. CHESTER LabNet, a subcontractor to RTI, and RTI will perform x-ray fluorescence (XRF) analysis. Desert Research Institute (DRI), another subcontractor to RTI, will perform organic/elemental carbon (OC/EC) analysis using the same method that is used in the Interagency Monitoring of Protected Visual Environments (IMPROVE) program: and semivolatile organic compounds (SVOC), and

optical density (OD) analysis on selected filters. Sound management requires a clear understanding of the roles, functions, and assignments of each position within the project structure. **Figure A.4.1** shows RTI's team members. **Table A.4.1** shows the responsibilities and lines of communication for each of the positions on this program.

Figure A.4.1. Schematic of RTI's team members and organization for the chemical speciation of $PM_{2.5}$ filter samples.

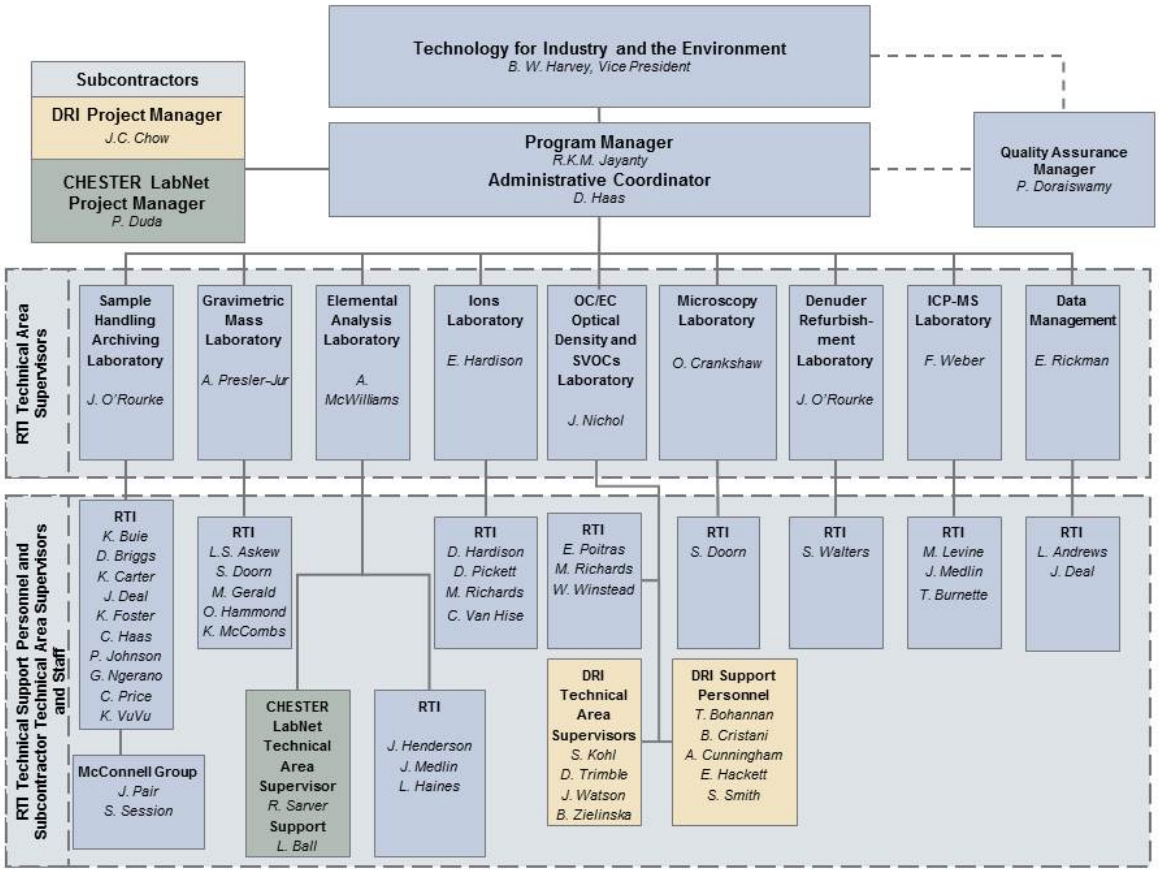


Table A.4.1. Personnel Responsibilities and Lines of Communication

Position	Responsibilities	Lines of Communication
Program Manager R. K. M. Jayanty	Accountable to corporate management for successful accomplishment of the project objectives.	Supervises project. Coordinates project activities with client and subcontractors. Reports to Vice President Bruce Harvey.
QA Manager Prakash Doraiswamy	Responsible for monitoring all aspects of QA/QC.	Reports to Program Manager. Works closely with technical area supervisors and staff. Performs peer-to-peer coordination with subcontractor QA staff.

Position	Responsibilities	Lines of Communication
Technical Area Supervisors Owen Crankshaw Paige Presler-Jur Eva Hardison Andrea McWilliams James O'Rourke Jeffrey Nichol Edward Rickman Frank Weber	Responsible for maintaining technical quality, data handling and transfer, and identifying and resolving technical problems. Responsible for staff training and assessment.	Reports to Program Manager. Works closely with technical staff and QA Manager.
Technical Staff	Performs technical tasks.	Interacts with other team members. Reports to Technical Area Supervisors.
CHESTER LabNet Paul Duda, Project Manager Rick Sarver Lisa Ball Emmely Briley Jess Mace	Responsible for receiving samples from RTI, performing XRF analyses, maintaining technical quality, data handling and transfer, and identifying and resolving technical problems for staff training and assessment.	Reports to RTI Program Manager.
DRI Judy Chow, Project Manager Barbara Zielinska, SVOC Dana Trimble, OC/EC R. J. Tropp J. G. Watson	Responsible for receiving samples from RTI, performing OC/EC by IMPROVE method and SVOC analysis on selected filters, maintaining technical quality, data handling and transfer, and identifying and resolving technical problems for staff training and assessment.	Reports to RTI Program Manager.

RTI coordinates its laboratory support activities with EPA/OAQPS and with the State, Local, and Tribal (SLT) agencies. Lab QA auditing and technical assistance are provided by EPA/ORIA as described in the Field QAPP (Quality Assurance Project Plan: PM2.5 Chemical Speciation Sampling at Trends, NCore, SLAMS, and Tribal Sites, USEPA/OAQPS, October 2011), Sections 4.0 and 4.3.2, and Figure 4-1.

A.4.1 Key Personnel

A.4.1.1 Program Manager and Administrative Program Coordinator

The CSN program is led by Dr. R. K. M. Jayanty, who provides overall supervision to ensure that the technical program is being performed in accordance with the EPA statement of work and according to this QAPP.

The RTI Program Manager's responsibilities include:

1. Maintaining cooperative working relationships with the EPA Project Manager, Delivery Order Project Officer (DOPO), and QA Manager in the following ways:

   Conference calls to be held biweekly initially, or as frequently as needed
   Meetings with EPA staff in RTP on an as-needed basis
   Written communications and e-mails to document planning and decisions
2. Facilitating interaction among team personnel
3. Ensuring that proper techniques and procedures are followed

4. Ensuring that reporting requirements are satisfied
5. Maintaining cost and schedule control
6. Adjusting schedules to meet the needs of the client
7. Reviewing and approving deliverables submitted to the client.

Ms. Diane M. Haas is the Administrative Program Coordinator for the CSN program and is responsible for financial and other project coordination activities within RTI.

A.4.1.2 QA Manager

Dr. Prakash Doraiswamy is the RTI QA Manager for this project. For the purposes of this project, he will report to Mr. Bruce Harvey, TIE Vice President, and to Dr. Jayanty, the Program Manager. Dr. Doraiswamy will monitor quality assurance/quality control (QA/QC) for the project. Dr. Doraiswamy and selected staff members will investigate problems and recommend corrective actions, perform periodic in-lab and data review audits, host external auditors during anticipated visits, and distribute EPA-provided Performance Evaluation (PE) samples and summarize the results of analysis of PEs.

A.4.2 Analytical Subcontractors

RTI has engaged CHESTER LabNet as a subcontractor to provide limited energy dispersive x-ray fluorescence spectroscopy (EDXRF) services for this program. RTI has also engaged DRI as a subcontractor for OC/EC analysis by the IMPROVE_A method, and SVOC analysis, and determination of OD on selected filters.

All subcontractor laboratories providing analytical services for this program have contributed to this project-specific QAPP and must provide their SOPs for EPA approval. If requested by EPA, subcontractors will undergo technical systems audits of their facilities and will analyze EPA-provided PE samples. RTI will maintain standards and document comparability of laboratories performing the same analyses through an intercomparison program for each type of analysis. Calibration check samples from the same source will be analyzed by both laboratories. The RTI XRF laboratory coordinates a filter reanalysis program in which selected filters are reanalyzed by the participating XRF laboratories (currently just RTI and Chester Labnet). Intercomparison results are summarized in annual quality assurance data reports. Subcontractors are also required to provide input for the quarterly metadata reports and the annual quality assurance data report.

The capabilities of each subcontractor are briefly outlined in the following subsections.

A.4.2.1 CHESTER LabNet

RTI will send XRF samples to CHESTER LabNet as long as CHESTER LabNet demonstrates that it can meet the quality, sample turnaround, and cost requirements for this program. The initial throughput capacity using the CHESTER LabNet Kevex 770 XRF for Protocol #6 was 25 samples per day. To boost productivity, CHESTER LabNet purchased a second Kevex XRF, numbered 771. Samples were analyzed on both the 770 XRF and the 771 XRF to test for equivalency, and a report titled “Tests of Equivalency for Two XRF Instruments Operated by CHESTER LabNet,” which showed acceptable equivalency of the two XRFs, was submitted to EPA and approved. With these two approved instruments, CHESTER LabNet has a

total capacity of approximately 50 samples per day. CHESTER LabNet has purchased a third Kevex XRF for serving its other clients, but this instrument is not used for CSN analyses because no equivalency study has been performed.

RTI and Chester obtain their calibration standards from the same supplier (Micromatter Co). Both labs analyze a multi-element standard that is prepared by Micromatter, containing Si, Ti, Fe, Se, Cd, and Pb at levels of 5-10 $\mu g/cm^2$. The multi-element standard is analyzed with each tray of samples.

A.4.2.2 Desert Research Institute

The Desert Research Institute is the nonprofit research campus of the University and Community College System of Nevada (UCCSN). The main campuses are located in Las Vegas, NV (Southern Nevada Science Park) and Reno, NV (Dandini Research Park), with subsidiary campuses in Boulder City, NV, and Steamboat Springs, CO. DRI's environmental research programs are directed from three core divisions (Atmospheric Sciences, Earth and Ecosystem Sciences, and Hydrologic Sciences) and two interdisciplinary centers (the Center for Arid Lands Environmental Management and the Center for Watersheds and Environmental Sustainability). DRI's analytical capabilities on this program are described below.

IMPROVE_A OC/EC Analysis for URG 3000N Filter Samples

RTI has subcontracted with DRI to provide OC/EC analysis for filter samples obtained using the URG 3000N sampler following the same method as currently employed by the IMPROVE program. This analytical protocol, known as IMPROVE_A, was developed by DRI using the DRI Model 2001 Thermal/Optical Carbon Analyzer (manufactured by Atmoslytic, Calabasas, CA) and was placed in service on the IMPROVE program beginning January 1, 2005. The method is based on the technical requirements given in DRI's SOP. RTI and DRI have defined data transfer formats and procedures and have developed an SOP for IMPROVE OC/EC analysis.

The DRI Model 2001 analyzer used by DRI consists of essentially the same components as the Sunset Laboratory instrument used by RTI, although the configuration is quite different. The basic components of the system include a sample oven fitted with a laser-photodiode sensor, an oxidizer oven, a methanator, a flame ionization detector (FID), other components used to control oven temperature and gas composition and flows, and a computer workstation running software through which analysis parameters are controlled and data from the FID, photodiode sensor, and oven thermocouples are collected. All carbon volatilized from the filter is converted to CO_2 in the oxidizer, and the CO_2 is converted to methane (CH_4) in the methanator before passing into the FID, where it is measured. The laser is used to track and correct for the pyrolysis of OC that occurs during the inert combustion phase. The laser shines on the quartz filter section in the oven, and some of the light is reflected or scattered back onto a photodiode located on the same side of the filter and some of the light is transmitted through the filter. The laser-photodiode sensors are used to monitor reflectance and transmittance of laser light from the filter section during analysis.

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

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

Semivolatile Organics Compound Analysis

RTI has subcontracted with DRI to provide SVOC analysis on selected filter samples. DRI will analyze selected quartz fiber or Teflon filters and back-up sorbent traps for semi-volatile organic aerosol compounds using an extraction procedure that can accommodate multiple filters. DRI will extract semivolatile organic aerosol compounds from the filters and back up sorbent traps. The families of semi-volatile organic compounds (target analytes) to be quantitated for routine analysis are given in **Table A.6.1.** When requested, several filters may be combined for extraction to yield a more concentrated extract solution. Extracts will be analyzed for semi-volatile organic aerosol compounds using gas chromatography/mass spectroscopy (GC/MS) methodology. All analytical runs will be supported by QC analyses including replicate analyses. Sample extracts will be stored at DRI for at least 6 months and up to the life of the contract as requested by EPA.

Table A.6.1. Families of SVOCs to be Quantitated by GC/MS Methodologies

Family	Examples
n-alkanes	n-tricosane, n-tetracosane, n-pentacosane
iso-alkanes	Iso-hentracontane, iso-dotracontane
anteiso-alkanes	anteiso-triacontane, anteiso-hentriacontane
alkenoic acids	Cis-9-n-octadecenoic acid
aldehydes	nonanaldehydes
levoglucosan	levoglucosan
Polycyclic aromatic hydrocarbons	numerous
hopanes and steranes	numerous

Optical Density

RTI has subcontracted with DRI to provide OD (also known as "black carbon") analysis on selected filter samples. DRI will analyze selected Teflon filters for OD as described by Watson and Chow (1988). The densitometer used for the analysis is similar to the integrating plate method used by photographers to evaluate black-and-white negatives. Transmittance is measured before and after filter exposure, and the difference in the logarithms of the transmitted light is proportional to the absorption of the particle deposit. Transmittance is standardized using photographers' neutral-density filters that are commonly used for light attenuation in camera lenses and photographic enlargers. A high correlation between OD and IMPROVE EC has been found.

A.5 Problem Definition/Background

In 1997, the EPA promulgated the new National Ambient Air Quality Standards (NAAQS) for particulate matter (PM). The regulations (given in 40 CFR Parts 50, 53, and 58) apply to the mass concentrations (:g/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 $PM_{2.5}$ standard). To support these standards, a 1500-site mass

measurements network and a smaller $PM_{2.5}$ Chemical Speciation Network (CSN) were established. Gravimetric mass and chemical speciation analyses will also be performed for PM_{10} and coarse PM as part of the NCore program and for research studies as part of the CSN contract. Coarse PM, total mass and individual chemical species, will be determined either as PM_{10} minus $PM_{2.5}$ ($PM10_{-2.5}$) based on separate PM_{10} and $PM_{2.5}$ filter samples, or as coarse PM obtained by dichotomous sampling.

The ambient air data from the network, which measures solely the mass of particulate matter, are used for NAAQS comparison purposes in identifying areas that meet or do not meet the NAAQS criteria and in supporting designation of an area as attainment or non-attainment. The CSN consists of a set of core sites and additional non-core sites. Chemically speciated data are used to serve needs associated with development of emission mitigation approaches to reduce ambient PM concentration levels. Such needs include emission inventory establishment, air quality model evaluations, and source attribution analysis. Other uses of the data sets will be regional haze assessments, estimating personal exposure to PM and its components, evaluating potential linkages to health effects, and support for setting a secondary NAAQS for PM.

RTI supports the CSN by shipping ready-to-use filter packs and denuders to the field sites and by conducting gravimetric and chemical analyses of the several types of filters used in the samplers. This QAPP focuses on the QA activities associated with RTI's role in filter scheduling and distribution, performing the filter analyses, and validating and reporting the data.

Prior to operation of the core and additional sites, EPA ran a prototype network, informally known as the "mini-trends" network, in early 2000. This network was comprised of 13 monitoring stations in the continental U.S. Each site had two or more $PM_{2.5}$ chemical speciation monitors to enable various sampler intercomparisons. The mini-trends network ran from February 2000 to August 2000. RTI is currently supporting approximately 180 sites.

Beginning in May 2007, the CSN began operation of 57 URG 3000N samplers, which are used to obtain samples on quartz filters that are comparable to those being sampled by the IMPROVE network. The filter samples obtained using the 3000N sampler are analyzed by the IMPROVE_A method by subcontractor DRI. Outfitting the remaining sites in the CSN with URG 3000N samplers was complete in FY10. Sampling of quartz filters on the MetOne SASS sampler and analysis by the CSN method continued past the end of FY10 to support an intercomparison special study being conducted by EPA. Legacy CSN sampling and analysis also continued into 2011 at a small number of sites at the request of the air agencies.

Beginning with the laboratory contract that began in 2009, gravimetric and chemically speciated measurements were added for PM_{10} and coarse PM filters. The XRF method was modified to omit 15 rarely seen elements, and several new measurements were incorporated, including, for selected filters, inductively coupled plasma/mass spectrometry (ICP/MS), SVOC analysis, and optical density (OD); as well as determination of gas phase ammonia, nitric acid, and SO_2 using denuder technology.

A.6 Project/Task Description

The CSN laboratory contract involves four broad areas:

1. Supplying each site or monitoring agency with sample collection media (loaded filter packs and, when ordered, denuders) and field data documentation forms. RTI will ship the collection media to the sites or other designated locations specified by the monitoring agencies on a schedule specified by the DOPO.

2. Receiving the samples from the field sites and analyzing the sample media for mass and for an array of chemical constituents including elements (by EDXRF), soluble anions and cations, and carbonaceous species. Analysis of SVOCs, OD, gas-phase ammonia, ICP/MS, and examination of particles by electron or optical microscopy will be provided for selected samples.

3. Assembling validated sets of data from the analyses, preparing data reports for EPA management and the states, and entering data into the AQS data bank 60 days after initial data reports are first submitted to the DOPO and the states.

4. Establishing and applying a comprehensive QA/QC system. RTI's Quality Management Plan, this QAPP, and associated SOPs provide the documentation for RTI's quality system.

RTI will provide all the staff, facilities, analytical instrumentation, computer hardware and software, and consumable supplies necessary to carry out tasks from these work areas and will ensure that all contractual specifications are met.

A.6.1 Schedule

The present contract period extends from January 26, 2009 to January 25, 2014.

A.6.2 Sample Types and Quantities

Table A.6.2 shows the number of samples for the base period (January 26, 2009 through January 25, 2010) that were specified in RTI's contract with EPA/OAQPS. Similar quantities have been received in subsequent contract years, and this level of activity is expected to continue for the remainder of the contract unless program funding is reduced.

Table A.6.2. Sample Quantities for Base Period January 8, 2009 through January 7, 2010

Line Item	Description	Each	No. Samples
0001	$PM_{2.5}$ Gravimetric Mass	Each	100
0002	Elemental Analysis by EDXRF	Each	100
0003	Sulfate, Nitrate, Ammonium, Water-Soluble Sodium and Potassium	Each	100
0004	Magnesium Oxide/SC Denuder	Each	60
0005a	Organic, Elemental, and Total Carbon (CSN)	Each	5,850
0005b	Organic, Elemental, and Total Carbon (IMPROVE)	Each	13,650
0006	Suite 1-3	Each	19,500
0007	Ammonia Analysis and Denuder Refurbishment	Each	250
0008	Nitric Acid and SO2 analysis and Denuder Refurbishment	Each	100
0009	Semivolatile Organic Aerosol Analysis	Each	10
0010	Electron Microscopy Analysis	Each	50
0011	Optical Density Analysis	Each	10
0012	Organic Denuder Refurbishment	Each	50
0013	Elemental Analysis by ICP/MS	Each	100

A.7 Quality Objectives and Criteria for Measurement Data

A.7.1 Data Quality Objectives Process

The data quality objectives (DQO) process is a strategic planning approach used to prepare for a data collection activity in order 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 that allow an experimental design to be developed to meet decision criteria specified by stakeholders in the decision, as described in EPA QA/G-4, *Guidance for the Data Quality Objectives Process* (EPA, 1994).

A Chemical Speciation DQO Workgroup was established to develop and document DQOs for the $PM_{2.5}$ CSN. The primary DQO, detection of trends in the chemical speciation data, was defined as follows by participants in the EPA workgroup, who acted as stakeholders for the program, see: http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/dqo3.pdf .

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

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:

- Model evaluation, verification, and/or validation
- Emission inventory

- Source attribution
- Spatial and seasonal characterization of aerosol distributions
- 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.

A.7.2 Quality Objectives for Total Measurement Error

The DQO study also concluded that with sampling every third day for 5 years, trends greater than 5% (or less than –5%) per year can be detected for sulfate, calcium, and total carbon on a single-site basis. For nitrate, however, the annual trend must exceed ±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 5 years.

The Speciation Strategic Plan (U.S. EPA 1999b) quotes Measurement Quality Objectives (MQOs) for the overall measurement process that must be achieved in order to meet the DQO for trend detection. These MQOs, which should be interpreted as the total coefficient of variation (CV) attributable to sampling and analysis, are summarized in **Table A.7.3.** Analysis of the IMPROVE data and the model indicated that reduction of measurement errors below levels shown in this table is unlikely to result in any significant improvement in the ability to detect a trend within the parameters specified in the DQO statement. Note that there is no MQO-specified bias. In terms of completeness, the trend detection model was found to be relatively insensitive to sampling interval as long as approximately 1-in-3-day sampling is achieved. Thus, 1-in-3-day sampling was implemented at the original trends sites.

Table A.7.3. Recommended MQOs for Total Measurement Error

Analysis	MQO for Total Measurement Error (expressed as % CV)
Ions (anions and cations) by IC	10%
Total Carbon by TOR	15%
Elements by EDXRF	20%

Source: U.S. EPA 1999b

Total measurement error corresponding to the values given in Table A.7.3 may be estimated by combining individual components of random error using QC data collected by the laboratories and in the field. However, the best way to determine total error of measurement for comparison with the target MQOs given in Table A.7.3 is by statistical analysis of data from sites that operate collocated monitors. Estimates based on results from six CSN sites where collocated samplers are operated are included in the Annual Data Summary Reports.

Work during the first two CSN contracts (2000–2008) has helped to identify some 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 $\pm$5% for most species) does not appreciably help overall uncertainty. This is reflected in Table A.7.4, which reports the MQOs for total measurement error.

- Sensitivity issues – The majority of the $PM_{2.5}$ sampling for the CSN is being performed using the MetOne SASS sampler, which operates at a flow rate of 6.7 liters per minute and uses 46.2 mm filters. Compared with the IMPROVE program, this relatively low flow rate and large filter size results in a sensitivity deficit of up to 11-fold. This sensitivity difference is immaterial for gravimetric mass and species present in large amounts, such as sulfate, nitrate, and OC. Many trace elements analyzed by XRF that are usually detectible at high levels include iron, sulfur, and silicon. Inclusion of ICP/MS, a much more sensitive method than XRF, will help identify some of the trace elements but, because of cost, ICP/MS cannot be performed on the majority of CSN filters.

- OC artifact – The OC artifact is thought to be the result of adsorbed SVOCs from the gas phase and represents a non-particulate source of carbon. With the MetOne sampler, the OC artifact can amount to 2 $\mu g/m^3$ or more, which can bias the results by 20%–30% on a typical sample. Methods for correcting for the artifact are available but can never be perfect. Because of the relatively higher flow and smaller surface area, the OC artifact for samples taken with the URG 3000N or the IMPROVE samplers are much smaller than for those taken with the MetOne SASS. Samples taken with higher flow samplers, such as the $PM_{2.5}$ FRM sampler, will have intermediate magnitude of OC artifact.
- Uncertainty definitions – Work with receptor modelers during the first two CSN contracts has highlighted the importance of consistent definitions of uncertainty to be reported to the AQS database. The original formulation of uncertainty was based on the IMPROVE program's propagation of errors approach and relied on uncertainty values provided by the analytical instruments software (for XRF and OC/EC). To meet the needs of receptor modeling, it was important that the uncertainties be calculated in a consistent way across all analyzers. RTI, working with experts in the field of XRF analysis at EPA, UC Davis, and the XRF instrument vendors, developed an approach for harmonizing the uncertainties reported between different XRF

instruments. In the process, we also ensured that the total uncertainties for the other CSN analytical techniques (gravimetry, ion chromatography, OC/EC) were comparable with those for XRF and were realistic, based on the collocation results.

DQOs and MQOs for Speciated PM_{10} and PM_{coarse}

PM_{coarse} involves subtraction of results from two different filters. A straightforward approach to calculating precision would be to combine the individual uncertainties reported for the $PM_{2.5}$ and the PM_{10} filter, assuming additivity of variance. This may turn out to be a valid approach for simple species such as gravimetric mass; however, this approach is likely to significantly underestimate the random variability for other chemical species for a variety of reasons. Research necessary to develop expressions for accuracy and precision and the corresponding DQOs and MQOs applicable to PM_{coarse} is currently being conducted under contract EP-D-08-047, work assignment 4-07.

A.7.3 Measurement Quality Objectives

There are several components of total data variability included in the model used in the original DQO study. Of these, laboratory measurement error is the component that can be controlled and/or quantified most readily through the QA/QC program, even though it is significantly smaller than either the day-to-day variability in environmental pollutant levels (U.S. EPA, 1998) or the errors associated with sampling and handling (Flanagan et al., 2006).

The original set of MQOs for laboratory analyses were developed by considering the MQOs for total error shown in **Table A.7.4** and the known capabilities of the analytical methods to be used. In this table, systematic bias and random errors are aggregated into a single figure that was called "measurement error" in the DQO study.

Table A.7.4. Laboratory MQOs

Measurement	Measurement Error[a]	Completeness Goal[b]
Cations and Anions	±10% if C > 10×MDL[c] or ±MDL if < 10×MDL	90%
Carbon Species	±20% if C > 10×MDL	90%
Filter Weight	±10% if Wt > 6 µg/m[3]	90%
Elements (EDXRF)	±20% if C > 10×MDL	90%
SVOCs[d]	±10% if C > 10×MDL or ±MDL if < 10×MDL	90%
SEM and Optical Microscopic Examination[d]	N/A	90%
Denuder Analysis for Ions	TBD[e]	90%
Optical Density	TBD[e]	90%
Elements (ICP/MS)	TBD[e]	90%

[a] Measurement error is an aggregate figure that combines systematic bias and random error as described above.
[b] Completeness is based on the number of filters successfully exposed and returned to RTI for the specified analysis. Historically, the CSN laboratories have achieved completeness well in excess of 95% completeness on a continuing basis.
[c] MDL = Method detection limit. Typically determined as three times the standard deviation of seven or more replicate measurements of a reagent blank, matrix blank, or low-level calibration standard; however, other methods for determining the MDL may be used, depending on the analysis.
[d] SVOC and microscopic measurements were not made during the mini-trends portions of the project.
[e] TBD = To be determined as data are gathered under the proposed effort.

One justification for combining bias and random errors into a single figure is that, over the long time frame of the trends detection study (5 years), bias determinations will tend to fluctuate randomly, so it is appropriate to aggregate them with measurements of random error, particularly when multiple analyzers are used to perform the same analysis, as is done in the OC/EC, XRF, and ion chromatography laboratories.

Completeness is defined as the percentage of samples successfully analyzed divided by the number successfully sampled and returned to RTI. The DQO study found that 1-in-3-day sampling was adequate to meet the objective of trend detection after 5 years. Other sites not included in the trends portion of the network operated on either 1-in-3-day or 1-in-6-day sampling schedules.

A.7.4 References

Flanagan, J.B., R.K.M. Jayanty, E.E. Rickman, Jr., and M.R. Peterson. (2006). $PM_{2.5}$ Speciation trends network: evaluation of whole-system uncertainties using data from sites with collocated samplers. *Journal of the Air and Waste Management Association 56*:492–499. April.

U.S. EPA (1999a). *Particulate Matter ($PM_{2.5}$) Speciation Guidance Document (Third Draft)*, U.S. EPA, Research Triangle Park, NC. January 5, 1999.

U.S. EPA (1999b). Strategic Plan: Development of the Particulate Matter ($PM_{2.5}$) Quality System for the Chemical Speciation Monitoring Trend Sites, U.S. EPA, Research Triangle Park, NC, April 16, 1999.

U.S. EPA (1998). *Data Quality Objectives for the Trends Component of the $PM_{2.5}$ Speciation Network*, U.S. EPA, Research Triangle Park, NC, 1999. Available on AMTIC at http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/dqo3.pdf. (Accessed 08/09/2011)

U.S. EPA (1994). *Guidance for the Data Quality Objectives Process: EPA QA/G-4*, Report No. EPA/600/R-96/055, U.S. EPA, Washington, DC.

Watson, J.G, and J.C. Chow (November 8, 1988). The 1987–1988 Metro Denver Brown Cloud Study, Vol. II: Measurements. DRI Document No. 8810 1F2. Final Report.

A.8 Special Training Requirements/Certification

It is important that the analytical results produced by each analyst meet MQOs. Attainment of MQOs will be measured by attainment of acceptable recovery and precision from analysis of identified reference samples, "blind" test samples, and previously analyzed field samples.

Analysts new to the CSN program will be required to be experienced with the basic measurement techniques relevant to the analyses that they are to perform. These techniques include the operation of an analytical microbalance, XRF, ion chromatography, GC/MS, and electron and optical microscopy. Determination of OC/EC requires an analyst who has been trained to use the apparatus and to practice good laboratory techniques to avoid contamination of filters and standards.

With experience in the basic methodology, the analyst to be trained (hereafter referred to in Section A.8 as "the analyst") will read and understand the appropriate SOP. Under the direction of an analyst experienced in the method, the analyst will follow the SOP and use the method to analyze reference samples and, if available, samples that have been analyzed previously by an experienced analyst. These samples might include split filters, filter extracts, and whole filters for XRF and electron microscopy. This effort will be continued until the analyst achieves MQOs for recovery (or bias) and precision. The Technical Area Supervisor or mentor will also audit the performance of the analyst, checking such operations as calibration, data treatment, system maintenance, and record keeping. With both acceptable analytical results and a successful systems audit, the analyst will be considered ready to perform program sample analysis. Even then, the analyst will work under the direction of a mentor until the mentor believes the analyst is considered ready to work independently. Ongoing performance will be monitored by the program QA Manager through review of analytical data, which are identified by the analyst.

RTI will require gravimetric analysts to pass a test similar to the certification test administered to analysts working on the EPA's $PM_{2.5}$ Federal Reference Method Performance Evaluation Program (FRM PEP), which RTI helped to develop under another contract.

Permanent RTI employees, including high-level personnel and Technical Area Supervisor, are eligible to attend training courses relevant to the project areas. Both in-house and extramural training opportunities are provided to RTI's employees at its expense. Most employees attend one or more such courses each year. Project staff will be encouraged to attend courses such as manufacturers' training sessions or method-specific courses that are relevant to this program.

The training and acceptable performance will be documented in the analysts' training folder. This will include a record of reading and utilizing the SOP and verification by the Technical Area Supervisor and/or mentor that acceptable method performance has been demonstrated. These folders will include records of all performance standard analyses, formal training, and in-house training and testing.

A.8.1 Current Personnel

RTI believes that no further training is required for current personnel who have performed the chemical and gravimetric analyses in the past. Analysts and other personnel will receive copies of the QAPP and the relevant SOPs necessary to perform their duties. These documents will contain the requirements applicable to the performance of each analyst's job.

Relevant experience of current analytical staff are as follows:

Gravimetric Mass Determination

Paige Presler-Jur – 11 years of laboratory experience, including currently managing RTI's PM Gravimetry Laboratory ensuring that proper techniques and procedures are followed in the determination of gravimetric mass, maintaining adequate internal documentation, adjusting schedules to meet the needs of the project, and reviewing and approving deliverables submitted to the client.

Stacy Doorn – Over 15 years of relevant experience, including extensive experience in the preparation and analysis of samples by electron microscopy and over 10 years in the determination of gravimetric mass.

Maurice Gerald – Over 16 years of relevant experience, including 9 years in the determination of gravimetric mass and 8 months' prior experience working in the Sample Handling and Archiving Laboratory.

Okisha Hammond – Over 9 years of relevant laboratory experience, including 4 years in the determination of gravimetric mass.

Karen McCombs – 22 years of laboratory experience, including 9 years in the determination of gravimetric mass.

Ion Analysis

Eva Hardison – 33 years of relevant experience in the technical and fiscal management of ion chromatographic analysis, including 14 years of filter analysis experience for the National Park Service. Also, extensive experience in sample handling, data reduction/analysis, and report preparation.

David Hardison – 32 years of relevant analytical experience, including 9 years in performing ion analysis of filter extracts for the National Park Service, the American Lung Association, the EPA, and the California Air Resources Board.

Christine Van Hise – 15 years of relevant experience in sample handling and preparation, including over 3 years of experience in air filter extraction.

Dorrie Pickett – Over 20 years of relevant experience in sample handling and preparation, including over 4 years of experience in air filter extraction.

Metal Analysis

Andrea McWilliams – More than 10 years of relevant experience, including 8 years of experience operating, maintaining, and troubleshooting the ThermoNoran QuanX (EDXRF).

Paul Duda – (CHESTER LabNet) More than 20 years of relevant experience including 9 years of experience in air filter analysis by EDXRF and 9 years of experience as a LIMS administrator.

Richard Sarver – (CHESTER LabNet) More than 23 years of relevant analytical experience, including 18 years of experience in environmental air quality analysis, specializing in analysis of air particulates by EDXRF.

Organic/Elemental Carbon

Jeffrey Nichol - More than 30 years of experience in air quality monitoring, analysis, and quality assurance (QA), and 6 years of experience specific to OC/EC analysis. Has performed OC/EC analysis of quartz filters using the Sunset Laboratory's thermal/optical carbon analyzer and the DRI Model 2001 analyzer. Is also an ISO 9001:2008-certified Lead Auditor and serves as a Certified Instructor for training field operators in EPA's $PM_{2.5}$ PEP, Pb PEP, and the CSN programs.

Melville Richards – More than 25 years of relevant experience, including experience in ion chromatography and carbon analysis. Also, 6 years of experience in OC/EC analysis by the current EPA adaptation of NIOSH Method 5040.

OC/EC by IMPROVE Method

Judy Chow – (DRI) More than 30 years of experience in conducting air quality studies and performing statistical data analysis. Directs DRI's Environmental Analysis Facility (EAF). Supervises filter processing and chemical operations and develops cost-effective, yet accurate, methods for aerosol sampling and analysis. Prepared and revised sections of the U.S. EPA's air quality criteria document that pertained to chemical analysis and source emissions. Co-principal investigator on evaluation of aerosol measurement methods, sampling strategies, and databases for the U.S. EPA's guidance document on network design, continuous particulate monitoring, and aerosol measurement methods.

D. L. Trimble – (DRI) More than 16 years of experience in ambient air quality measurements and quality assurance. Serves as Laboratory Manager for DRI's EAF Carbon Analysis Laboratory, including data validation, reporting, and analysis of OC/EC measurements.

Steven Kohl – (DRI) More than 10 years of experience with scheduling and coordination of laboratory work. Responsibilities include the quality assurance and reporting of data generated by the inorganic analytical laboratory, as well as performing chemical analysis of aerosol samples by x-ray fluorescence. Also manages field studies, maintains a vast array of field sampling equipment, and supervises three laboratory

technicians. Before coming to DRI, Mr. Kohl developed immunochemical pesticide assays for use in fiber optic biosensors for environmental monitoring applications for EPA. Mr. Kohl will serve as DRI's EAF Laboratory Coordinator.

Richard Tropp – (DRI) More than 30 years of experience conducting air quality studies, statistical data analysis, and quality assurance. Project Manager for $PM_{2.5}$ FRM laboratory support to the states of Texas and Oklahoma. Provides coordination among laboratory groups, field personnel, contractors, and subcontractors. Provided technical support to EPA in preparing $PM_{2.5}$ regulatory proposal and promulgation packages. Outside reviewer of Section 2.12 of EPA's QA Handbook.

John Watson – (DRI) More than 30 years in environmental sciences, including the planning and conducting of major air pollution studies. Serves as QA Manager and senior technical advisor for the EAF. Has undertaken reviews of visibility science and regulation and is currently investigating the comparability of existing methods for carbon analysis and ways to obtain better, more useful information.

Microscopy

Owen Crankshaw – More than 21 years of relevant experience with scanning electron microscopy (SEM) and transmission electron microscopy. Specifically experienced in analysis of PM_{10} and $PM_{2.5}$ samples, including the analysis of Teflon, polycarbonate, and fibrous glass/quartz filters.

Semivolatile Organic Compound Analysis

Barbara Zielinska – (DRI) More than 30 years of experience in the development, enhancement, and application of collection and analysis methods for trace atmospheric organic species present in both gaseous and particulate phases. Work includes the development of analytical methods for measuring biologically active compounds in primary and secondary particulate organic matter; atmospheric transformations of organic compounds; ozone precursors; and particle-associated and VOC emissions from various sources, including diesel- and gasoline-powered vehicles, wood combustion, and meat cooking. Currently a member of EPA's Clean Air Scientific Advisory Committee (CASAC) and a regular reviewer for the professional journals *Environmental Science & Technology* and *Atmospheric Environment*.

Sample Handling

James O'Rourke – More than 20 years of relevant experience in sample handling and preparation and denuder refurbishment. Specifically trained in handling and shipping of hazardous materials. Experience in logistics of shipping and receiving large numbers of samples through EPA radon proficiency testing program and American Industrial Hygiene Association Environmental Lead Proficiency Analytical Testing program.

Jessie Deal – More than 9 years of relevant experience supporting the $PM_{2.5}$ chemical speciation project, which includes handling, packaging, and maintaining records for

different types of air filters used for air sampling studies. Serves as assistant supervisor of the sample handling laboratory and oversees operations in Mr. O'Rourke's absence.

Database Development/Management

Edward Rickman – More than 20 years of relevant experience in design and implementation of environmental and QA databases, including a database for EPA's OAQPS $PM_{2.5}$ Performance Evaluation Program and preparation of programs and queries to combine information from EPA's Envirofacts Oracle Data server with additional information from other (off-line) sources. Also experienced in statistical evaluation of test data and analytical methods.

Linda Andrews – More than 12 years of relevant experience in data management and database design. Participated in various database development efforts, which included designing a relational database; creating necessary data entry forms, queries, reports, and functions; providing technical support or management of data; and creating relationship diagrams and data dictionaries for database documentation. Also responsible for final flagging and uploading CSN data to AQS after review by the SLT air agencies.

Quality Assurance

Prakash Doraiswamy – More than 10 years of relevant experience in data reduction, data analysis, and specific recent experience in QA/QC of data from the CSN program. Has extensive experience in QA of data from the CSN program as part of data analysis and model evaluation efforts. Unique knowledge and experience in both analytical and modeling data applications. While at DRI, co-authored the final QA report for the Fresno Supersite and the QAPP for a carbon methods comparison project sponsored by the California Air Resources Board, reviewed recent advances in $PM_{2.5}$ measurement methods, and compared multiple continuous and filter-based measurements of OC/EC.

Denuder Refurbishment

James O'Rourke – Over 20 years of relevant experience in supervision, filter sample preparation and analytical chemistry. Experience with the design and operation of PM samplers employed in the CSN and related speciation programs. Experience with the analysis of silica samples for the American Industrial Hygiene Association Environmental Lead Proficiency Analytical Testing program. Over a 25 year career at RTI, has supported a number of EPA sponsored projects including indoor radon, aldehydes and ketones in indoor air, and Method 29 multi metals analysis.

A.8.2 Summary of Experience and Training

The qualifications of each analyst are maintained in training folders, along with a record of courses taken, special in-house training, and results of performance audits.

Highlights of the present status of experience and training of RTI personnel include the following:

- Gravimetric mass laboratory staff have given instructional workshops and prepared SOPs to train analysts for the $PM_{2.5}$ Performance Evaluation Program.

- The RTI ion chromatographic team has performed air filter analysis for the National Park Service for the IMPROVE program. $PM_{2.5}$ ion analysis has been performed in support of EPA evaluation of $PM_{2.5}$ samplers, for the California Air Resources Board, and for a variety of other clients.

- Three staff members have trained other personnel in the use of single channel $PM_{2.5}$ samplers and in the handling and shipment of filters for the FRM PEP.

- Several members of the RTI staff have been actively involved in evaluating commercially available speciation samplers and have participated in operating them at sites across the country.

- At least three members of the staff have served as sample custodians or sample managers to send and receive filters, prepare denuder surfaces, and send and retrieve COC forms and field data sheets for each of the available speciation samplers.

- RTI XRF operator Andrea McWilliams has successfully completed training courses in the operation and application of the ThermoNoran EDXRF unit and understands the problems associated with the analysis.

- CHESTER LabNet personnel have successfully completed training courses in the operation of XRF units, has participated in numerous audits, and understands the problems associated with the analysis.

- RTI operators of the thermo-optical analysis method for carbon species have shown good agreement with other laboratories through sample analysis intercomparisons and analysis of certified standards.

A.8.3 New Personnel

RTI will hire new personnel as necessary to meet the needs of this program. These personnel will typically be involved with routine, but important, activities such as assembling sample packages in the Sample Handling and Archiving Laboratory (SHAL), 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 has been implemented to ensure that new personnel or personnel learning a different function are fully proficient in their responsibilities.

RTI's approach to assessing and training new hires (and cross-training of existing employees) is as follows:

- New personnel are interviewed and their credentials carefully assessed with regard to prior experience and aptitude for the assigned task. Candidates are interviewed by the Technical Area Supervisor and by at least one other senior-level project participant, such as the Program Manager, QA Manager, or a Technical Area Supervisor in another area.

- RTI regular and temporary personnel to be hired for sample shipping and receiving in the SHAL must have excellent work habits and must be particularly careful and attentive to detail. These individuals must also be comfortable with working under tight deadlines imposed by contractual turnaround times. References will be contacted to verify that the applicant meets these particular qualifications with regard to work habits.

- New hires in the analytical laboratories must have experience or aptitude equivalent to 2 years of experience, but individuals are assessed on a case-by-case basis by the Technical Area Supervisor. References are contacted to verify that the applicant has the required laboratory skills and aptitude.

- For individuals hired as permanent RTI employees, a probationary period of 6 months is provided, at which time the employee may be terminated for failing to meet required job standards; temporary employees may be dismissed at any time. The majority of training is on-the-job and is provided by the Technical Area Supervisor or by a staffer who has already mastered the task area. The specific SOPs are the main training material used.

- All SOPs will be written in sufficient detail to allow a new staff member with the requisite training and experience to perform the task. Any departures from the written SOPs will require consultation with the Technical Area Supervisor for that area. Departures from SOPs necessitated by systematic or recurring problems should result in corrective actions, which may include revision of the SOP.

- All new hires will work under close supervision of the Technical Area Supervisor. The individual may work unsupervised only after the Technical Area Supervisor provides a memo to the individual's training file. Analysts must demonstrate proficiency with analyzing standards and duplicates of previously analyzed samples. These results will be included in the training file.

A.9 Documentation and Records

Table A.9.1 provides a summary of the documentation and records that will be maintained in each functional area for this program. Management records will include monthly data reports, correspondence with the EPA Project Officer, and correspondence and orders from the DOPOs. Consolidated requests from the DOPOs will be received and examined by the Program Manager and will be circulated to all of the laboratories for advanced planning and materials procurement.

Table A.9.1. Management Records

Document Name	Brief Description	Format	Storage Location
Laboratory Request Forms	Used by the laboratories to order materials, schedule shipments, and plan future level of effort (the Program Manager checks the request and distributes it to the laboratories)	Hard copy and electronic	Copies to SHAL and labs
Monthly Data Reports	Monthly data reports to EPA	Electronic	Program Office
Correspondence	Contractual correspondence with EPA and subcontractors	Electronic	Program Office
Purchase Requisitions	Copies of all approved purchase orders	Electric	Staffnet
Conference Call Notes	Notes made during conference calls between the Program Manager, DOPOs, and EPA/OAQPS	Electronic	Program Office
E-mail	All of the Program Manager's project-related e-mail correspondence	Electronic	RTI mail server/CD Program Office

A.9.1 QA/QC Records

Table A.9.2 shows the QA/QC records that will be maintained.

Table A.9.2. QA/QC Records

Document Name	Brief Description	Format	Storage Location
Training Files	Records substantiating the training and proficiency of analysts relevant to this program	Hard copy	Program Office
Audits, Question-naires, and Results	Results of internal QA surveys and audits	Hard copy or electronic	Program Office and QA Office
QAPP	Master version of QAPP, including pending revisions	Hard copy and electronic	Program Office and QA Office
SOPs	Current version of all SOPs	Hard copy and electronic	Program Office, QA Office, and Subcontractor
Intercomparison Study Results	Results validating comparability of EDXRF or OC/EC results if done by two different laboratories	Hard copy and electronic	Program Office and QA Office
Corrective Action Response Memoranda	Results of identified QA problems and their resolutions	Hard copy	Program Office and QA Office

A.9.2 SHAL Records

Table A.9.3 shows the records that will be maintained by the SHAL.

Table A.9.3. SHAL's Records

Document Name	Brief Description	Format	Storage Location
Delivery Order	Instructions from DOPOs for sampling module needs	Hard copy and electronic	Program Office and SHAL
Chain-of-Custody Forms	Forms used to track sample module shipments between RTI and the states	Hard copy, triplicate form (copies 1 and 3 to RTI, copy 2 to field site)	SHAL
Laboratory Chain-of-Custody Forms	Forms used to track groups of aliquots between the SHAL and RTI's internal laboratories or subcontractor laboratories	Hard copy; may be computerized in the future	SHAL and laboratories
SHAL Schedule	Schedules shipments, receipt of containers, and assembly and disassembly of modules according to delivery orders supplied by DOPO	Hard copy	SHAL
Sampling Module Parts Received	Details parts received from states to be used at sampling sites	Electronic	Database
Bin Inventory Form	Lists current inventory of module parts for a specific site stored in a plastic bin in the SHAL	Electronic	Database
Module Assembly Form	Details the assembly of a module for a specific sampling event	Hard copy	SHAL
Container Contents Form	Inventory of modules sent in a shipping container to a specific sampling site	Hard copy	SHAL
Shipment Air Bill	Waybill for transport of containers to sampling site or aliquots to contractor laboratories	Hard copy	SHAL
Incoming Shipment Form	Identifies containers received at the SHAL on a particular date/time	Hard copy	SHAL
Incoming Container Content Form	Details modules received in a container returned from a sampling site	Hard copy	SHAL
Analysis List for Sampling Event	Details requested analysis for a particular sampling event	Electronic	Database
Aliquot Form	Matches filters/pieces of filters to analysis	Hard copy	SHAL
Aliquot Log-Out Form	Lists aliquots that have left the SHAL and have been sent to a laboratory for analysis	Hard copy/notebook	SHAL
Incoming Aliquot Form	Inventory of aliquots being returned to the SHAL from a laboratory	Hard copy/notebook	SHAL
Archive Bin Report	Lists aliquots in a particular storage box sent to archive	Electronic	Database
URG Flash Card Data From URG 3000N	Continuous record of flow and other operational information	Flash memory cards	Database

A.9.3 Analytical Laboratories' Records

RTI and subcontractor analytical laboratories will maintain the generally applicable records listed in **Table A.9.4.**

Table A.9.4. Analytical Laboratories' Records

Document Name	Brief Description	Format	Location
Internal Tracking Forms	Forms used to track sample batches between the SHAL and RTI's internal laboratories	Hard copy and electronic	Returned to the SHAL
Laboratory Notebooks	Includes the following types of notebooks and bound data sheets: Analysts' notebooks Instrument maintenance logs Reagent preparation logs Materials acceptance tests	Hard copy	Each laboratory
Calibration Certificates and Records	Includes certificates of NIST traceability and similar records	Hard copy	Each laboratory
Control Charts or Equipment	QC information displayed in sequence to help diagnose problems with analytical instruments; usually include acceptance limits that are periodically recomputed	Hard copy or spreadsheet	Each laboratory
SOPs	Current copies of SOPs relevant to the analyses performed in a particular laboratory	Hard copy	Each laboratory
QAPP	A current copy of this QAPP; the Lab Supervisor must ensure that each analyst has access to a current copy of the QAPP	Hard copy	Each laboratory
Analytical Results Database	Results for each chemical analysis with identifying information	Spreadsheet or DBMS	—
Analytical QC Database	Includes all QC information for each weighing session including standard weights, duplicates, field blanks, and laboratory blanks	Spreadsheet or DBMS	—

A.9.4 Gravimetric Mass Laboratory Records

The gravimetric mass laboratory will maintain records shown in **Table A.9.5.**

Table A.9.5. Gravimetric Mass Laboratory Records

Document Name	Brief Description	Format	Location
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	Spreadsheet or hard copy	Gravimetric mass laboratory
Filter Conditioning Information	Indicates the dates filters were conditioned and stability test results	Hard copy	Gravimetric mass laboratory

Document Name	Brief Description	Format	Location
Calibration Certificates and Records	Includes certificates of NIST traceability and similar records	Hard copy	Gravimetric mass 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	DBMS	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 (may be computerized in the future)	Copy retained by gravimetric mass laboratory; original returned to the SHAL
Laboratory Logbooks	Individual analysts' comments; instrument maintenance logs	Hard copy	Each laboratory
Control Charts	QC information displayed in sequence to help diagnose problems with analytical instruments; usually includes acceptance limits that are periodically recomputed	Hard copy or electronic spreadsheet	Each laboratory

In addition to the records shown in Table A.9.5, the gravimetric mass laboratory will receive a monthly filter order from the SHAL to accommodate program sampling requests. The DOPOs receive the sampling requests from the various state agencies and consolidate these requests into delivery orders, which are sent to the RTI CSN program office. Information derived from the delivery orders is distributed to the SHAL, data management, and the laboratories, so that the SHAL operations, materials (e.g., filters and reagents), and laboratory personnel can be scheduled as necessary. Each month, the SHAL supervisor will calculate the projected number of Teflon filters that will be needed to meet that month's sampling and field blank requirements. This projection is sent to the gravimetric mass laboratory via e-mail so that a sufficient number of filters can be ordered in advance.

A.9.5 XRF Laboratory Records

The XRF laboratory will maintain records shown in **Table A.9.6.**

Table A.9.6. XRF Laboratory Records

Document Name	Brief Description	Format	Location
Calibration Certificates and Records	Includes certificates of NIST traceability and similar records	Hard copy	XRF Laboratory
"Method" Database	Includes x-ray generation information and other information required to automate the XRF analyses	Computer files	XRF Laboratory
QC Records	Results of calibrations, SRM recoveries, and replicate precision	Computer files	XRF Laboratory
Raw Data Records	Results of PM analyses	Computer files, database files	Instrument PC; database; Program Office
Laboratory Notebooks	Individual analysts' comments; instrument maintenance logs	Hard copy	XRF Laboratory
Instrument User's Manual	Information for setting up, using, and troubleshooting the XRF instrument	Hard copy	XRF Laboratory or analyst's office

A.9.6 IC Laboratory Records

The IC laboratory will maintain records shown in **Table A.9.7.**

Table A.9.7. IC Laboratory Records

Document Name	Brief Description	Format	Location
Calibration Certificates and Records	Includes certificates of NIST traceability and similar records	Hard copy	IC Laboratory
"Method" Database	Contains the information required to automate the analyses	Computer files	IC Laboratory
QC Records	Results of calibrations, SRM recoveries, and replicate precision	Computer files	IC Laboratory and database
Raw Data Records	Results of PM analyses and analysis of selected denuder extracts	Computer files, spreadsheets, database files	Instrument PC, analyst's PC, database computer
Laboratory Notebooks	Individual analysts' comments, instrument maintenance logs	Hard copy	IC Laboratory
Instrument User's Manual	Information for setting up, using, and troubleshooting the IC instruments	Hard copy	IC Laboratory

A.9.7 OC/EC Laboratory Records

The OC/EC laboratory will maintain records shown in **Table A.9.8.**

Table A.9.8. OC/EC Laboratory Records

Document Name	Brief Description	Format	Location
Calibration Certificates and Records	Includes certificates for gases and other chemicals used for calibration	Hard copy	OC/EC Laboratory
"Method" Parameter Files	Contains the information required to run the analysis	Computer files	OC/EC Laboratory computers
QC Records	Results of instrument blanks, calibrations, standard recoveries, and replicate precision	Computer files and hard copy	OC/EC Laboratory
Raw Data Records	Results of PM analyses (including supporting data that are not uploaded to the database)	Spreadsheets, hard copy, database	OC/EC Laboratory computers, Data validation analyst's PC, database computer
Laboratory Notebooks	Individual analysts' comments; instrument maintenance logs	Hard copy	OC/EC Laboratory
Instrument User's Manual and/or Manufacturer's Instructions	Information for setting up, using, and troubleshooting the OC/EC instruments	Hard copy	OC/EC Laboratory

A.9.8 Denuder Refurbishment Laboratory Records

The Denuder Refurbishments Laboratory will maintain records shown in Table A.9.9.Table A.9.9. Denuder Refurbishment Laboratory Records

Document Name	Brief Description	Format	Location
Personnel Training Records	Date and description of training or inspection	Hard copy	Denuder Lab
Denuder Refurbishment Information	Date, number, and type of denuders refurbished and technician name	Hard-copy, notebook	Denuder Lab
SOP	SOPs for coating various types of denuders	Hard-copy, loose-leaf binder	Denuder Lab
Reagent Purity Records	Information for denuders to be quantitatively analyzed	Hard-copy, notebook	Denuder Lab

B.1 Sampling Process Design (Experimental Design)

The experimental design, including design of the sampling network and sampling locations, is outside the program scope and is not addressed in this QAPP. Refer to EPA planning documents available on the U.S. EPA's AMTIC Web site.

B.2 Sampling Methods Requirements

Actual collection of samples is outside the scope of this laboratory QAPP and is not addressed herein. The CSN Field QAPP prepared for OAQPS contains a full description of sample acquisition, including sample COC, which meshes closely with operations of the SHAL. The Field QAPP is available on the AMTIC Web site.

B.3 Sample Handling and Custody Requirements

Note: This section relies heavily on design of RTI's sample handling system, including the SHAL. Please refer to the applicable SOP for more details.

This section describes the sample handling and custody process for all sampling modules to be provided to the sites, as well as sample tracking internally and between RTI and its subcontractors. In this document, the term "sampling module" is used in a generic sense to denote the sampling media and holder associated with a specific sampled air stream in a single speciation sampler. A sampling module is the smallest unit (in one or several pieces) shipped back and forth between RTI and a sampling site.

A sampling module includes denuders (in addition to filter media) and transport hardware if either (or both) is required. All sampling modules and associated sample media will be tracked individually in the database management system (DBMS). An overview of the entire sample handling system is shown in **Figure B.3.1.**

B.3.1 Sample Handling Delivery Order Process

RTI prepares and ships appropriate sampling media (including the required filters) to each state (or sampling site within the state) as needed to meet the sampling schedule for each site covered in the consolidated request received from the DOPOs. The PM checks the consolidated request and distributes it to the SHAL and other laboratories for planning purposes. Based on the schedule defined by all the consolidated requests, RTI schedules and sends modules to the addresses indicated for the state monitoring agencies. Details of the information contained in the consolidated requests, and RTI's interactions with the state air monitoring agencies, will be defined in collaboration with EPA. State personnel collect the required samples and return them to RTI, which logs the samples into its tracking system, performs all required speciation analyses, enters and validates the data, enters data meeting Level 1 criteria into the AQS, forwards all analysis data to the states that requested the analyses, and reports all activities to the DOPOs. Provisions also are made for archiving samples and for resolving technical quality issues and contract dispute issues.

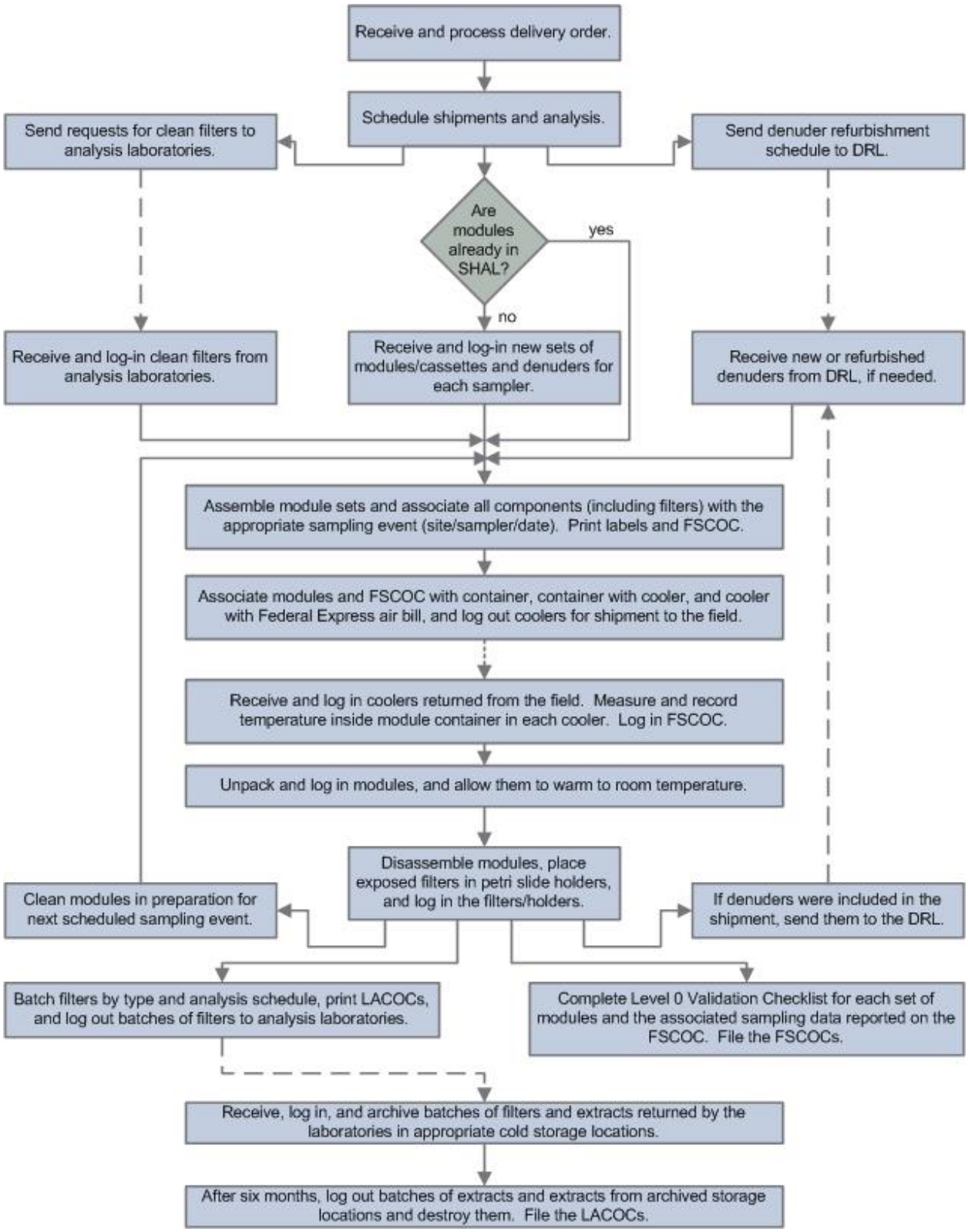


Figure B.3.1. Overview of sample handling and custody system.

The following subsections describe the processes associated with filter and sample handling and archiving, the physical and chemical analyses required for each filter in each type of speciation sampler, and the data handling and analyses required to obtain concentration data of known quality. The sample handling and tracking process is described in more detail in the SHAL SOP.

B.3.2 Chain of Custody

Note: An example of the field COC information sheet is shown in the Field QAPP available on the AMTIC Web site.

RTI will provide COC documentation with all sample shipments to track and ensure that samples are collected, transferred, stored, and analyzed by authorized personnel; sample integrity is maintained during all phases of sample handling and analysis; and an accurate record is maintained of sample handling and treatment from the time of its collection, through the laboratory analytical process, to the eventual relinquishing of all data to the DOPOs and the state clients.

The COC documentation that accompanies the sampling modules to and from the field will include a three-part carbonless form for sending and receiving samples from the field sites. The COC forms are computer generated so that they are customized for each type of sampler. All media (filters and other types of sampling media, if any) will be listed on the COC form for each sampling event. The COC form will include areas in which the field operators can enter critical data, including the total sample volume for each filter channel.

Internal custody forms will also be used to distribute individual sets of filters to the various laboratories for analysis. These forms are computer generated based on information already entered into the database, such as the assigned aliquot numbers.

B.3.3 Processing System for PM Chemical Speciation Modules

RTI has designated 10 laboratories that are involved in the program, and these are described below:

1. **Sample Handling and Archiving Laboratory (SHAL)**. Personnel in the SHAL will be responsible for assembly of components (including clean filters and refurbished denuders) into sampling modules, shipment of sampling media and modules to the states (or sampling sites within the states), receipt of samples from the states, disassembly and cleaning of sampling modules, distribution of filters (and other sampling media, if applicable) to the individual laboratories for analysis, and final archiving of filters and filter extracts for 6 months. COC and field sampling data sheets are generated by SHAL personnel, who will also log out and log in all filter samples (going to the field or laboratories and returning) and all archived filters and extracts. Flash memory cards from the URG 3000N samplers are read into the database as part of the SHAL disassembly procedure.

2. **Denuder Refurbishment Laboratory (DRL)**. Personnel in the DRL are responsible for refurbishment of all denuders and extraction of denuders employed to collect and quantify acidic and basic gases. The DRL must have a hood and sink for work with volatile solvents and for cleaning spent denuders. The DRL will coordinate with the SHAL to prepare and track denuders as they are needed.

3. **Gravimetric Mass Laboratory (GML)**. Personnel in the GML are responsible for all activities associated with $PM_{2.5}$ gravimetric mass determinations on Teflon filters.

4. **Elemental Analysis Laboratory (EAL)**. Personnel in the EAL are responsible for all elemental (selected elements, sodium through lead, by atomic number) analyses. RTI will analyze the majority of the samples. CHESTER LabNet will assist with elemental analysis support for the contract.

5. **Cations/Anions Laboratory (CAL)**. Personnel in the CAL are responsible for all ion analyses. This will include both anions (sulfate and nitrate) and cations (ammonium, sodium, and potassium) on sample filters and denuder extracts. They are also responsible for acceptance testing and cleaning, if necessary, of nylon and other filters used for collection and measurement of target anions and cations.

6. **RTI Organic Carbon/Elemental Carbon Laboratory (OC/ECL)**. Personnel in the OC/ECL are responsible for total, elemental, organic, and fractions analyses on quartz filters that are done by the NIOSH method. The RTI OC/EC Lab is also responsible for cleaning and acceptance testing the quartz filters used in the URG 3000N samplers, which are subsequently analyzed by DRI by the IMPROVE_A method.

7. **DRI OC/EC Laboratory**. Personnel in DRI's OC/EC laboratory are responsible for carbon analysis by the IMPROVE method.

8. **Semivolatile Organics Laboratory (SVOL).** Personnel in the DRI SVOL are responsible for measuring individual SVOCs extracted from $PM_{2.5}$ collected on selected quartz filters and from backup sorbent traps.

9. **Microscopy Laboratory (ML)**. Personnel in the ML are responsible for all optical and electron microscopy of selected filters (with or without elemental particle analysis).

10. **ICP/MS Laboratory.** Personnel in RTI's ICP/MS laboratory will analyze selected filter extracts as directed.

Figure B.3.2 shows a flow diagram for filter processing by filter type. Teflon filters are used for determination of gravimetric mass and trace elements (sodium through lead) concentrations; some Teflon filters may be analyzed for ions. Quartz filters are used for determination of total, organic, elemental, and fractional concentrations. Nylon filters are used for determination of cations (ammonium, sodium, and potassium) and anions (sulfate and nitrate).

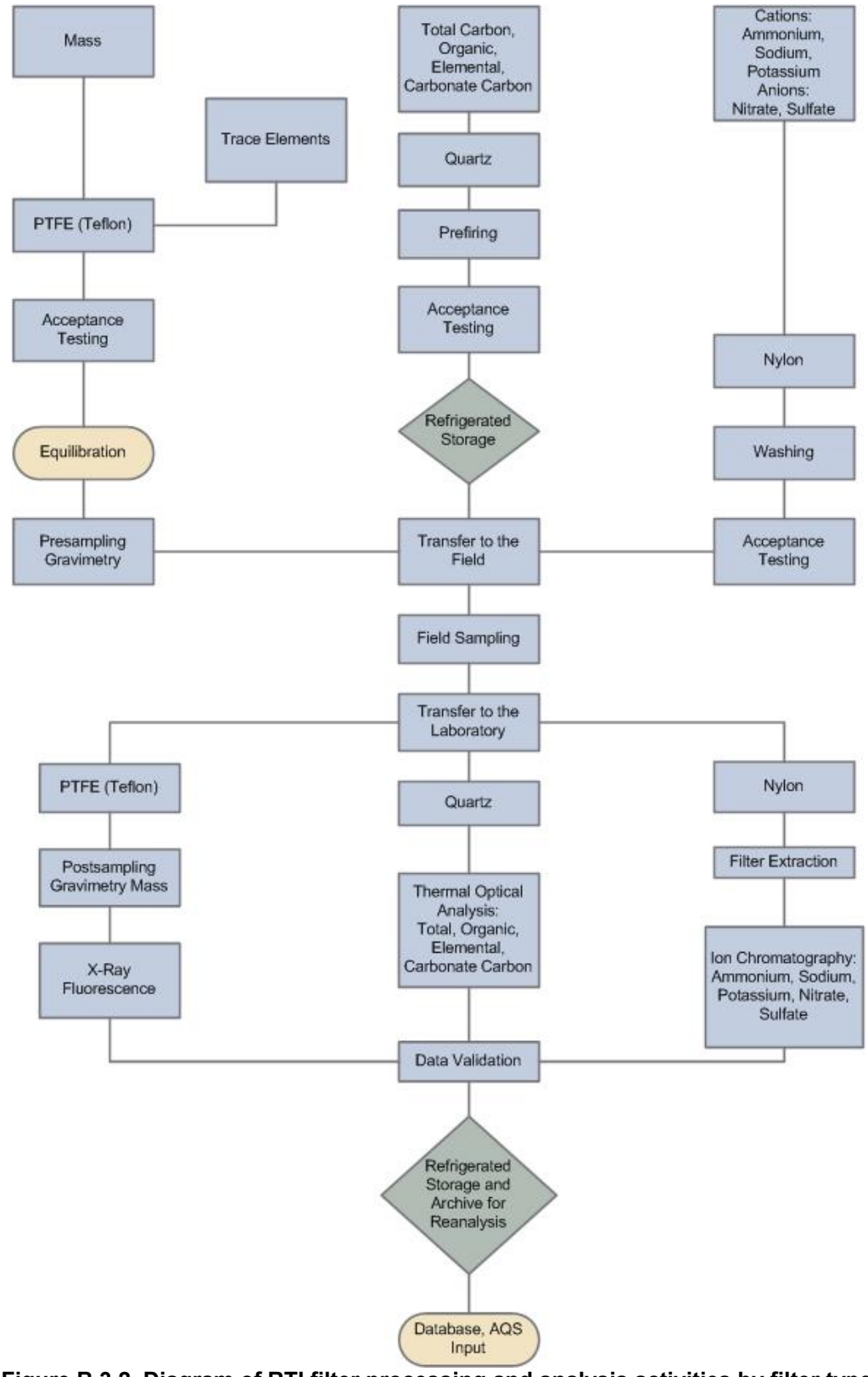
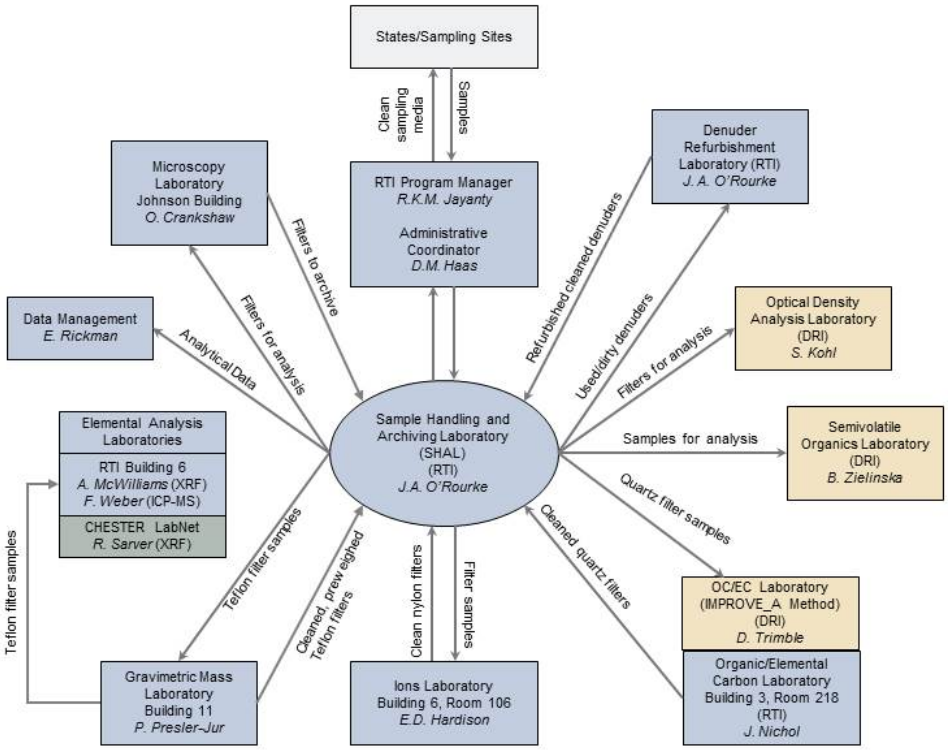


Figure B.3.2. Diagram of RTI filter processing and analysis activities by filter type (arrangement may vary by sampler model).

Figure B.3.3 shows the anticipated movement of filters and extracts through RTI laboratories described above. The focal point for shipping and receiving sampling media and for archiving analyzed filters and extracts is the SHAL. The other laboratories, except for the DRI, are responsible for cleaning and acceptance testing of new filters and for analyses of samples collected on those filters. The main items moving between the various laboratories are shown in the figure, but other pathways are possible.

Figure B.3.3. Movement of filters and extracts through RTI and subcontractor laboratories.



After final weighing in the gravimetric mass laboratory, custody of the exposed Teflon filters is transferred to Ms. Andrea McWilliams, supervisor of the XRF laboratory. Ms. McWilliams distributes the filters to the two XRF laboratories, CHESTER LabNet and RTI. After XRF analysis, the filters are returned to Ms. McWilliams who sends them either to the filter archive or to the CAL if ion analysis is required.

Table B.3.1 shows the sampling media used in each type of $PM_{2.5}$ speciation sampler, the species collected on each type of filter, and the RTI laboratory (or laboratories) that will measure those species on that filter. All of the sampler models use at least one each of the three types of filters (Teflon, nylon, and quartz) used in the $PM_{2.5}$ speciation program.

B.3.3.1 Assembly of Sampling Modules

Sampling modules sent to the field must be clean, properly assembled with clean and unflawed filters and denuders, and shipped in a timely manner. Personnel in the SHAL will clean and inspect all hardware associated with sampling modules and visually inspect each filter (for a pinhole or crease, evidence of chaffing or flaking, discoloration, or any other defect) and each denuder as each module is assembled. Any items that appear flawed are rejected. SHAL personnel will carefully pack all modules for a given sampler at a given location in the same cooler for shipment to the appropriate destination. All modules are assembled according to the manufacturer's instructions and with the sampling components requested by the state agencies and approved by the DOPOs. These operations are fully described in SOPs specific to each model of sampler.

B.3.3.2 Shipping to and from the Field

Filter cassettes, sampling modules, and any additional required components are shipped in specially designed insulated shipping containers to each sampling site or other location designated by the states through the DOPOs. EPA has established an account for shipping with a national provider (currently UPS).

Scheduling of shipping dates to and from the state agencies is a key part of the SHAL's operation. RTI will continue to prepare shipping schedules for all sampling locations, and the shipping schedules will be distributed through the DOPOs.

Sufficient commercially available, leak-proof, "blue-ice" gel packs are added to each cooler to maintain a transit temperature at or below 4°C. Each state agency is responsible for freezing the ice packs and packaging the shipment so that it maintains a temperature at or below 4°C. Shipments are returned to RTI overnight by Federal Express as described above. The temperature of each shipment is determined upon delivery at the SHAL using a temperature probe with digital readout. Temperature upon receipt is recorded on a Level 0 validation form.

Table B.3.1. Sampler Component and Laboratory Speciation Analysis Matrix

Sampler	Module or Flow Channel	Device	Mass	Elements XRF, ICP-MS	Anions^{++} SO_4^{-2}, NO_3^-	Cations,$^{++}$ NH_4^+, Na^+, K^+	TC, OC, EC	Optical Density	SVOC	Micros-copy	HNO_3, and SO_2 (gas)$^{++}$	NH_3 (gas)$^{++}$
URG 3000N Sequential carbon aerosol sampler	Module 1	Quartz filter					●		●			
SASS	Channel 1	Teflon filter	●	●				●		●		
	Channel 2	Nylon filter with MgO coated denuder			●	●						
	Channel 3***	Quartz filter					●		●			
FRM	Single channel per sampler$^+$	Teflon filter	●	●				●		●		
		Nylon filter with MgO coated denuder			●	●						
		Quartz filter					●		●			
All sampler types	Analytical Denuders: Any channel, as required	Phosphorous or citric acid coated										●
		MgO or Na_2CO_3 coated									●	
PMCOARSE	To be determined											

EC = elemental carbon, HNO_3 = nitric acid, ICP-MS = inductively coupled mass spectrometry, K^+ = potassium ion, Na^+ = sodium ion, NH_3 = ammonia, NH_4^+ = ammonium ion, NO_3^- = nitrate ion, Na_2CO_3 = sodium carbonate, OC = organic carbon, SO_2 = sulfur dioxide, SO_4^{-2} = sulfate ion, SVOC = semi-volatile organic compound, TC = total carbon, XRF = X-ray fluorescence

$^+$ Three FRM samplers can be used in parallel as three separate channels to collect $PM_{2.5}$ samples for speciation analyses.

$^{++}$ Sorbed gases NH_3, HNO_3, and SO_2 are measured by using ion chromatography as NH_4^+, NO_3^-, and SO_4^{-2}, respectively.

***Only used if the original CSN OC/EC analysis is to be performed.

B.3.3.3 Disassembly of Sampling Modules

Upon their return to RTI, sampling modules are logged into the database and disassembled by SHAL personnel. Each filter is sealed in a new, clean, labeled petri slide holder and sent to the appropriate laboratory for analysis. Any denuders used in the module will be refurbished or extracted and analyzed, if required, and all other components will be cleaned prior to reuse.

B.3.3.4 Internal Tracking of Analytical Samples

Figure B.3.4 shows the internal tracking form that is used to transfer batches of filters removed from the sampling modules in the SHAL to the respective RTI laboratories. Several filters are transferred in a typical batch, so there is not a one-to-one correspondence between the external COC form (which corresponds to a set of modules for a single field exposure) and the internal tracking form. In typical use, filters of like type that are received on the same day are listed on a single internal tracking form. These filters need not be from the same source, so long as they are going to the same laboratory for similar analyses. A similar sample request form is used to transfer samples from RTI to its external analytical subcontractors.

B.3.3.5 Archiving of Filters and Extracts

See *Standard Operating Procedure for Long-Term Archiving of PM Filters and Extracts* for more detailed information. After completion of the analyses, the following may remain, depending upon the model of sampler used and the arrangement of filters:

- Teflon filters (following XRF) (filters extracted for ion analysis cannot be archived)
- Teflon filter extracts in 50 mL plastic tubes (following IC)
- Denuder extracts in 50 mL plastic tubes (following IC)
- Nylon filter extracts in 50 mL plastic tubes (following IC)
- Quartz filters (following subsampling for OC/EC analysis)
- Quartz filter extracts in glass bottles (following SVOC analysis)
- Teflon or other filters (following microscopic or optical density analysis).

Quartz filters that are analyzed by RTI are archived in petri-slide holders, sorted by location into petri-slide trays, and sorted by sampling date within a tray. Full trays of quartz filters are placed in heavy-duty plastic zippered bags and placed in plastic bins in a freezer maintained at or below -15°C. Individual filters are indexed for rapid retrieval by Archive Bin ID, Tray ID, and Aliquot ID. Computer-generated reports are available to facilitate retrieval by sample date, site, or state. Quartz filters sent to DRI for analysis are archived by DRI at their facility. At DRI, the quartz filters are stored by batch. The sample database can be queried based on batch number, RTI order number, or sample ID, providing easy access to filters in the archive. RTI provides information to DRI on the type of filter, site, sample date, etc., which allows DRI to retrieve any quartz filter based on these criteria as well.

Forms Listed in Order Added to Batch

Batch: E12674P

E12674P

Form Batch Created 2/7/2008 **Flags Reviewed** ☑

Entry 1 ☑ **DATE** 2/12/2008

Entry 2 ☑ **DATE** 2/7/2008 **Complete** ☑

COC Form ID	Location	Sampling Date
Q155549D	Burlington	1/31/2008
Q155787P	Roxbury (Boston)	1/31/2008
Q153019K	Simi Valley	1/31/2008
Q156027W	Henrico Co.	1/31/2008
Q154139V	Chamizal	1/31/2008
Q155971N	Elizabeth Lab	1/31/2008
Q155821A	Sydney	1/31/2008
Q1544496	JFK Center	1/31/2008
Q154105L	Capitol	1/31/2008
Q154587F	Urban League	1/31/2008
Q155583F	CPW	1/31/2008
Q155481A	Alabama (TN)	1/31/2008
Q152789F	Fairbanks State Bldg	1/31/2008
Q152891C	Phoenix Supersite	1/31/2008
Q154505X	Woolworth St	1/31/2008
Q152991F	San Jose - Jackson Street	1/31/2008
Q152857A	Fresno - First Street	1/31/2008
Q155999Z	Gulfport	1/31/2008
Q1529255	Reno	1/31/2008
Q1560550	Lawrenceville	1/31/2008
Q154311P	Jefferson Elementary (10th and Vine)	1/31/2008
Q1542774	Arnold - R&P	1/31/2008
Q1555153	Albany Co HD	1/31/2008
Q151526Q	Mayville Hubbard Township site	1/31/2008
Q155915F	Chicopee	1/31/2008
Q151492X	G.T. Craig	1/31/2008

Tuesday, February 26, 2008 *Page 1 of 2*

Figure B.3.4. RTI Laboratory COC form used in tracking.

Teflon filters are archived in petri-slide holders, sorted by location into petri-slide trays, and sorted by sampling date within a tray. Full trays of Teflon filters are placed in heavy-duty plastic zippered bags and placed in plastic bins in a refrigerator or cold room maintained at or below 4°C (but not below freezing). Individual filters are indexed for rapid retrieval by Archive Bin ID, Tray ID, and Aliquot ID.

Filter extracts (nylon or Teflon) are archived for 6 months in extraction vials and grouped in lab batches, which are placed in heavy-duty plastic zippered bags in plastic bins in a refrigerator or cold room maintained at or below 4°C (but not below freezing). Individual extracts are located by Archive Bin ID, Batch ID, and Aliquot ID.

B.3.3.6 Denuder Preparation

Denuders are placed upstream of sampler filters in certain speciation sampling configurations to remove interfering acidic and basic gases and gas-phase SVOCs. The acidic gases of concern to the Chemical Speciation Network include nitric acid and SO_2. The reason for removal of such gases is to preclude their collection on the filter as reaction product artifacts. For example, if nitric acid vapor from ambient air was allowed to reach the nylon filter, it may react with basic substances there or with the filter itself to form nitrate salts; thus the nitrate ion concentration would be higher than that due to nitrate PM alone. In certain instances, it may also be desirable to remove SVOCs from the air stream due to their potential for adsorption or reaction upon reaching the PM collection filter.

RTI will also prepare denuders specially designated for quantitative extraction. These denuders will be prepared with special attention to the purity of the coating reagents, and backgrounds levels of the species to be analyzed (ammonium, nitrate, and sulfate) will be determined for each batch of denuders. Special precautions to ensure low background levels will be taken for denuders that are to be extracted for analysis of ambient gas-phase ammonia, nitric acid, and SO_2.

RTI will provide support for the operation and use of denuders associated with all types of samplers to be used in the speciation network. Denuder specifications for the samplers will be provided upon start-up of this segment of the monitoring program.

The state (or local agency within the state) planning to employ denuders in its PM speciation sampling scheme will inform the EPA Regional Speciation Coordinator of this fact at the same time that a request for analytical services on filters is made. This initial request for denuder use should be made well in advance of the intended date of use to allow for shipment of denuder equipment to the RTI laboratory, denuder cleaning and coating, and QC. The EPA DOPOs will notify RTI's Program Manager of the state's need for denuders (and filters) and details on special filter pack arrangements associated with the denuders. The sampling schedule is also set. The state must provide a sufficient number of denuders and accessories to meet the demands of their sampling schedule, provide appropriate shipping containers, and carefully pack and ship the new denuders to RTI by Federal Express. Several complete sets of denuders may be required, depending upon the sampling schedule.

Upon receipt of the new denuders and accessories, RTI will clean and coat the denuder devices according to one or more of the following SOPs:

- *Standard Operating Procedure for Coating and Extracting Annular Denuders with Sodium Carbonate*
- *Standard Operating Procedure for Coating Annular Denuders with Magnesium Oxide*
- *Standard Operating Procedure for Coating Annular Denuders with XAD-4 Resin*
- *Standard Operating Procedure for Coating Aluminum Honeycomb Denuders with Magnesium Oxide*
- *Standard Operating Procedure for Coating and Extracting Compact Parallel-Plate Denuders for Ammonia Determination*
- *Standard Operating Procedure for Coating and Extracting Denuders for Capture of Ammonia and Its Measurement.*

All prepared, refurbished, or purchased denuders are sealed airtight and stored in a secure location free of acidic or basic gases and SVOCs. They will then be shipped to the sampling sites for installation on the samplers. The SASS samplers' denuders are installed in the sampling module prior to shipment to the field.

The denuders to be installed at the site sampler are shipped to the requesting state or local agency. Denuders are listed on the COC form that will accompany each shipment to a particular speciation sampler. A record of the number of uses or length of time in use of a particular denuder is maintained by the SHAL so that the denuder is refurbished or replaced according to schedule. All MgO denuders are currently replaced after approximately 30 exposures, and Na_2CO_3 denuders are replaced after each sampling event.

The denuders, COC forms, and field data sheets are returned with the filter samples to RTI from the sampling sites by Federal Express. Upon receipt, the denuders are inspected for damage. The state is responsible for replacement or repair of denuder components damaged in the field; the shipping company is responsible for damage caused during transit. RTI will repair or replace items damaged during handling in its laboratory. The denuders will then be cleaned and/or refurbished for the next round of use according to the established schedule. Unless otherwise directed, RTI will not save extracts from rinsing or cleaning the denuder surfaces and will not analyze the extracts for components. Following cleanup, the undamaged denuders will be refurbished. The newly coated denuders are sealed airtight and stored in a clean, secure location until they are needed.

B.4 Analytical Methods Requirements

B.4.1 Gravimetric Mass Determination

Standard Operating Procedure for $PM_{2.5}$ Gravimetric Analysis describes the procedure to be used for gravimetric mass determination in RTI's laboratory.

B.4.2 EDXRF Analysis for Elements

Standard operating procedures used by RTI and CHESTER LabNet for EDXRF analysis are listed below:

RTI

Standard Operating Procedures for X-Ray Fluorescence Analysis of $PM_{2.5}$ Deposits on Teflon Filters

CHESTER LabNet

Standard Operating Procedures for the Sample Receipt and Log In

Standard Operating Procedures for the Analysis of Elements in Air Particulates by XRF (Kevex 771)

Standard Operating Procedures for the Analysis of Elements in Air Particulates by XRF (Kevex 770 and 772)

Standard Operating Procedures for the Kevex Spectrometer Data Generation, Interpretation, and Reporting

Standard Operating Procedure for the Kevex XRF Spectrometer Calibration

B.4.3 Extraction and Analysis of Anions and Cations

For an overview of RTI's laboratory facility and procedures for extraction and analysis of anions and cations, including nitrate and sulfate, see:

Standard Operating Procedure for Cleaning Nylon Filters Used for Collection of $PM_{2.5}$ Material

Standard Operating Procedures for $PM_{2.5}$ Anion Analysis

Standard Operating Procedures for $PM_{2.5}$ Cation Analysis

B.4.4 Carbon Analysis

RTI's laboratory facility and procedures for organic, elemental, carbonate, and total carbon analysis by the CSN TOT method are detailed in the *Standard Operating Procedure for the Determination of Organic, Elemental, and Total Carbon in Particulate Matter Using a Thermal/Optical-Transmittance Carbon Analyzer*.

DRI's laboratory facility and procedures for OC/EC analysis by the IMPROVE_A/TOR-TOT method are detailed in the *DRI Standard Operating Procedure: DRI Model 2001 Thermal/Optical Carbon Analysis (TOR/TOT) of Aerosol Filter Samples – Method IMPROVE_A*.

RTI's laboratory facility and procedures for OC/EC analysis by the IMPROVE_A/TOR-TOT method are detailed in three SOPs:

- *Standard Operating Procedures for Temperature Calibration of the Sample Thermocouple in a Sunset Laboratory or a DRI Model 2001 Carbon Aerosol Analyzer*
- *Standard Operating Procedure for the Determination of Carbon Fractions in Particulate Matter Using the IMPROVE_A Heating Protocol on a Sunset Laboratory Dual-Mode Analyzer*

- *Standard Operating Procedure for the Determination of Carbon Fractions in Particulate Matter Using the IMPROVE_A Heating Protocol on a DRI Model 2001 Analyzer*

While the CSN/TOT analysis and the IMPROVE/TOR-TOT analysis are similar in technical approach, and both require heating ramps under non-oxidizing conditions followed by heating ramps under oxidizing conditions, the two methods are fundamentally different in the way they define carbon fractions. The CSN/TOT analysis is a timed analysis with fixed times at each temperature step in the heating profile, and the IMPROVE/TOR-TOT analysis is an event-driven analysis with the sample remaining at a given temperature step until evolution of carbon from the filter drops to near zero, subject to a minimum residence time of 150 seconds and a maximum residence time of 580 seconds at each temperature step. A CSN/TOT analysis runs for a total of 12 minutes; an IMPROVE_A/TOR-TOT analysis may take anywhere from about 18 minutes to 70 minutes.

The maximum temperatures for the various fractions are also different as are the way that "Peaks" are defined. For the CSN/TOT analysis, the five OC peaks are defined as their contributions to OC. For CSN/TOT, the sum of the five OC peaks is always equal to OC. For the IMPROVE_A/TOR-TOT method, the four OC peaks and the three EC peaks are independently calculated without regard to the OC/EC split and pyrolyzed carbon has a negative value if the OC/EC split comes before the addition of oxygen. **Table B.4.1** below describes and compares the carbon fractions measured for both methods and the conditions (e.g., non-oxidizing or oxidizing atmosphere and maximum temperature) under which each fraction is measured.

B.4.5 Semivolatile Organic Compounds

SVOCs will be analyzed by RTI's subcontractor DRI. The analysis is detailed in DRI's *Standard Operating Procedures for Analysis of SVOC by GC/MS.*

B.4.6 Characterization of Particles by Electron and Optical Microscopy

RTI will provide SEM and optical microscopy for characterization of particulate samples. RTI has extensive experience in the analysis of airborne PM by both optical and electron microscopy techniques, having analyzed a large number of PM_{10} filters by optical microscopy for several state air quality agencies and a significant number of air filters for commercial firms.

B.4.6.1 Scanning Electron Microscopy

SEM can be employed to characterize individual particles collected on a filter. Particles may be sized and the morphology described on an individual basis. The composition of a particle may be determined by EDXRF. Characterization of a large number of particles provides information as to the particle size, distribution, and chemistry of the PM. Any of several filter media can be used to collect particulate material, but smooth-surface filters such as polycarbonate filters are far superior for the purposes of analysis by SEM. The procedures for analysis by particulate material by SEM are described in detail in *Standard Operating Procedure for Sample Preparation and Analysis of PM_{10} and $PM_{2.5}$ Samples by Scanning Electron Microscopy.*

Table B.4.1. Carbon Fractions Reported

Atmosphere/ Fraction	CSN/TOT†		IMPROVE_A/TOR-TOT‡	
	Analyte Name	Maximum Temperature	Analyte Name	Maximum Temperature
He&He-O_2/OCT	OC	900°C	OCT	580°C
He&He-O_2/OCR	Not Calculated	N/A	OCR	580°C
He/1st OC Peak	Pk1_OC	310°C	OC1	140°C
He/2nd OC Peak	Pk2_OC	480°C	OC2	280°C
He/3rd OC Peak	Pk3_OC	615°C	OC3	480°C
He/4th OC Peak	Pk4_OC	900°C	OC4	580°C
He-O_2/PCT	Pyrol_C	Varies	PCT	varies
He-O_2/PCR	Not Calculated	N/A	PCR	varies
He-O_2/ECT	EC	920°C	ECT	840°C
He-O_2/ECR	Not Calculated	N/A	ECR	840°C
He-O_2/1st EC Peak	Not Calculated	600°C	EC1	580°C
He-O_2/2nd EC Peak	Not Calculated	675°C	EC2	740°C
He-O_2/3rd EC Peak	Not Calculated	750°C	EC3	840°C
He-O_2/4th EC Peak	Not Calculated	825°C	N/A	N/A
He-O_2/5th EC Peak	Not Calculated	920°C	N/A	N/A

† Chemical Speciation Network/Thermal-Optical-Transmittance Analysis, adopted by EPA in 2000. Older models of Sunset carbon analyzer did not calculate individual EC peaks. Dual-model sunset carbon analyzers calculate the individual EC peaks.
‡ Interagency Monitoring of Protected Environments/Thermal-Optical-Reflectance & Transmittance Analysis, adopted as IMPROVE_A in 2005.

B.4.6.2 Optical Microscopy

The RTI optical microscopy laboratory is fully equipped with both stereo-binocular and polarizing light microscopes (PLM) capable of both reflected and transmitted light analysis. Photomicrography capabilities allow for documentation of particle characteristics. No RTI SOP currently exists for optical examination of filter media. Procedures will be carried out at the direction of the DOPOs, and reporting criteria and formats will be established at the time of the initial requests.

Analysis by optical microscopy allows for examination of particles having apparent diameters less than 0.25 µm. Optical characteristics such as color, refractive indices, birefringence, and morphology (size and shape) can be determined, which may aid in the identification of particles. The Teflon filter commonly employed in $PM_{2.5}$ sampling is not a suitable substrate for analysis by optical microscopy because the thickness and translucent nature of the filter severely limits the transmittal of light. Additionally, the surface of the filter is highly irregular, making it very difficult to observe individual particles. Other filter media such as mixed cellulose ester (MCE) or polycarbonate provide substrates that are more suitable for analysis by optical microscopy.

B.5 Quality Control Requirements

B.5.1 Quality Criteria for Gravimetric Analyses

All QA/QC procedures and processes employed by RTI in the performance of gravimetric analysis of filters will meet or exceed the requirements outlined in EPA's QA Handbook Guidance Document 2.12. RTI will also stay current with weighing procedures developed by other authorities such as NIST and ASTM. RTI will assess procedural innovations, and, in consultation with EPA, will adopt changes to improve the quality of the CSN data. For example, the weighing session software that has been developed by RTI for the CSN program automatically prompts for duplicate and standard weighings to ensure that these QC checks are performed at the required frequency in each weighing session.

A summary of nine laboratory QC samples that accompany gravimetric measurements and their acceptance criteria is given below.

1. At least two Class 1 working mass reference standards traceable to the National Institute of Standards and Technology (NIST) are weighed at the beginning and end of each weighing session, with weights not to vary by more than 3 µg from the designated value. If the tolerance is exceeded, corrective actions will be taken. After any problems with the balance or with the weights have been identified and addressed, any filters not bracketed by acceptable standard checks will be reweighed.

2. At least one working standard is weighed after every tenth filter weighed, with the weight not to vary by more than 3 µg from the designated value. If this tolerance is exceeded, corrective actions will be taken as described above.

3. Standard weight measurements are monitored by QC charts (or equivalent) throughout the year to determine if any bias has developed in the weights or the balance.

4. Replicate weighings are made at a frequency of 33% of pre-sampling (tare) filters and 10% of post-sampling filters; if the weights differ by more than 15 µg, the laboratory supervisor for the project will be consulted and corrective action will be taken.

5. At least one laboratory blank is weighed during each weigh session, with the weight not to vary by more than 15 µg from the initial weight. If this tolerance is exceeded, troubleshooting of the entire weighing process will be conducted in coordination with the laboratory supervisor.

6. Post-sampling weights for field blanks are not to exceed initial weights by more than 30 µg. If the weight difference of any of the field blanks exceeds 30 µg, the laboratory blanks are checked. If the laboratory blanks are within 15 µg, the state agencies will be notified to troubleshoot possible contamination in the field.

7. The microbalances are calibrated annually or more frequently, as needed, by a Mettler technician.

8. The 100 and 200 mg primary and working mass reference standards are recertified annually against NIST-traceable mass standards at a state weights and measures laboratory holding a NIST certificate of traceability. [Note that filters currently used for gravimetric mass determination are bracketed by these two reference weights. If a new type of filter is adopted for the CSN program in the future, appropriate reference standards would be used to bracket the expected filter weights.]

9. The accuracy of the temperature and relative humidity (RH) recorders are verified annually. See section B.6.1 for detailed descriptions of the temperature and RH control requirements.

B.5.1.1 Gravimetric Disaster Recovery Plan

Raw weighing data, including internal QC checks, are recorded in the gravimetric database application written for the laboratory in Microsoft Access by RTI Data Management personnel. For backup and archiving purposes, the raw data are stored on the RTI chemical speciation program's dedicated database server. Data logger spool files are downloaded directly from each data logger to the server. Database backup and restore procedures are described in greater detail in Section B.10 of this QAPP. Hard copies of raw data will also be printed for backup purposes.

In addition to the program's database backup and recovery plan, the gravimetric mass laboratory will have a severe weather/utilities interruption response plan. This plan will be filed in the Microanalytical Sciences Department's administrative office and will instruct laboratory personnel in the response actions to be taken in the event of power outage, water outage, severe inclement weather, and so forth. The intent of this plan will be to minimize the impact of unavoidable weather events or utilities interruption on laboratory operation, sample throughput, and data quality.

B.5.2 Quality Criteria for Ion Analysis

The quality criteria applicable to analysis of cations and anions are provided in **Table B.5.1.**

Table B.5.1. QC Criteria for Ion Chromatography (Anions and Cations)

QC Sample	Frequency	Acceptance Criteria	Corrective Action
Multipoint calibration	Daily, before analysis of field samples	Acceptable agreement with previous calibration results plotted on a control chart	Identify and correct the problem before analyzing field sample
Method Detection Limit (MDL)	Annually or after major instrument change	Acceptable agreement with instrument manufacturer's specification	Troubleshoot IC instrument
QC samples prepared with laboratory reagents at concentrations higher and lower than expected sample concentrations (one high, one low)	1) Daily, before analysis of field samples, and 2) After every 10 field samples during a run	±10% of nominal value	1) Identify and correct the problem before analyzing field samples, and 2) Field samples not bracketed by acceptable QC samples must be reanalyzed after corrective actions
Commercial, NIST-traceable standard solution	Daily, before analysis of field samples	±10% of nominal value	Identify and correct the problem before analyzing field samples
Reagent blanks	1) Daily, before analysis of field samples, and 2) After every 20 field samples during a run	(1 and 2) less than the MDL for each ion	1) Identify and correct the problem before analyzing field samples, and 2) Field samples not bracketed by acceptable QC samples must be reanalyzed after corrective actions
Duplicates (of field samples)	After every 20 field samples during a run	Relative difference less than 10% for concentrations ∃10 times the MDL (less than 100% for concentrations at the MDL)	Field samples not bracketed by acceptable QC samples must be reanalyzed after corrective actions
Spiked duplicates	One for every 20 field samples during a run	Spike recovery between 90% and 110%	Field samples not bracketed by acceptable QC samples must be reanalyzed after corrective actions have been taken

B.5.2.1 Ion Disaster Recovery Plan for Data

The Ion Lab supervisor or analyst copies raw data (.txt) and calculated data (.csv) files from the hard drives of each lab computer to a 1GB disk storage partition on an NT file server located in a separate RTI building. Data stored on the NT file server are backed up nightly. Other data security measures include copying data files to the lab supervisor's PC for data analysis, validation, and reporting and frequent backups to CD-R media. At least two archive CDs are burned before any data are deleted from either a lab PC or the NT file server (typically done to free up disk storage space), and the two archive CDs are kept in separate buildings at RTI.

B.5.3 Quality Criteria for EDXRF

B.5.3.1 RTI

QC elements practiced by RTI are shown in **Table B.5.2.**

Table B.5.2. RTI QC Procedures to Analyze EDXRF Elements

Item	Inspection Frequency	Inspection Parameter	Control Limits	Corrective Action
Calibration	As needed	—	—	—
Calibration verification	Weekly	Measure elements on NIST SRMs 1832 and Micromatter QC standards	90%–110%	Investigate and recalibrate; reanalyze any affected filters
Instrument precision	Every tray of samples	Comparison of measured value and value at time of calibration for 6 elements	Relative % of error is ≤ 5%	Tray reanalysis
Reproducibility	5%	Duplicate analysis of 5% of batch	Difference of ≤ 50% for values with original value ≤ 3x its uncertainty	Investigate: and possible reanalysis of entire batch

B.5.3.1.1 XRF Disaster Recovery Plan for Data

Data safety and security are ensured by frequent transfer of computerized raw data from the XRF PC in RTI's Building 6 to portable hard drive media, which is stored in Building 7, Room 219.

B.5.3.2 CHESTER LabNet

QC procedures for the analysis of elements by EDXRF, their frequency of application and control limits, and corrective actions as performed by CHESTER LabNet are shown in **Table B.5.3.**

Table B.5.3. CHESTER LabNet's QC Procedures Used to Analyze EDXRF Elements

Item	Inspection Frequency	Inspection Parameter	Control Limits	Corrective Action
Calibration	As needed	--	--	--
Calibration verification	Weekly	Measure elements on NIST SRMs 1832 and Micromatter QC standards	90 to 110%	Investigate, possible recalibrate
Instrument precision	Every tray of samples	Comparison of measured value and value at time of calibration for 6 elements	Relative % of error - ≤ 5%	Tray reanalysis
Reproducibility	5%	Duplicate analysis of 5% of batch	Difference of ≤ 50% for values with original value ≤ 3x its uncertainty	Investigate and possible batch reanalysis

The two-sigma (95% confidence level) detection limits in units of ng/cm^2 are calculated from the analysis of a blank Teflon filter as follows:

$$\text{detection limit for element I} = 2\delta_1 = \frac{2(2B_i)^{1/2}}{s_i t}$$

where,

B_i = the background counts for element I,
s_i = the sensitivity factor for element I, and
t = the counting livetime.

Theoretically, detection limits may be decreased by simply increasing the counting livetime. In practice, a point of diminishing returns is reached for real-world samples in which the background increases along with the analyte signal. At this point, further improvement in detection limits by increasing the counting time is not possible.

Note: CHESTER LabNet's MDLs are being reported as 3-sigma limits for compatibility with other STN MDLs.

B.5.4 Quality Criteria for OC/EC Analysis

The QC criteria applicable to the carbon speciation analysis in RTI's OC/EC Laboratory are provided in **Table B.5.4.a** for RTI and **B.5.4b** for DRI.

Table B.5.4a. QC Criteria for OC/EC Analysis by CSN/TOT and IMPROVE_A/TOR-TOT Methods in RTI's OC/EC Laboratory

QC Element	Frequency	Acceptance Criteria	Corrective Action
RTI CSN/TOT Analysis			
Method Detection Limit (MDL)	Annually	MDL # 0.5 μg C/cm^2	Investigate the source of the problem and initiate corrective action, if necessary, to correct the problem before analyzing samples
Calibration peak area	Every Analysis	Within 95%–105% of average calibration peak area for that day	Discard the results of that analysis and, if necessary, repeat the analysis with a second punch from the same filter
Instrument blank	Daily	Blank #0.3 μg/cm^2	Determine if the problem is with the filter or the instrument and, if necessary, initiate corrective action to identify and solve any instrument problem before analyzing samples
Three-point calibration	Weekly	Correlation Coefficient (R^2) ≥0.998 [with force-fit through 0,0]	Determine the cause of the nonlinearity and initiate actions that will identify and solve any problem that may have arisen; then repeat the three-point calibration, which must yield satisfactory results before samples are analyzed
Calibration check	Daily	1) 90%–110% recovery, and 2) Calibration peak area 90%–110% of average for the weekly 3-point calibration	Initiate corrective action, if necessary, to solve the problem before analyzing samples

QC Element	Frequency	Acceptance Criteria	Corrective Action
Duplicate analyses	10% of Samples	1) TC Values greater than 10 μg/cm^2—less than 10% RPD, 2) TC Values 5–10 μg/cm^2—less than 15% RPD, 3) TC Values less than 5 μg/cm^2—within 0.75 μg/cm^2	Flag analysis results for that filter with non-uniform filter deposit (LFU) flag
RTI IMPROVE_A/TOR-TOT Analysis			
Method Detection Limit (MDL)	Annually	MDL ≤ 0.6 μg C/cm^2	Investigate the source of the problem and initiate corrective action, if necessary, to correct the problem before analyzing samples
Calibration peak area	Every Analysis	Within 95%–105% of average calibration peak area for that day	Discard the results of that analysis and, if necessary, repeat the analysis with a second punch from the same filter
Instrument blank	Daily	Blank ≤0.6 μg/cm^2	Determine if the problem is with the filter or the instrument and, if necessary, initiate corrective action to identify and solve any instrument problem before analyzing samples
Full Calibration [sucrose(aq) , KHP (aq), CH_4/He and CO_2/He]	Six Months	Slope [force-fit through 0,0], recovery, and calibration peak area all within 95% to 105% of average slope, average recovery, and average peak area for each run and for each standard.	Determine the cause of the problem and initiate actions that will identify and solve any problem that may have arisen; then repeat the calibration with the standard that appeared to be most different. The individual calibrations for the four standards and their collective results must yield satisfactory results before samples are analyzed
Auto Cal Check	Daily	Peak area for each of the three CH_4/He injections must be within 95% and 105% of the average for the three.	Determine the cause of the problem and initiate corrective action, if necessary, to correct the problem; and obtain acceptable Auto Cal results before analyzing samples.
Calibration check (15 µL sucrose standard)	Daily	1) 90%–110% recovery, and 2) Calibration peak area 90%–110% of average for the weekly 3-point calibration	Initiate corrective action, if necessary, to solve the problem before analyzing samples
Duplicate or replicate analyses	10% of Samples	1) OC or TC ≥ 10 µg/cm^2—less than 10% RPD, 2) OC or TC < 10 µg/cm^2—within 1.0 µg/cm^2, 3) EC ≥ 10 µg/cm^2—less than 20% RPD, 4) EC < 10 µg/cm^2—within 2.0 μg/cm^2	Flag analysis results for that filter with non-uniform filter deposit (LFU) flag.

Table B.5.4b. QC Criteria for OC/EC Analysis by IMPROVE_A/TOR-TOT Methods in DRI's OC/EC Laboratory

Requirement	Calibration Standard	Calibration Range	Calibration Frequency	Performed By	Acceptance Criteria	Corrective Action
System Blank Check	N/A	N/A	Beginning of analysis day.	Carbon Analyst	≤0.2 µg C/cm^2.	Check instrument and filter lots.
Leak Check	N/A	N/A	Beginning of analysis day.	Carbon Analyst	Oven pressure drops less than 0.52 mmHg/s.	Locate leaks and fix.
Laser Performance Check	N/A	N/A	Beginning of analysis day.	Carbon Analyst	Transmittance >700 mV; Reflectance >1500 mV	Check laser and filter holder position.
Calibration Peak Area Check	NIST 5% CH_4/He gas standard.	20 µg C (Carle valve injection loop, 1000 µl).	Every analysis.	Carbon Analyst	Counts >20,000 and 95-105% of average calibration peak area of the day.	Void analysis result and repeat analysis with second filter punch.
Auto-Calibration Check	NIST 5% CH_4/He gas standard.	20 µg C (Carle valve injection loop, 1000 µl).	Beginning of analysis day.	Carbon Analyst	95-105% recovery and calibration peak area 90-110% of weekly average.	Troubleshoot and correct system before analyzing samples.
Manual Injection Calibration	NIST 5% CH_4/He or NIST 5% CO_2/He gas standards.	20 µg C (Certified gas-tight syringe, 1000 µl).	End of analysis day.	Carbon Analyst	95-105% recovery and calibration peak area 90-110% of weekly average.	Troubleshoot and correct system before analyzing samples
Sucrose Calibration Check	10µL of 1800 ppm C sucrose standard.	18 µg C.	Thrice per week (began March, 2009).	Carbon Analyst	95-105% recovery and calibration peak area 90-110% of weekly average.	Troubleshoot and correct system before analyzing samples
Multiple Point Calibrations	1800 ppm C Potassium hydrogen phthalate (KHP) and sucrose; NIST 5% CH_4/He, and NIST 5% CO_2/He gas standards.	9-36 µg C for KHP and sucrose; 2-30 µg C for CH_4 and CO_2.	Every 6-months or after major instrument repair.	Carbon Analyst	All slopes ±5% of average.	Troubleshoot instrument and repeat calibration until results within stated tolerances.
Sample Replicates	N/A	N/A	Every 10 analyses.	Carbon Analyst on same or different analyzer	±10% when OC, EC, TC ≥10 µg C/cm^2 or <±1 µg/cm^2 when OC, EC, TC <10 µg C/cm^2	Investigate instrument and sample anomalies and rerun replicate when difference > ±10%.
Temperature Calibrations	Tempilaq (Tempil, Inc., South Plainfield, NJ, USA).	Three replicates each of 121, 184, 253, 510, 704,	Every 6-months, or whenever the	Carbon Analyst	Linear relationship between thermocouple	Troubleshoot instrument and repeat calibration until

Requirement	Calibration Standard	Calibration Range	Calibration Frequency	Performed By	Acceptance Criteria	Corrective Action
		and 816 °C.	thermocouple is replaced.		and Tempilaq values with R^2>0.99.	results are within stated tolerances.
Oxygen Level in Helium Atmosphere	Certified gas-tight syringe.	0-100 ppmv.	Every 6-months, or whenever leak is detected.	Carbon Analyst using a GC/MS system.	Less than the certified amount of He cylinder.	Replace the He cylinder and/or O_2 scrubber.

B.5.4.1 RTI OC/EC Lab Disaster Recovery Plan for Data

At RTI, copies are regularly made of the raw data (.txt) and calculated data (.csv) files from the hard drives of each lab computer attached to a Sunset Lab analyzer and the Access database of each lab computer attached to a DRI Model 2001 analyzer. These files are saved to a 1-GB disk storage partition on a file server located in a separate RTI building. Data stored on the file server are backed up nightly. Other data security measures include copying all lab data files to the PC of the staff member responsible for performing data analysis, validation, and reporting, and making frequent backups to CD-R or DVD-R media. At least two archive CDs or DVDs are burned before data are deleted from either a lab PC or the file server (typically done to free up disk storage space), and the two archive CDs or DVDs are kept in separate buildings at RTI. At DRI, data is archived as per their standard archival and back-up procedures.

B.5.5 Quality Criteria for Denuder Refurbishments

Denuders are used for the CSN program in two different applications. The first application is the stripping of acid gases (e.g., sulfur dioxide and nitrogen oxides) from the airstream upstream of nylon filters. If not removed prior to sampling, these gases can appear as anion artifacts when the filters are analyzed. Magnesium oxide (MgO) is used with the SASS honeycomb denuder to remove these gases. The sorbent material is not analyzed after use, and QC criteria relate primarily to adequacy and uniformity of coating.

The second potential application for denuders in the CSN program is for quantitative sampling of ammonium gas. As of this writing (August 2011), ammonia sampling has not been performed for routine CSN sampling. Consequently, the sampling uncertainties and QC requirements applicable to preparing and testing these denuders have not been fully assessed and tested, or approved by EPA.

Quality control steps applicable to acid gas denuder refurbishment and quantitative denuders for ammonia gas are provided in **Table B.5.5.**

Table B.5.5. QC Criteria for Denuder Refurbishments

QC Element	Frequency	Acceptance Criteria*	Corrective Action
Coating solution storage	After each coating session	Sodium carbonate solutions to be refrigerated at ~4°C. MgO slurry to be stored tightly capped while stirring	Prepare fresh coating solution if not refrigerated or if MgO slurry has dried
Absence of MgO-clogged denuder passage ways	After each coating	Visually inspect each denuder for clogged passage ways	Remove the obstructions; use nitrogen gas to clean debris; if necessary, clean and recoat
Final inspection	After each coating	As applicable, check each denuder for damage, O-ring quality, and absence of debris affecting proper seating of denuder	Remove damaged denuders from service; replace aged, cracked, or missing O-rings; clean O-ring surfaces with damp lab wipe
Denuder Storage	After denuder coating is dry	To protect denuders from exposure before installation in module, cap or bag them	Reclean and recoat denuders exposed to room air for more than 4 days
Reagent purity	For denuders to be analyzed quantitatively – upon opening new containers of coating material	Phosphorous Acid 99% other reagents as specified in SOP**	Use different reagent source; optionally recrystallize in the laboratory
Denuder lot background contamination	For denuders to be analyzed quantitatively – each preparation lot should have 1 or 2 reextracted	TBD* (Background levels approaching 1.0 µg NH_3 per denuder have been achieved during method development tests***)	Reject denuder lot; determine source of contamination; re-make the denuder lot
Field Blank denuder ion background	For denuders to be analyzed quantitatively -- Minimum of one per shipment	TBD*	Investigate source of field contamination
Denuder extraction effectiveness	For denuders to be analyzed quantitatively	TBD* (90%–110% goal)	Investigate effectiveness of extraction protocol

*Final QC criteria for quantitative measurement of ammonia gas will be developed in cooperation with EPA.
**Standard Operating Procedure for Coating and Extracting Compact Parallel-Plate Denuders for Ammonia Determination, RTI International, March 1, 2010.
*** Eaton, W. Cary, Wall, Constance V., and Walters, Steven J., October 2009. "Refinement and Field Testing of Denuder Technology for Quantification of Basic and Acidic Gases to Support EPA PM2.5 and CASTNET Ambient Air Monitoring Network Research." RTI International Institutional Research and Development Final Report.

B.5.6 Uncertainty Determination

Uncertainty values reported to AQS with each concentration record will include components of both analytical and the volumetric uncertainty. The reported uncertainties are estimated "1-sigma" valued (one standard deviation). No blank corrections are assumed other than laboratories' instrumental baseline corrections, which are an integral part of each analysis. The equations to calculate the total uncertainty for the CSN analytes are included in **Appendix 1**.

B.5.7 Method Detection Limits

The method detection limits (MDLs) for the $PM_{2.5}$ CSN analytes are shown in **Appendix 2** and are reported annually in the data summary reports provided to EPA and posted on AMTIC. MDLs are typically reported as three times the standard deviation of seven or more replicate measurements of a reagent blank, matrix blank, or low-level calibration standard. MDLs for gravimetric mass are determined from net weights (post-weight minus pre-weight) for historical QC blanks and lot stability blanks. MDLs for PM_{10} and PM_{coarse}, and for new analytical methods will be added to this QAPP when they become available. In some cases these may be identical to those for $PM_{2.5}$.

B.6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

B.6.1 Gravimetric Mass Laboratory

Two different relative humidity and temperature recording devices are used in the gravimetric mass laboratory to verify that measurements are correct and that variances around the chamber are taken into account. **Table B.6.1** details chamber environment inspection criteria, including how to appropriately document the inspection and troubleshoot if the inspection fails.

Table B.6.1. Inspection Criteria for Gravimetric Mass Laboratory

Item	Inspection Frequency	Inspection Parameter	Action if Item Fails Inspection	Documentation Requirement
Weigh Chamber temperature	Daily	20°–23°C	1) Contact RTI HVAC Department 2) Call service provider that holds maintenance agreement	1) Document in weigh room log book 2) Notify Lab Manager
Weigh Chamber humidity	Daily	30%–40%	1) Contact RTI HVAC Department 2) Call service provider that holds maintenance agreement	1) Document in weigh room log book 2) Notify Lab Manager

EPA Document 2.12 states that filters will not be weighed if the relative humidity and temperature measurements in the weighing environment are not within acceptance criteria (RH = 30%–40% with a control of ∀5% and temperature = 20E–23EC with a control of ±2E) for the preceding 24 hours. Critical criteria tables included in March 2000 guidance from OAQPS on the use of data flags for $PM_{2.5}$ AQS data offer slightly relaxed acceptance criteria (RH = 30%–40% with a control of ±5% *standard deviation* and temperature = 20E–23EC with a control of ±2E *standard deviation*). Gravimetric lab personnel will ensure that filters are equilibrated for at least 24 hours before weighing. In the event of protracted chamber downtime that would cause the laboratory holding time to be exceeded, the analyst must decide whether to weigh the filters without the full 24 hours of equilibration, to weigh the filters when relative humidity and/or temperature measurements in the weighing environment have exceeded acceptance criteria, or to wait until the chamber controls are functional, thus exceeding holding time limits. This choice has little impact on overall data validity, as the consequence of each choice is the same: an AQS

validity status flag of 2, "operational criteria exceeded." In each case, the analyst must specify the data flag and insert a brief explanation of the problem in the spreadsheet that is sent to data management.

Table B.6.2 details the weigh room schedule and who will be responsible for performing the maintenance.

Table B.6.2. Gravimetric Mass Laboratory Maintenance Schedule and Responsibility

Item	Maintenance Frequency	Responsible Party
▪ Multi-point Micro-balance ▪ Internal calibration ▪ Maintenance ▪ External calibration	Daily Yearly or as needed Yearly or as needed	▪ Balance Analyst ▪ Mettler Toledo service representative
Comparison of NIST Standards to laboratory working and primary standards	Yearly or as needed	RTI Laboratory Supervisor
Cleaning weigh room	Monthly	Balance Analyst
Sticky floor mat (just outside weigh room)	Monthly or as needed	Balance Analyst
HVAC system preventive maintenance	Yearly	RTI HVAC Personnel

B.6.2 Ion Chromatographic Laboratory

In the ion chromatographic laboratory, several different instruments are routinely tested and maintained**. Table B.6.3** details the items to inspect, how to appropriately document the inspection, and action items if the inspection fails. **Table B.6.4** details the IC maintenance schedule and who will be responsible for performing the maintenance.

Table B.6.3. Inspection Criteria for Ion Analysis Laboratory

Item	Inspection Frequency	Inspection Parameter	Action if Item Fails Inspection	Documentation Required
IC column back pressure	Each day of use	Column-specific; supplied by Dionex	1) Check for blockage 2) Replace column if necessary	Record pressure in instrument log book
IC background conductivity	Each day of use	Eluent specific; within control limits	1) Check eluent flow 2) Check suppressor 3) Call Dionex tech support if necessary	Record conductivity in instrument log book
Baseline	Each day of use	Steady; no "pulsing"	1) Check for leaks 2) Check for air bubbles in conductivity cell 3) Call Dionex tech support if necessary	Record corrective action in instrument log book

Table B.6.4. Ion Analysis Laboratory Maintenance Schedule and Responsibility

Item	Maintenance Frequency	Inspection Parameter	Responsible Party
IC system preventive maintenance	Yearly	Check all valves, fittings, flows; replace as needed	Dionex service representative
Check for leaks at valves and column fittings	Daily	Check for leaks	IC analyst
Ultrasonic bath	Monthly	Check for power	IC analyst

B.6.3 EDXRF Laboratory

B.6.3.1 RTI

In RTI's XRF laboratory, the XRF instrument is subjected to routine testing and maintenance. **Table B.6.5** details the items to inspect, documentation to record inspection, and the action items if the inspection fails. **Table B.6.6** details RTI's XRF maintenance schedule and the responsibilities of the person performing the maintenance.

Table B.6.5. Inspection Criteria for RTI EDXRF Laboratory

Item	Inspection Frequency	Inspection Parameter	Action if Item Fails Inspection	Documentation Required
Energy calibration	Daily	Wavelength alignment of the instrument	This is an automated process	Document in instrument's run log book.
Calibration verification	Weekly	Percent recovery of seven elements on thin-film NIST standards	Adjust instrument calibration factors	Document in instrument's run log book; the results are stored in XRF database.
Ongoing calibration verification	Run with every tray of samples	90%–110% recovery using a multi-element sample containing Ti, Fe, Cd, Se, Pb, and SiO deposits of 5-10µg/cm^2	Re-check instrument calibration and adjust if necessary; re-analyze samples	Document in instrument's run log book
Fast Discriminator (FD)	As needed	FD value is located on the system status; if the FD is set too low, low energy peaks can be lost; if the FD is set too high, the dead time readings can be inaccurate and higher than normal	Service required	Document in service notebook

Table B.6.6. RTI EDXRF Laboratory Maintenance Schedule and Responsibility

Item	Maintenance Frequency	Responsible Party
Vacuum pump maintenance and oil level check	Monthly, as needed	XRF analyst
Stability test	As needed, depends on Ecal; this test checks for instability due to changes in the x-ray tube output or peak shift both of which will be detected	XRF analyst
State-mandated radiation safety checks	Semi-annually	Safety Officer and XRF analyst

B.6.3.2 CHESTER LabNet

In the EDXRF laboratory, the EDXRF instrument is subjected to routine testing and maintenance. **Table B.6.7** details the items to inspect, how to appropriately document the inspection, and action items if the inspection fails. **Table B.6.8** details the EDXRF maintenance schedule and who will be responsible for performing the maintenance.

Table B.6.7. Inspection Criteria for CHESTER LabNet EDXRF Laboratory

Item	Inspection Frequency	Inspection Parameter	Action if Item Fails Inspection	Documentation Required
Fundamental calibration	Weekly	Percent recovery of 11 elements on thin-film NIST standards	Instrument recalibration	Document in instrument log book
Ongoing calibration	Every 10 samples	95%–105% recovery of six elements	Reanalysis, check fundamental calibration	Document in instrument log book
Excitation condition check	Every sample	Within analysis uncertainty	Reanalysis	Document in instrument log book

Table B.6.8. CHESTER LabNet XRF Laboratory Maintenance Schedule and Responsibility

Item	Maintenance Frequency	Responsible Party
Pump maintenance and oil level check	Weekly	XRF analyst
Chiller maintenance and coolant level check	Weekly	XRF analyst
Replenish liquid nitrogen in Dewar	Weekly	XRF analyst

B.6.4 ICP/MS Laboratory

Selected filters will be analyzed by ICP/MS to achieve higher sensitivity than is possible with the XRF method used for the bulk of the filter samples. The list of elements analyzed by ICP/MS is shown in **Table B.6.9.**

Table B.6.9. Elements to be Analyzed by ICP/MS

Aluminum*	Antimony	Arsenic	Beryllium	Cadmium
Chromium	Cobalt	Copper	Barium	Lead
Manganese	Mercury	Nickel	Selenium	Silver

*ICP-MS analysis is not recommended using Whatman Teflon filters due to background levels present in the stiffening ring.

Filter samples are removed from cold storage or received after analysis by XRF. Sample information is entered into the extraction logbook. The filters are loaded into 50 mL, acid-cleaned centrifuge tubes, with the loaded side facing inward. A 25 mL aliquot of extraction solution is added to cover the filter in the tube. The tubes are capped and placed in a heated ultrasonic bath for 3 hours to extract the metals on the filter. The samples are allowed to cool, centrifuged, and a 5 mL aliquot of the supernatant liquid is removed for ICP-MS analysis. The ICP-MS is optimized daily with a tuning solution, and the samples are analyzed against a new calibration curve for each analytical sequence.

Two Thermo X-Series Inductively Coupled Plasma Mass Spectrometers are used for this procedure. Both instruments are equipped with collision cell technology and the following major components:

- Torch box, RF generator, lens stack, quadrapole, and electron multiplier detector
- Personal computer with the Thermo PlasmaLab software
- Vacuum pump and turbo pump
- Refrigerated water recirculator
- Uninterruptible Power Supply (UPS), which supplies the entire instrument, PC, and chiller with 15 minutes of uninterruptible power in full operation and 2 hours of vacuum support in standby mode
- 240-position autosampler housed in a HEPA-filtered enclosure to protect against atmospheric contamination.

Standards are prepared from NIST-traceable, commercially purchased stock solutions. A series of concentrations ranging from 0.25 ppb to 500 ppb along with a blank are prepared to bracket expected analyte concentrations. The range of calibration standards will be adjusted based on the indigenous concentration of individual elements in the samples.

A check standard is prepared from a second source of commercially purchased NIST-traceable stock standards to verify the validity of the calibration curve. The check standard is prepared at a concentration that is not a point on the calibration curve and near the midpoint of the calibration range. The check standard is analyzed following calibration and before the analysis of any samples at a frequency of one per every 10 samples, and at the end of analysis. All sample results to be reported must be bracketed by passing standard checks.

Calibration is performed at the beginning of each analytical run. The correlation coefficient must be ≥ 0.995 for each element. The result for each standard concentration on the curve must be +/– 10% of the expected value for the point to be valid. The initial calibration check, which is prepared from a separate standard source than the calibrants, must pass at +/–

10% of the expected concentration for each element. The initial calibration blank must be less than the reporting limit for each element. If an element fails to meet the calibration criteria, a new calibration must be run and the associated samples reanalyzed for the given element.

Several different quality control activities are performed as part of the analysis procedure. These activities, their frequency, and the measures of acceptable performance are given in **Table B.6.10.**

Table B.6.10. Quality Control Activities for ICP/MS Analysis Sequences

Activity	Frequency	Measure of Acceptable Performance
Calibration	Every sequence	Correlation coefficient of ≥ 0.995
QC blank	Analyzed after calibration, every 10 samples, and at the end of the sequence	All elements below method reporting limit
QC check sample	Analyzed after calibration, every 10 samples, and at the end of the sequence	90%–110% recovery
MDL	Every 6 months	n/a
Duplicate analysis	One per 20 samples	n/a – flag LDU if > 20%

The detection limit for each element is calculated by analyzing seven replicates of a known standard concentration and multiplying the standard deviation of the replicates by three. The uncertainty for the measurement is the percent relative standard deviation, which is calculated by the instrument operating software for the triplicate readings taken on each sample.

B.6.5 Organic/Elemental Carbon (OC/EC) Laboratory

B.6.5.1 RTI OC/EC Laboratory

In the RTI OC/EC laboratory, the two Sunset Laboratory CSN thermal-optical transmittance (TOT) analyzers and the two IMPROVE_A/TOR-TOT analyzers (a Sunset Laboratory dual mode and a DRI Model 2001) are routinely tested and maintained. **Table B.6.11** details the analyzer maintenance schedule and who will be responsible for performing the maintenance.

Table B.6.11. OC/EC Laboratory Maintenance Schedule and Responsibility

Item	Maintenance Frequency	Responsible Party
OC/EC analyzers	As needed (daily checks are performed on key components)	RTI OC/EC analyst
Analytical balance	Yearly or as needed	Mettler Toledo, Inc., service representative
Muffle furnace	As required	RTI OC/EC Analyst

B.6.5.2 DRI OC/EC Laboratory

In the DRI OC/EC laboratory, the twelve dual reflectance/transmittance (TOR/TOT) analyzers are routinely tested and maintained. **Table B.6.12** details the analyzer maintenance schedule and who will be responsible for performing the maintenance.

Table B.6.12. OC/EC Laboratory Maintenance Schedule and Responsibility

Item	Maintenance Frequency	Responsible Party
TOR or TOR/TOT Analyzer	As needed (daily checks are performed on key components)	DRI OC/EC analyst
Analytical balance	Yearly or as needed	Quality Control Services (routine) or Mettler Toledo, Inc., service representative (as needed)

B.7 Instrument Calibration and Frequency

B.7.1 Gravimetric Mass Laboratory

The microbalances are externally calibrated and serviced, if necessary, at least annually or as needed when problems are detected. RTI keeps records on the service dates and calibration results. NIST-traceable standards are tracked to determine if any bias is entering into the system. These standards are recertified annually. Control charts based on a standard weight are maintained to track long-term drift and other time-dependent changes in microbalance performance.

Calibrations in RTI's analytical laboratories are performed on each day of analysis. See the respective SOPs for more details.

B.7.2 Ion Chromatography Laboratory

Multipoint calibration (0.05 to 25.0 ppm) is performed daily. Calibration is followed by analysis of QA/QC samples. Included are:

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

Initially, only the calibration curve from 0.05 to 10.0 ppm is used for the calculation of the anion/cation concentrations. All field sample ion concentrations that exceed 10.0 ppm are recalculated with the 25.0 ppm standard added to the calibration curve.

B.7.3 EDXRF Laboratory

RTI and CHESTER LabNet obtain their calibration standards from the same supplier (Micromatter Co.). Both labs analyze a multi-element standard that is prepared by Micromatter containing Si, Ti, Fe, Se, Cd, and Pb at levels of 5–10 μg/cm^2. The multi-element standard is analyzed with each tray of samples.

B.7.3.1 RTI

Energy calibration is performed using a copper calibration standard provided by ThermoNoran. This is an automated test to adjust the pulse processor gain so that the detected x-rays appear at the correct energy. Failure to perform this test daily could result in inaccurate quantitative results, misidentification, or failure to detect one or more elements. Peak calibration is performed by analyzing the following thin-film standards:

Purchased from Micromatter, Co. **Table B.7.1** lists the elements and compounds on thin Mylar film that are to be analyzed for the CSN.

Table B.7.1. Elements Present on Micromatter, Co. Standard

Analyte	Analyte	Analyte
Sodium or Chlorine as NaCl	Chromium as Cr metal	Rubidium or Iodine as RbI
Magnesium as Mg metal	Manganese as Mn metal	Strontium as SrF2
Aluminum as Al metal	Iron as Fe metal	Silver or Mercury as Ag-Hg Amalgam
Silicon as SiO	Cobalt as Co metal	Cadmium or Selenium as CdSe
Gallium or Phosphorus as GaP	Nickel as Ni metal	Indium as In metal
Sulfur as CuSx	Copper as Cu metal	Tin as Sn metal
Potassium or Iodine as KI	Zinc as ZnTe	Antimony as Sb metal
Calcium as CaF2	Arsenic as GaAs	Barium as BaF2
Titanium as Ti metal	Selenium as Se metal	Cerium as CeF3
Vanadium as V metal	Bromine or Cesium as CsBr	Lead as Pb metal

Calibration verification is performed weekly by analyzing the following NIST thin-film standards provided by EPA. The expected value and the uncertainties are published with the NIST standards:

NIST SRM 1832 multi-elemental XRF thin film standard certified values are shown in **Table B.7.2.**

Table B.7.2. Certified Values of Elements Present on NIST Standard Reference Material No. 1832

Analyte	Certified Value (µg/cm^2) SRM 1832
Aluminum	15.1 ± 0.98
Silicon	35.5 ± 1.14
Calcium	20.1 ± 1.30
Vanadium	4.83 ± 0.49
Manganese	4.62 ± 0.49
Cobalt	1.05 ± 0.06
Copper	2.45 ± 0.16

Re-calibration is performed on an as-needed basis.

B.7.3.2 CHESTER LabNet

Energy calibration is performed using Kevex Standard No. 2036 and the IXRF software calibration option in which a low-energy line is measured at the Al K_2 line (1.487 KeV) and a high-energy line is measured at the Cr K_2 line (8.047 KeV). The program will then assign channel number 149 as the Al peak centroid and channel 805 as the Cu peak centroid, thereby calibrating each channel increment at 10 eV.

Peak calibration is performed by analyzing the following thin-film standards:

1. Micromatter, Inc., vapor deposit of single or two non-interfering elements onto thin mylar film
2. EPA organo-metallic acetate film, usually with two non-interfering elements
3. NIST SRMs 1832 and 1833 multi-element vapor deposits on glass films.

Peaks should be Gaussian-shaped with at least 2,000 counts in the central channel (centroid). Methods for calculating peak location data, calibration factors, and interference factors correction for $PM_{2.5}$ particle size are presented in Chester LabNet SOPs and accompanying discussion.

Recalibration is performed on an as-needed basis. Calibration verification is performed weekly using Calibration Verification Standards (NIST SRMs 1832 and 1833). Control limits are the uncertainties published with the NIST standards; for results outside of control limits, fundamental recalibration of the instrument is performed, followed by reanalysis of the NIST standards.

B.7.4 OC/EC Laboratories

B.7.4.1 RTI OC/EC Laboratory

As shown **in Table B.7.3,** calibration of a CSN/TOT analyzer is checked daily using an external standard and during every analysis using an internal standard. The external standard is prepared by spiking a clean section of quartz filter with 10 µL of a standard sucrose solution, which corresponds to a filter loading of about 21 µgC. The internal NIST-traceable standard is

5% methane in helium. A set of three concentrations of sucrose external standards (10 µL of each, giving a range corresponding to about 4-42 µgC) of filter is run weekly.

Also shown **in Table B.7.3,** calibration of an IMPROVE_A/TOR-TOT analyzer is checked daily using both an internal standard and an external standard and during every analysis using an internal standard. The daily internal standard check consists of automated injections of the internal standard (5% CH_4/He) in a non-oxidizing atmosphere (pure He), an oxidizing atmosphere (2% O_2/He), and at the end of the run. The daily external standard is prepared by spiking a clean section of quartz filter with about 27 µgC in 15-µL of a standard sucrose solution. The NIST-traceable internal standard is 5% methane in helium. A set of five injections (5 to 20 µL, giving a range corresponding to about 9-36 µgC) each of a sucrose external standard and a KHP external standard and six injections (100 to 1500 µL, giving a range corresponding to about 2-36 µgC) each of NIST-traceable external CH_4/He and CO_2/He gas standards are used for a full calibration semi-annually or after significant instrument repairs.

Table B.7.3. RTI OC/EC Instrument Calibration and Frequency

Laboratory	Instrument	Calibration: Frequency
RTI OC/EC Laboratory	CSN/TOT carbon analyzer	Three-point external calibration: run initially to demonstrate linearity; run once a week thereafter One-point external calibration check: run daily to confirm that FID response has not changed by more than ± 10% since the last three-point calibration End-of-run calibration peak with 5% CH_4/He: every analysis (counts within 95% to 105% of average for the day)
RTI OC/EC Laboratory	IMPROVE_A /TOR-TOT carbon analyzer	Semi-Annual calibration with four separate standards: separate 6-pt cals with 5% CH_4/He and 5% CO_2/He and separate 5-pt cals with a sucrose solution and a KHP solution (average slopes for the four separate calibrations within 95%-105% of average slope; recovery and internal standard counts for each run within 95%-105% of average for that standard) Daily Auto Cal check: Injection of CH_4/He standard in He, He/O_2, and end of run (area counts for the 3 injections must be within 95%-105% of the average for the three) Daily calibration check: mid-level injection of sucrose standard (recovery 90-110%, internal standard counts within 90%-110% of average counts for last full semi-annual calibration) End-of-run calibration peak with 5% CH_4/He standard, every analysis (counts must be >20,000 and within 95%-105% of average counts for the day)

B.7.4.2 DRI OC/EC Laboratory

As shown in **Table B.7.4,** the DRI carbon analyzers are calibrated in three ways in this order:

1. Semi-annual (or after instrument repair) full calibration using KHP, sucrose, CH_4/He, and CO_2/He standards;
2. Daily calibration checks using injections of the two gas standards (CH_4/He, and CO_2/He); and
3. Automatic injection of the CH_4/H_2 gas standard as an internal standard at the end of each analysis.

Table B.7.4. DRI OC/EC Instrument Calibration and Frequency

Laboratory	Instrument	Calibration: Frequency
DRI OC/EC Laboratory	IMPROVE_A /TOR-TOT carbon analyzer	Semi-Annual: Separate 5-pt cals with 5% CH_4/He, 5% CO_2/He, sucrose solution, and KHP solution (average slopes for the four separate calibrations; new slope 90%–110% of 5% previous slope if no instrument repairs) Calibration injections of the two NIST traceable gas standards; reverse two cal gases and the carrier gases (O_2/He and He) between morning and afternoon injections (counts should be same) End-of-run calibration peak with 5% CH_4/He calibration gas performed as part of routine program (counts > 20,000)

B.8 Inspection/Acceptance Requirements for Supplies and Consumables

Supplies and consumables are inspected by the laboratory supervisor or laboratory technicians to determine if they are acceptable for use on the project.

B.8.1 Filters

RTI will purchase, inspect, and verify filter lots to be used for the CSN according to specific procedures applicable to each type of filter and for other sampling media such as reagents used to prepare denuders.

RTI will purchase the appropriate number of filters and other sampling media to supply the needs of the monitoring organizations, as directed by the DOPO. The quantity of filters ordered will be sufficient to provide spares to replace defective filters and to satisfy all QA/QC needs (e.g., laboratory blanks and field blanks). Cassettes, if required, are provided by the state sampling authority responsible for field monitoring. The number of cassettes must be sufficient to allow for shipments to the sampling sites as well as preparation of upcoming shipments from RTI.

Regardless of the filter type or the project's specific analytical requirements, filters of all types must be examined individually prior to use to ensure that one or more of the following defects does not exist:

- **Pinholes.** A small hole or tear in the filter matrix that appears when examined over a light table.
- **Loose material.** Any extra loose material or particulate contamination on the filter surface.
- **Separation of reinforcing ring.** Any separation or discontinuity of the seal between the filter matrix and the outer retaining or reinforcing ring.
- **Discoloration.** Any visible discoloration that indicates problems during the filter's manufacture or packaging.
- **Filter non-uniformity.** Any obvious difference in the spatial uniformity of the filter matrix structure or color. Analytical techniques that rely on the uniformity of aerosol deposition (e.g., XRF) are particularly sensitive to filter defects of this type.
- **Other.** Defined as any other defect (e.g., wrinkling, warping) that might prevent a filter from providing accurate measurement data.

The other acceptance criteria applicable to the different filter types are described in the following sections.

B.8.1.1 Teflon Filters

RTI will purchase the appropriate number of Teflon filters (Whatman, Catalog No. 7592-004) as directed by the DOPOs. The quantity of filters ordered will be sufficient to provide spares to replace defective filters and to satisfy all QA/QC needs (e.g., laboratory blanks and field blanks). Cassettes, if required, must be provided by the state sampling authority. The number of cassettes should be sufficient to allow for shipments to the sampling sites as well as preparation of upcoming shipments from RTI. Acceptance testing of Teflon filters (and other filter types) to be used for ion sampling should be based on analysis of a minimum of 2% per lot (or two filters). Lots must be rejected when the levels of individual anion or cation species exceed 1µg/filter.

B.8.1.2 Nylon Filters

Nylon filters (Whatman, 47 mm diameter, 1 micron pore size) are purchased from the McConnell Group (Cat. No. TM185967). These filters are prepared as follows:

1. Rinse twice in deionized water, approximately one minute per rinse
2. Using TCLP apparatus, rotate for 7 hours in a 2-liter polypropylene jar completely filled with deionized water; drain and repeat for approximately 24 hours
3. Dry in a 40°C oven for ½ to 1 hour.

Nitrate, sulfate, sodium, ammonium, and potassium levels in each lot should be less than 1µg/filter each based on 2% analysis per lot. Prepared nylon filters should be sealed and refrigerated until needed for field sampling.

B.8.1.3 Quartz Filters

The Whatman 47 mm diameter quartz filters and the Pall Tissuquartz 25mm diameter filters are prepared by RTI in-house. The procedure is as follows:

- The 47 mm filters are typically prefired in batches of 100, in a muffle furnace at 900°C for 3 hours. The 25mm filters are prefired typically in batches of 100 for 4 hours.

- The filters are acceptance tested once they have cooled for at least 2 hours, under a low flow of nitrogen in the furnace which has been turned off.

- Either 2% or a minimum of 2, whichever is more, of the filters are randomly selected from the cleaned batch for total carbon testing according to National Institute for Occupational Safety and Health (NIOSH) Method 5040. The results of the acceptance testing show evidence of inadequate cleaning or contamination that may have occurred during transport.

- If any filter analyzed gives, a measured blank total carbon level exceeding 1µg/cm2 for the 47mm filters and 1.5µg/cm2 for the 25mm filters, the filters from that batch will be rejected or recleaned.

- Batches of the 25mm quartz filters that pass the acceptance-testing criterion (≤1.5 µg/cm^2 total carbon) are assigned a Batch Number. Batches of acceptance-tested filters are placed individually in petri slide holders, which are placed in a resealable plastic bag labeled with the Batch Number. The resealable plastic bag is stored in a freezer at ≤-15°C until the filters are used.

- Batches of the 47mm quartz filters that pass the acceptance-testing criterion (≤1 µg/cm^2 total carbon) are assigned a Batch Number, which is used to associate the history of the filters with the batch and to track the batch until the filters are assigned individual identification numbers in the Sample Handling and Archiving Laboratory. Batches of acceptance-tested filters are placed individually in petri dish holders, which are placed in a resealable plastic bag labeled with the Batch Number. The resealable plastic bag is stored in a freezer at ≤-15°C until the filters are used.

- Filters are kept in a freezer until just prior to loading into modules.

The reason for the difference in the acceptance criteria is the size of the filter punch used for the analysis: The 25mm diameter filter used for the IMPROVE_A OC/EC method requires a punch that has an area of about 0.5 cm^2, and the 47 mm diameter filter used for the CSN/TOT OC/EC method requires a punch that has an area of about 1.5 cm^2. RTI will store batches of prepared filters in a freezer until they are needed in preparation for field sampling. Before loading onto the cartridges or modules for field sampling, each quartz filter is carefully inspected for uniformity in size, shape, thickness, and appearance. Any filters that are visually flawed will be discarded.

B.8.2 Criteria for Other Materials

Other RTI laboratories for Ion Analysis, Carbon Analysis, and Denuder Refurbishment will use the types and quality of reagents, purified water, and other materials specified in the respective SOPs.

B.9 Data Acquisition Requirements (Non-direct Measurements)

This work does not 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.

B.10 Data Management

This section describes Data Management System (DMS) Quality Control/Quality Assurance (QC/QA) as well as how the DMS promotes overall QC/QA program activities.

B.10.1 Overview

The core of the DMS is a custom database, using Microsoft SQL Server as a relational database server. Custom user programs for data entry and processing were written in Access 2000. To minimize data entry errors, the system imports laboratory data directly from electronic data files produced by laboratory instrumentation systems.

RTI created preset sampling configurations to ensure that samples were scheduled, prepared, and processed consistently. Each sampling event is scheduled for a specific sampling configuration. These configurations specify which sampling media are used by specific sampler channels, what flow rates are appropriate for sampling, which analyses are to be performed on each sampling medium, and how the calculations for each analysis are to be performed.

The system tracks each sampling module, event, and sampling medium with a unique identification number (ID). To prevent data entry errors, barcode readers are used extensively and each ID contains a check digit to reduce errors in manual entry.

Data reports are copied to a separate external Web server for review by the site data contacts. Data revisions are submitted via e-mail and incorporated into the SQL Server database. An AQS-ready data file is then prepared for import into AQS.

B.10.2 DMS Design Features

Careful identification of each sampling module and sampling event is essential in combining the correct analytical results with the correct sampling event. Many features have been designed into the DMS to prevent common data entry errors. Unique identifiers are generated for each sampling event, module, and sampling medium. These identifiers are used to link modules with configurations, sampling events, and analyses. Barcode scanners are used for data entry to reduce the chance of data entry errors. In addition, all identifiers have check digits to permit the data entry programs to immediately catch most manual data entry errors. Database referential integrity also prevents linkage of any sampling module, event, or sampling medium that has not been previously created in the database system.

B.10.2.1 Sample Identifiers

Each item that is tracked by the DMS is assigned a unique identification number (ID). Tracked items include record sheets such as the Field Sampling Chain-of-Custody Form, as well as equipment such as sampler modules, shipping containers, and analysis aliquots in storage. ID numbers that are not automatically generated at the time of data entry (i.e., those that are entered from a local workstation) are obtained from preprinted barcode stickers. The stickers are generated with a unique leading character that specifies the type of item being generated and with a trailing checksum character. The leading character is used by data entry applications to prevent entry of a data item's ID into the wrong field on a form. As an example, a module ID cannot be entered into the aliquot (analytical sample) ID field because module IDs begin with "I" and aliquot IDs begin with "A." The trailing checksum character is used by data entry applications to detect and prevent most common transposition and single character entries. **Table B.10.1** shows the labels currently in use by the CSN Program.

Table B.10.1. Label Identifiers for Tracking CSN Records and Equipment

Prefix	Label Type
Q	Field Sampling Chain of Custody
A	Aliquot
I	Sampler Module ("Inventory")
R	Measurement Request ID
C	Shipping Container (Cooler)
B	Storage Bins
L	Bin Storage Location
H	Aliquot Shipment Batches (to laboratories)
Y	Aliquot Archiving Box

B.10.2.2 Barcode Scanners

Handheld laser scanning barcode readers are used at all SHAL processing stations to read barcode ID labels. These readers are inserted into the client workstation's keyboard connection and provide a rapid and reliable means of entering ID labels used in sample processing.

B.10.2.3 Relational Integrity

SQL Server permits establishment of foreign key constraints between fields in related tables. These constraints provide automatic enforcement of database referential integrity. Enforcement occurs at the server level and is not dependent on application-level programs. Referential integrity constraints prevent entry of a record in a dependent (child) record without a corresponding record in the independent (parent) table. This prevents entry of records that are not linked to other database items. Similarly, an independent (parent) record cannot be deleted while records that depend on that record exist. This prevents the creation of orphaned records.

As an example of referential integrity, laboratory results for a laboratory sample (aliquot) cannot be entered unless the laboratory sample number was previously entered into the Aliquots Table (at the time the sample was created). Thus, attempts to enter laboratory results from other programs or from programs that have incorrect sample identification would be prevented. Attempts to delete an aliquot that has analytical data would also be prevented, as this would orphan the analytical results (i.e., leave results that have no corresponding sample information).

B.10.2.4 Double Entry of Field Data

Sample event information (such as elapsed sample time, volume, barometric pressure, temperature, and sampler QC information) for scheduled events are transmitted from the field on a multi-copy Field COC Form. To prevent data entry errors, information on these forms are double entered and compared by a comparison program. Any discrepancies are resolved before transfer of the double-entered data to the main database.

B.10.2.5 Direct Transfer of Laboratory Data

All laboratory data are sent from the laboratory to the DMS as an electronic file via e-mail. The laboratory data are obtained directly from instrument data system outputs that contain

the sample identifier and the measured value. Laboratory personnel add additional QC information during their QC review process. The resulting laboratory data files are directly transferred into the database using custom import programs. This direct transfer prevents data entry errors that could result from manually retyping data into the DMS.

B.10.2.6 Training and Development Databases

Separate training and development databases have been established for operator training and program development purposes, respectively. This permits us to train operators and develop new software without risk of modifying the actual program database. All output (forms, reports, etc.) from these databases contain clear labels to identify them as training or development reports. This prevents their accidental usage in the actual program. In addition, all data entry forms are color coded to clearly identify when a database other than the actual program database is in use. This prevents accidental entry of data into the training or development database when it was intended to be entered into the actual database.

B.10.2.7 Database Backup and Recovery

The information contained in the SQL Server database is backed up to tape on a nightly basis. Tape copies are maintained off site by RTI's IT department. Detailed procedures are covered in RTI's Speciation Data Disaster Recovery Plan.

B.10.3 Automated and Semi-Automated QC Limit Checks for Outlier Detection

The database contains provisions to add data quality flags to most data records. These data flags allow the annotation of data to indicate specific problems and or conditions that might affect data quality. Flags may be added to entire sampling events, individual sampler flow channels, analytical samples (aliquots), or individual analysis results. The flags are expanded during the reporting process so that flags that reflect an entire sampling event apply to all results in that event, flags affecting a sampler flow channel apply to all results using that channel, etc.

A number of automated range checks are currently in place. Outlier checks, also known as "Level 1 checks," are done based on mass balance, anion-cation balance ratios, and other metrics. Assigning the limits for these outlier checks required the development of sufficient historical data to establish a baseline to set appropriate QC limits. **Tables B.10.2** and **B.10.3** show the statistical QC limits that have been developed for $PM_{2.5}$ based on experience during the mini-trends pilot program. The upper and lower limits were based on the 2nd and 98th percentile points on the distributions of the mini-trends data. For blanks, the concentrations were flagged at the upper 95^{th} percentile. Similar validation limits will be developed for speciated PM_{10} and PM_{coarse} when sufficient data has been gathered.

Additional strategies for establishing acceptance limits should be discussed between RTI and EPA.

Table B.10.2. Statistical Validation Limits for Routine Data

Percentile	Tail	Validation Test	Sample Type	Limit, µg	Analyte(s)	Outlier Flag
2.0	LOWER	$PM_{2.5}$ Mass Conc.	ROUTINE	2.98	$PM_{2.5}$ Mass Conc.	QL1
2.0	LOWER	Anion/Cation Ratio	ROUTINE	0.86	All ions	QAC
98.0	UPPER	Anion/Cation Ratio	ROUTINE	2.82	All ions	QAC
2.0	LOWER	Mass Ratio	ROUTINE	0.60	All analytes	QMB
98.0	UPPER	Mass Ratio	ROUTINE	1.32	All analytes	QMB
2.0	LOWER	Sulfur/Sulfate Ratio	ROUTINE	0.25	Sulfate ion, XRF	QCR
98.0	UPPER	Sulfur/Sulfate Ratio	ROUTINE	0.45	Sulfate ion, XRF	QCR

Table B.10.3. Statistical Validation Limits for Blanks

Tail	Analyte(s)	Sample Type	Limit µg	Analyte	Outlier Flag
UPPER	$PM_{2.5}$ Mass	FIELD BLANK	50.00	$PM_{2.5}$ Mass	QL1

The Internal Flags shown in the last column are used to keep track of flagged data within the RTI database and are also shown on the monthly data reports; however, these are not accepted by AQS and must be converted into valid AQS validity status codes and AQS null value codes prior to delivery to AQS. **Table B.10.4** shows how different types of internal flags are converted into AQS codes. There is no one-to-one correspondence between the Internal Flags and the AQS Codes, so the QC reviewer or SHAL supervisor will assign the AQS Codes based on the identified reason for the violation of the screening limits. Because the causes for outliers is often unknown even after careful review of the available documentation, "generic" AQS codes must be used in these cases, as shown in the table.

Table B.10.4. Mapping of Outlier Flags onto AQS Codes

Objective Cause Found for Level 1 Outlier	AQS codes assigned	
	If NOT Invalid (Suspicious)	If Invalid
Lab Error	[1]	AR
Filter Damage	[1]	AJ
Module Assignment Error	(N/A)	AQ or AR
Sampler Malfunction	(N/A)	AN
Unusual Conditions Noted by Operator	[1]	[2]
Unknown Cause	5	AS or AM
Range Checks (Table 10.3)	(N/A)	5

[1] = Use the applicable AQS validity status code
[2] = Use the applicable AQS null value code
(N/A) = Not Applicable

Additional range checks based on fixed criteria are also performed and AQS flags are assigned as shown in **Table B.10.5.**

Table B.10.5. Automated Checks Based on Fixed Criteria

Parameter	Limits	AQS Null Value Code
Exposure Duration, t_{exp}	$23 < t_{exp} < 25$ hrs	AN – Machine malfunction AQ – Collection error AV – Power failure Other code as appropriate
Holding Time before removal from sampler, $t_{pick\text{-}up}$	$t_{pick\text{-}up} < 48$ hrs	None – As per EPA direction
Average Flow Rate, F_{avg}	Within 10% of target flow rate	AH – Flow rate out of range

B.10.4 Report Preparation and QA Screening

Monthly data reports are screened carefully as described in the following sections prior to delivery to the state monitoring organizations.

B.10.4.1 Data Set Completeness and Integrity

Crosstab Reports showing site locations (rows) and sampling dates (columns) are generated and examined to get an overall picture of data completeness and integrity of data assignments. Missing or anomalous results are investigated and corrected by the data processing staff with the assistance of SHAL and QA personnel. The following crosstab tables are generated to facilitate this screening process:

1. **COC Form number for each event** – Field blanks, routine samples, and unscheduled blanks are displayed in a rectangular table. Missing cells in the table indicate missed exposures or missing data. When empty cells are observed, the data processing manager should be contacted to determine why the data have not been reported. If an investigation indicates that no data were received, then the SHAL supervisor should be consulted to find out if there was a problem with the shipment.

2. **Total counts of AQS-deliverable records** – Each sampler type should generate a specific number of AQS record counts. Exceptions typically are the result of missing analytical results or of processing records. RTI tries to hold reporting on events until all analysis results have been received. If no additional analysis data are expected for a particular exposure, the data manager will fill the records with "missing data" flags so that the data can be delivered and the exposure purged from the data delivery queue.

3. **Counts of invalid or suspicious analyte records** – Systematic stretches of invalid data for a site may indicate that a site is having problems or that filter shipments to the site should be discontinued.

4. **Sampled date vs. scheduled date** – Any event where these "date" records do not agree is investigated by examining the Field Sample COC (FSCOC) form and by contacting the monitoring agency, if necessary. If a sample was actually run on the wrong date, the data are transmitted to AQS with the date actually run. If the date is incorrect due to a typographical or other error, it is corrected.

B.10.4.2 Entry and Verification of Data Changes from the States

Changes requested by the state agencies are entered into RTI's database by the data processing staff as the comments are received from the respective DOPOs.

When the acceptance period for comments closes for a particular data delivery batch, the text-formatted AQS file is generated. This is checked for integrity using crosstab tables and other simple reporting methods. Record counts per event and sampling date checks are particularly helpful in detecting problems with the record set. After any anomalies are corrected, the AQS text file is regenerated and transmitted to EPA's AQS database as discussed in the next section.

B.10.5 AQS Data Entry

Routine (actual sampled), Field, and 24-Hour Blank data are currently sent to AQS. **Table B.10.6** summarizes all of the AQS parameter codes applicable to the $PM_{2.5}$ Chemical Speciation analytes. **Table B.10.7** presents the AQS parameter codes for field data parameters. Units for all analytes are micrograms per cubic meter under ambient conditions (i.e., not corrected to standard temperature and pressure). The nominal sampling period is 24 hours. Similar tables for PM_{10} and PM_{coarse} will be developed when the QAPP is finalized or when the parameter codes become available.

The validity status of AQS data is reported in two ways: Data that are qualified in some way but still may be useful for some purposes are assigned Validity Status Codes. These codes, shown in **Table B.10.8,** do not overwrite the data value, which provides data users with the option to include the data item in their analyses. Alternatively, data that are judged to be invalid receive an AQS Null Value Code. In the current AQS system, the Null Value Code overwrites the data value such that the AQS user cannot access the data. The Null Value Codes applicable to the CSN Program are shown in **Table B.10.9.**

Table B.10.6. Analytes and AQS Parameter Codes ($PM_{2.5}$ Only)

AQS Parameter Codes: PM2.5 (LC)	Analyte	Symbol	Analysis
88102	Antimony	Sb	EDXRF (trace elements)
88103	Arsenic	As	EDXRF (trace elements)
88104	Aluminum	Al	EDXRF (trace elements)
88107	Barium	Ba	EDXRF (trace elements)
88109	Bromine	Br	EDXRF (trace elements)
88110	Cadmium	Cd	EDXRF (trace elements)
88111	Calcium	Ca	EDXRF (trace elements)
88112	Chromium	Cr	EDXRF (trace elements)
88113	Cobalt	Co	EDXRF (trace elements)
88114	Copper	Cu	EDXRF (trace elements)
88115	Chlorine	Cl	EDXRF (trace elements)
88117	Cerium	Ce	EDXRF (trace elements)
88118	Cesium	Cs	EDXRF (trace elements)
88126	Iron	Fe	EDXRF (trace elements)
88128	Lead	Pb	EDXRF (trace elements)
88131	Indium	In	EDXRF (trace elements)
88132	Manganese	Mn	EDXRF (trace elements)
88136	Nickel	Ni	EDXRF (trace elements)
88140	Magnesium	Mg	EDXRF (trace elements)
88152	Phosphorus	P	EDXRF (trace elements)
88154	Selenium	Se	EDXRF (trace elements)
88160	Tin	Sn	EDXRF (trace elements)
88161	Titanium	Ti	EDXRF (trace elements)
88164	Vanadium	V	EDXRF (trace elements)
88165	Silicon	Si	EDXRF (trace elements)
88166	Silver	Ag	EDXRF (trace elements)
88167	Zinc	Zn	EDXRF (trace elements)
88168	Strontium	Sr	EDXRF (trace elements)
88169	Sulfur	S	EDXRF (trace elements)
88176	Rubidium	Rb	EDXRF (trace elements)
88180	Potassium	K	EDXRF (trace elements)

AQS Parameter Codes: PM2.5 (LC)	Analyte	Symbol	Analysis
88184	Sodium	Na	EDXRF (trace elements)
88185	Zirconium	Zr	EDXRF (trace elements)
88301	Ammonium	NH_4^+	Ion Chromatography, Cations
88302	Sodium	Na^+	Ion Chromatography, Cations
88303	Potassium	K^+	Ion Chromatography, Cations
88305	Organic Carbon STN	OC_TOT	OC/EC TOT
88306	Nitrate	NO_{3-}	Ion Chromatography, Nitrate
88307	Elemental Carbon STN	EC_TOT	OC/EC TOT
88332	PK1_OC STN	PK1_OC	OC/EC TOT
88333	PK2_OC STN	PK2_OC	OC/EC TOT
88334	PK3_OC STN	PK3_OC	OC/EC TOT
88335	PK4_OC STN	PK4_OC	OC/EC TOT
88336	PYROLC STN	PKYROLC	OC/EC TOT
88355	OC IMPROVE TOT	OCT	Organic and elemental carbon IMPROVE_A
88357	EC IMPROVE TOT	ECT	Organic and elemental carbon IMPROVE_A
88370	OC IMPROVE TOR	OCR	Organic and elemental carbon IMPROVE_A
88374	O1 IMPROVE	OC1	Organic and elemental carbon IMPROVE_A
88375	O2 IMPROVE	OC2	Organic and elemental carbon IMPROVE_A
88376	O3 IMPROVE	OC3	Organic and elemental carbon IMPROVE_A
88377	O4 IMPROVE	OC4	Organic and elemental carbon IMPROVE_A
88378	OP IMPROVE TOR	PCR	Organic and elemental carbon IMPROVE_A
88380	EC IMPROVE TOR	ECR	Organic and elemental carbon IMPROVE_A
88383	E1 IMPROVE	EC1	Organic and elemental carbon IMPROVE_A
88384	E2 IMPROVE	EC2	Organic and elemental carbon IMPROVE_A
88385	E3 IMPROVE	EC3	Organic and elemental carbon IMPROVE_A
88388	OP IMPROVE TOT	PCT	Organic and elemental carbon IMPROVE_A

Table B.10.7. Field Data and AQS Parameter Codes

AQS Parameter Code	Property	Units
68103	Min Ambient Temp	EC
68104	Max Ambient Temp	EC
68105	Avg Ambient Temp	EC
68106	Min Barometric Pressure	torr
68107	Max Barometric Pressure	torr
68108	Avg Barometric Pressure	torr

Table B.10.8. AQS Validity Status Codes

AQS Validity Status Code	Flag Name
IA	African Dust
IB	Asian Dust
IC	Chem. Spills and Industrial Accidents
ID	Cleanup After a Major Disaster
IE	Demolition
IF	Fire – Canadian
IG	Fire – Mexico/Central America
IH	Fireworks
II	High Pollen Count
IJ	High Winds
IK	Infrequent Large Gatherings
IL	Other
IM	Prescribed Fire
IN	Seismic Activity
IO	Stratospheric Ozone Intrusion
IP	Structural Fire
IQ	Terrorist Act
IR	Unique Traffic Disruption
IS	Volcanic Eruptions
IT	Wildfire – U. S.
IU	Wildland Fire Use Fire – U. S.
1	Critical Criteria Not Met
2	Operational Criteria Not Met
3	Possible Field Contamination
4	Possible Lab Contamination
5	Outlier – Cause Unknown
6	Data Prior to QAPP Approval
A	High Winds
C	Volcanic Eruptions

AQS Validity Status Code	Flag Name
E	Forest Fire
F	Structural Fire
H	Chemical Spills & Indust. Accidents
I	Unusual Traffic Congestion
J	Construction/demolition
O	Infrequent Large Gatherings
Q	Prescribed Burning
R	Clean up after a Major Disaster
S	Seismic Activity
T	Multiple Flags; Misc.
V	Validated Value
W	Flow Rate Average out of Spec.
X	Filter Temperature Difference out of Spec.
Y	Elapsed Sample Time out of Spec.

Table B.10.9. AQS Null Value Codes

AQS Code	Flag Name
BI	Sample Lost or Damaged in Shipment
AA	Sample Pressure out of Limits
AB	Technician Unavailable
AC	Construction/repairs in Area
AD	Shelter Storm Damage
AE	Shelter Temperature Outside Limits
AF	Scheduled but Not Collected
AG	Sample Time out of Limits
AH	Sample Flow Rate out of Limits
AI	Insufficient Data (Cannot Calculate)
AJ	Filter Damage
AK	Filter Leak
AL	Voided by Operator
AM	Miscellaneous Void
AN	Machine Malfunction
AO	Bad Weather
AP	Vandalism
AQ	Collection Error
AR	Lab Error
AS	Poor Quality Assurance Results
AT	Calibration
AU	Monitoring Waived
AV	Power Failure (Powr)

AQS Code	Flag Name
AW	Wildlife Damage
AX	Precision Check (Prec)
AY	QC Control Points (Zero/span)
AZ	QC Audit (Audt)
BA	Maintenance/routine Repairs
BB	Unable to Reach Site
BC	Multi-point Calibration
BD	Auto Calibration
BE	Building/site Repair
BF	Precision/zero/span

B.10.6 Data Management in the Laboratories

The individual analytical laboratories are responsible for managing their data prior to its entry into the CSN Program's database. The procedures for data management vary significantly between laboratories and are described in the respective SOPs.

B.10.7 Management and Reporting of Field Audit Data

RTI will provide data entry and reporting support for field calibration and audit data. These will include parameters of flow rate, temperature, pressure, and clock time checks. Details regarding data input and reporting have not been worked out as of the time of this writing, however principles described above will be followed in developing the data management processes and procedures for these new data.

C.1 Assessments and Response Actions

RTI will participate in any laboratory assessment or proficiency program established by EPA, and will maintain any analyst or laboratory certification required for the program.

The QA Manager for this project, Dr. Prakash Doraiswamy or his designee, will perform periodic technical systems audits of the RTI activities. These audits will cover all aspects of RTI's work, including sample receipt, custody, conditioning, weighing, shipping, data reduction and reporting. These audits are scheduled to be performed annually.

Prior to each audit, a checklist will be prepared, based on this QAPP, the SOPs, and applicable guidance documents. After the audits, the QA Manager will summarize the results in a memorandum to Dr. Jayanty within two weeks. These memoranda will clearly spell out any areas in which corrective action is necessary. If any serious problems are identified that require immediate action, such as a large, systematic analytical bias, the QA Manager will convey these to Dr. Jayanty verbally or through electronic mail the day that such problems are identified. Corrective actions are the responsibility of Dr. Jayanty and will be documented in a memorandum to the file and all relevant project staff, including the QA Manager. The QA Manager will verify the effectiveness of any formal corrective actions and summarize these in memoranda to Dr. Jayanty.

Since these memoranda constitute the corrective action system for this project, all memoranda will be retained in the QA Manager's files, where they will be available for internal or external review.

As SPM, Dr. Jayanty will conduct ongoing informal surveillance of project activities. If new staff members eventually perform some of the activities that others are initially responsible for, the experienced personnel and/or technical supervisors will perform ongoing surveillance of the new persons' work to ensure that the quality of the results is comparable with the previous results.

C.1.1 External Quality Assurance Assessments

RTI's PM speciation laboratories, including subcontractor laboratories, participate in external QA assessments as requested by EPA. The on-site audits and assessments as of this writing are listed below. The most current assessments and reports are available at the PM2.5 Speciation Quality Assurance section of EPA's AMTIC website, http://www.epa.gov/ttn/amtic/pmspec.html.

- EPA/NAREL:
  - Experimental Inter-comparison of Speciation Laboratories (June 15, 2011), (accessed 5/7/2012).
  - 2010 DRI laboratory Technical Systems audit (June 1, 2011), (accessed 5/7/2012).

- UC Davis Laboratory Audit (January 11, 2011), http://www.epa.gov/ttn/amtic/pmspec.html accessed 8/10/2010).

- Experimental Inter-comparison of Speciation Laboratories (June 15, 2010) , http://www.epa.gov/ttn/amtic/pmspec.html accessed 8/10/2010).

- October 2009 Technical Systems Audit Report of South Coast AQMD Chemical Speciation Laboratory (April 2, 2010), (http://www.epa.gov/ttn/amtic/pmspec.html accessed 8/10/2010).

- Technical Memorandum: Report of the Sept 2009 Technical Systems Audit of RTI's PM2.5 Speciation and Support laboratories (November 24, 2009), (http://www.epa.gov/ttn/amtic/pmspec.html accessed 8/10/2010).

- Technical Memorandum: Experimental Inter-comparison of Speciation Laboratories (September 9, 2009), (http://www.epa.gov/ttn/amtic/pmspec.html accessed 8/10/2010).

- Multilab Speciation PE Report (November 24, 2008), (http://www.epa.gov/ttn/amtic/pmspec.html accessed 8/10/2010).

- May, 2007 Technical Systems Audit of DRI's Laboratory

- July 2005 EPA audit of RTI Chemical Speciation Lab Operations

- October 2003 PM2.5 Chemical Speciation Trends Network Lab Audit Report 12/05/03, www.epa.gov/ttn/amtic/files/ambient/pm25/spec/audit03.pdf

– EPA audit of RTI Chemical Speciation Laboratory Operations 03/20/02, www.epa.gov/ttn/amtic/files/ambient/pm25/spec/rtiaudit2.pdf

– A report on the study to evaluate specific laboratory performance as part of the QA oversight of the PM2.5 speciation program 01/30/02, www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pememo.pdf

– "Chemical Speciation Laboratory Audit Report", 02/02/01, www.epa.gov/ttn/amtic/files/ambient/pm25/spec/audit.pdf

– "Performance Evaluation Samples for PM2.5 Chemical Speciation Network", 02/02/01, www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pesreport.pdf

– "PM2.5 Chemical Speciation Laboratory Audit Report", 09/01/00, www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pereport.pdf

- "Performance Evaluation Samples for PM2.5 Chemical Speciation Network", 09/01/00, www.epa.gov/ttn/amtic/files/ambient/pm25/spec/

- The State of Louisiana audits the Gravimetry Laboratory under the Louisiana Environmental Laboratory Accreditation Program. RTI performs PM2.5 filter weighings for the State. The most recent on-site assessment was performed November 13-14, 2008.

C.2 Reports to Management

Within 20 business days from receipt of the last sample in a monthly delivery batch, RTI posts the results of filter analyses together with the level 0 and level 1 validation flags to web site where they can be accessed by the EPA DOPO and State or local contact who submitted the delivery order. Upon approval by the State or local agency contacts, the data are posted to the AQS electronic data base. Draft and final composite annual data summary reports are issued by RTI to the EPA Project Officer.

The SPM or designee approves the monthly data postings and the annual reports. The SPM and the QA Manager are notified whenever there is a QA problem and will be apprised of corrective actions taken to solve the problem. The QA Manager will perform yearly technical audits and will submit a report to the project office within two weeks of the audits. Annual determinations of limit of detection, precision, an accuracy and a summary of results of analysis of external performance evaluation samples will also be submitted as part of the Annual Data Summary Report.

The following is a list of regularly scheduled technical and quality-related reports that will be provided to EPA:

1. **Level 0 Validation Report (Checklist)**. Data entry checking of the Custody Forms and Level 0 validation checklist is performed by double entry, with comparison done at RTI. This provides better accuracy than manually reviewing sampler forms to catch errors. Data flags generated during the Level 0 validation process are attached to each data record and are reported monthly to the DOPOs and monitoring agencies as part of regular monthly reporting described in items 3 and 4, below.

2. **Level 1 Validation Report (Checklist).** Cation/anion balance, sulfur/sulfate balance, and reconstructed mass balance reports (spreadsheets) are generated from the DBMS. Other statistical reports are done using data from the DBMS during monthly validation to assist validation personnel in identifying problems. Additional statistical reports are being developed as needed based on experience with the chemical speciation data. Data flags generated during the Level 1 validation process are attached to each data record and are reported monthly to the DOPOs and monitoring agencies monthly as part of items 3 and 4, below.

3. **Monthly Traceability Report.** A report to show traceability between components and analytical results for each sampling event is produced using the DBMS. "Traceability" means correctly relating the identity of filters, analytical results, etc.,

to the correct event. Electronic copies of this report are prepared and made available to each of the following: the state agencies submitting the delivery orders, the DOPOs, and the EPA Regional QA Laboratory. The information for the monthly traceability report is included as part of the Monthly Analytical Reports described in the next item.

4. **Monthly Analytical Reports (Electronic and hard copies).** Data for this report are generated from RTI's DBMS using the field and analytical data and the flags produced during Level 0 and Level 1 validation. RTI has developed SQL queries to produce the reports and spreadsheets. Electronic copies of these reports are made available to the DOPOs, the state agencies submitting the delivery orders, and EPA/OAQPS through RTI's password-protected website. These data users are notified by e-mail of the availability of new data sets as soon as they have been approved by the QA Officer and have been moved to the website.

5. **Quarterly Metadata Summary Reports** of laboratory/field changes and issues that impact data quality will be prepared by RTI with input from its subcontractors. These reports will include a complete listing of field changes (e.g., sites that shut down or changes to sampler types and dates of operation), laboratory changes (e.g., changes to lab procedures or operations and specific dates for the samples affected); and data collection or analysis issues and dates for samples affected or invalidated. Reports will be chronological and will succinctly describe the issues or changes, and the samples that were affected. One electronic copy of the report will be prepared and delivered to EPA OAQPS for posting on an EPA web site.

6. **Annual Data Summary Report.** RTI worked closely with EPA during the initial $PM_{2.5}$ CSN contracts to develop a comprehensive report responsive to data users' needs without being unnecessarily complex. This report provides a comprehensive overview of performance and summarizes quality issues, corrective actions, data completeness, MDLs, operational problems, blank levels, laboratory QC results, and precision estimated using data from sites where collocated samplers are situated. Other information such as reports of external TSAs and performance audits also may be included as available. An electronic copy of the finalized annual report is posted to AMTIC after EPA approval.

D.1 Data Review, Validation, and Verification Requirements

The following describes RTI's approach to data review, validation, and verification for $PM_{2.5}$ filter analysis. Similar procedures will be developed for the other forms of PM as the new program progresses. The QC criteria given elsewhere in this QAPP will be used as the data validation requirements. Any data that fails routine validation checks will be flagged for review by the monitoring agencies. Large or systematic exceedance criteria may also trigger a corrective action investigation by the RTI QA Manager.

Analytical data are validated using data from laboratory blanks, calibration checks, standard spikes, and laboratory duplicates. Based on QC verification data, a filter or other sample may be invalidated prior to submitting results to AQS, or the result may be flagged. Reasons for invalidation may include, but are not limited to, damaged filter, laboratory or field blank contamination, balance malfunction, and invalid holding times. Table B.10.8 provides the data validity flags currently available for $PM_{2.5}$ data in AQS. RTI will implement any additional or alternative flags that may be defined for $PM_{2.5}$ chemical speciation data.

D.2 Validation and Verification

RTI is responsible for validating analytical data produced in its laboratories. Subcontractor laboratories will apply Level 0 and Level 1 screening to data produced in their laboratories. RTI is responsible for overall, final data review, validation, and verification and for data reporting.

D.2.1 Level 0 Validation

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

Sources for the information used to screen data for Level 0 validation include the analyst's notes (logbooks and data forms), sample labels, COC forms, package shipping labels, and inspection results for filters and other sample media. Validation flags in the Level 0 data will also include the data flags for items such as power failures, temperature flags, and insufficient data for the averaging period generated by the speciation sampler in the field.

Occasionally, RTI personnel may become aware of an excessive rate of problematic samples from a particular monitoring organization. Such problems might include inadequate packing, excessive numbers of damaged filter media, and incorrectly or inadequately completed forms. RTI will work with the monitoring organization to bring about corrective action. Also, the RTI PM will contact the DOPOs (or the appropriate contact designated by the DOPOs) to inform him/her of the problem.

D.2.2 Level 1 Validation

Level 1 data are reviewed more fully for technical acceptability and reasonableness based on information such as routine QC sample results, data quality indicator (DQI) calculations, performance evaluation (PE) samples, internal and external audits, statistical screening, internal consistency checks, and range checks. Unacceptable long-term performance of the analytical system can also be uncovered in the process of documenting the DQIs of completeness, precision, accuracy, and detection limits, and comparing those indicators with the program's goals or DQOs.

In response to major or systematic problems identified by any of these procedures, corrective actions will be taken and data may be flagged or invalidated. Corrective actions based on Level 1 screening results will include, for example, the following:

- Investigating the specific conditions that contributed to an anomalous results for a single laboratory sample or related group of samples
- Contacting the site operator or monitoring agency to find out if there were any meteorological or other conditions that might lead to anomalous results
- Increasing the number of routine instrument checks such as multipoint calibrations, blanks, duplicates, and spikes
- Repeating analyses for the affected samples, if possible
- Reviewing logs and other records for transcription errors and evidence of operational problems or equipment malfunction.

Level 1 screening is conducted primarily after the data have been loaded into the data management system but before the data sets are transmitted to the state agencies for review. Initial screening of data is performed by data management personnel using screening criteria developed by the QA Manager and the laboratory personnel. Data validation flags generated during Level 1 screening are reviewed by the QA Manager; however, the QA Manager often requires input from one of the Technical Area Supervisors to address the problem. Data problems that originate outside the scope of RTI's operations are reported to the appropriate DOPO.

RTI will take any necessary corrective actions on problems identified during Level 0 and Level 1 data review activities and input from the state monitoring agencies during their review cycle.

Level 1 designation will be assigned to a set of data after the laboratory has performed all QC activities and has addressed all identified issues. Level 1 data will be transmitted to AQS along with AQS codes generated during the data validation process, as well as the changes requested by the monitoring agencies during their review.

D.2.3 Screening of Subcontractor Data

Although CHESTER LabNet will conduct their own Level 0 and Level 1 screening of the EDXRF data, RTI must further validate its results at Level 0 to ensure a consistent data set. In doing so, RTI will ensure that the sample identifications and COC information from the subcontractor are consistent with RTI's records. This process will consist primarily of comparing

the original sample numbers, dates, types, and so on, with the data received from the subcontractor. Of particular importance is ensuring that sample results from the subcontractor match up exactly with data from the other analyses for each exposure. Discrepancies in sample attribution uncovered during Level 0 screening will be investigated and rectified before the data are reported.

RTI will not perform detailed Level 1 screenings on the subcontractor's EDXRF data because this would duplicate efforts already expended. However, data from EDXRF are included in certain Level 1 checks such as reconstructed mass balance and sulfur/sulfate ratio.

RTI's screening of DRI's OC/EC includes assignment checks based on date, site, and the various ID numbers assigned to filters, aliquots and sampling events. Monthly validation queries are run that incorporate the DRI data, including reconstructed mass balance, invalid data counts by site and date. Data from DRI are also scanned for unusually high blank values and possible filter swaps between routinely sampled filters and blanks.

D.2.4 Data Corrections

RTI will investigate and attempt to make corrections to all laboratory problems. Corrections to quantitative data such as concentrations will not be applied unless they are defensible and are based on documented information. Questionable data will be flagged appropriately. The following paragraphs briefly discuss the types of data corrections that are typically encountered in this work.

D.2.4.1 Mass

Mass measurements will not be corrected for blank levels. Early in the development of the fine particulate program, a problem was encountered with Teflon filters with rings in which the manufacturer used an adhesive to attach the rings. Solvent continued to volatilize from the adhesive over several weeks, making it difficult to achieve constant weight. The filter manufacturer has since corrected this problem. If any other examples of time-dependent variances in mass measurements are found through analysis of blank filters, RTI will address these in consultation with EPA.

D.2.4.2 Elemental Analysis

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

- Escape peaks from secondary targets (e.g., chlorine K∝ from the titanium secondary target, titanium K∝ from the iron secondary target) are corrected by the instrument software.
- Inter-element interference corrections are carried out as described in the XRF SOPs.
- Attenuation corrections for light elements (Na through S) will be applied. The appropriate values for the correction factors differ by particulate size fraction ($PM_{2.5}$, PM_{10}, or $PM_{10-2.5}$), and XRF instrumental conditions.
- Filter lot-specific background levels will be accounted for in the instrumental method.

D.2.4.3 Ions

RTI's experience has indicated that artifacts and interferences pose no problem to the analysis of $PM_{2.5}$ ions using state-of-the-art IC systems. High-resolution columns and excellent chromatographic data processing software provide acceptable precision and accuracy. Precision and accuracy results for ions on filters similar to those used in the CSN are included in the ion analysis SOP.

D.2.4.4 OC/EC

This method is subject to a number of potential interferences. RTI will use its best judgment in applying corrections, will fully document any such corrections, and will discuss them with EPA before the data are submitted to AQS. RTI does not apply corrections or adjustments to account for the OC sampling artifact; however, if EPA provides the equations to be used for making such a correction, RTI will process the data back to 2009 and will post it to AQS.

Carbonates and bicarbonates present in some filter samples may cause interference in the OC/EC analysis. Two alternative procedures may be used to measure carbonate carbon. The first approach includes analysis of a second portion of the filter sample after it has been acidified (i.e., exposed to HCl vapor, which removes carbonate as CO_2) 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.

D.2.4.5 SVOCs

As with IC, state-of-the-art GC/MS provides high resolution of compounds (i.e., accurate qualitative analysis). Artifacts and interferences are more likely to be encountered in the sample extraction and cleanup stages. The following activities should ensure that artifacts such as analyte loss and poor recovery do not pose a significant risk to achieving acceptable analysis results:

- Field blanks
- Method blanks
- Field controls or matrix spikes
- Laboratory controls (spiked sample matrices)
- Method controls (spiked extraction solvent)
- Replicate extract analyses.

D.3 Reconciliation with User Requirements

RTI will ensure that its measurement data meet requirements as expressed in this QAPP and in the Chemical Speciation Guidance documents. RTI and its subcontractors will work closely with EPA to ensure that all required performance characteristics are met. RTI will do the following to ensure that our performance meets contract requirements and client expectations:

- Regular communications between the Program Manager and the DOPOs, the EPA Project Officer, and EPA technical leader. Communications will include conference calls scheduled biweekly or as needed, e-mail and written correspondence, and meeting with EPA/OAQPS personnel in the Research Triangle Park, NC, area.
- An organized system of corrective action notification and follow-through. Significant quality-related problems will be assigned corrective action request (CAR) numbers. The CARs will be tracked by the area supervisor and the QA Manager to ensure that quality problems are addressed in a systematic way. This system will enable the Program Manager to allocate the resources necessary to resolve problems, to prioritize corrective actions, and to track the accomplishment of corrections.

Another key aspect of ensuring the smooth operation of the CSN laboratories is the handling of communications with the various participants in the program. Most programmatic communications with outside participants including EPA/OAQPS, the DOPOs, and the state agencies flow through the Program Manager. The only exceptions to this rule will be dealings on a technical level with EPA personnel (e.g., to define data delivery formats for AQS) and contacts between shipping/receiving personnel at RTI and the state agencies for the purpose of expediting or locating specific shipments. No one at RTI other than the Program Manager is authorized to alter schedules, increase or decrease the number of samples to be analyzed, or change the schedule of shipments to/from a state agency. All such requests must go through the RTI Program Manager.

Appendix 1:
Uncertainty Calculations

Uncertainty values reported to AQS with each concentration record will include components of both the analytical and the volumetric uncertainty. The reported uncertainties are estimated "1-sigma" values (one standard deviation). No blank corrections are assumed other than laboratories' instrumental baseline corrections, which are an integral part of each analysis. The equations below describe how RTI will calculate the total uncertainty for the CSN analytes. A list of symbols is given at the end of this section. Uncertainties for PM_{10} are likely to be determined in the same manner as for $PM_{2.5}$. Uncertainties for PM_{coarse} will initially be determined by statistically combining the uncertainties of the two filters (PM_{10} and $PM_{2.5}$) used to calculate the PM_{10}–$PM_{2.5}$ fraction. The reasonableness of all uncertainties is subject to verification by techniques such as statistical analysis of data from collocated sites.

1.1 General Equation for Uncertainty

The mass uncertainty (micrograms per filter) will be calculated as shown in equation (1) for gravimetric mass and Ion Chromatography. Uncertainty for XRF elements are calculated as per equation (4). OC/EC uncertainty will be calculated once EPA decides on an approach for artifact correction and uncertainty calculation. The use of the *max* function prevents the calculated uncertainty for an exposed filter from being less than the average uncertainty for blanks. In most cases, the first term should be the larger.

$$\sigma_{M\,i,j} = \max\left(\sqrt{\sigma^2_{Ai} + \sigma^2_{Vk} \cdot M^2}\ ,\ \sigma_{Bi}\right) \tag{1}$$

The mass uncertainty is converted to concentration units (micrograms per cubic meter) according to equation (2).

$$\sigma_{C\,i,j} = \sigma_{M\,i,j} / V \tag{2}$$

1.2 Gravimetric Analysis

Determination of gravimetric mass requires two separate weighings, each of which contributes to the total uncertainty. A 47 mm Teflon filter used in the STN program weighs 145,000 micrograms, while the deposits on the filter are typically on the order of a few hundred micrograms. The total mass of loaded and clean filters is thus approximately the same (i.e., on the order of 145,000 micrograms). RTI has conducted experiments demonstrating that loaded filters have approximately the same repeatability as blank filters. Therefore, a constant value is assumed for the analytical uncertainty, $\sigma_{Ai,}$ used in equation 1, independent of filter loading.

Data obtained from filter lot acceptance blanks have provided a good data set on which to calculate uncertainties for clean filters. The standard deviation of a large population of replicate filter weighings from 2002 and 2003 was determined in order to set the baseline parameters σ_{Ai} and σ_{Bi} in equation 1. These are multiplied by a factor of the square root of 2 to account for the fact that two weighings are involved for each reportable mass concentration value.

1.3 XRF Elements

For XRF elements, an analytical uncertainty value for each analyte is calculated by the manufacturers' software, using an algorithm based on counting statistics for each sample. RTI has found that in order to report more consistent uncertainties for data generated by different analyzers, the manufacturer's uncertainties must be harmonized to ensure that the same components of uncertainty are used. This process is described in two documents that have been prepared by RTI and are posted on the AMTIC Web site:

Harmonization of Interlaboratory X-ray Fluorescence Measurement Uncertainties – Overview – http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/xrfuncertov.pdf

Harmonization of Interlaboratory X-ray Fluorescence Measurement Uncertainties – Detailed Discussion – http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/xrfdet.pdf

For the RTI XRF Lab, the XRF software does not calculate an uncertainty for an analyte when the peak and concentration values are zero. The formula shown in equation 3 was developed to calculate an uncertainty when the peak or concentration values are zero. This formula takes into account the background count rate in counts per second (B), livetime (t), and scaling factor (A).

$$\text{Instrument Uncertainty} = \text{slope} * A * \text{sqrt}\,(3 * \text{sqrt}\,(B * t) + B * t) / t \quad (3)$$

The total harmonized uncertainty is then calculated as:

Total Harmonized XRF Uncertainty

$$U_i = \sqrt{\delta^2_{i,attenuation} + \delta^2_{i,calibration} + \delta^2_{i,field-sampling\ \&\ handling} + \delta^2_{i,instrument\ peak\ counts}} \quad (4)$$

Where
U_i = total harmonized XRF Uncertainty for element i
δ_i = uncertainty for each component for element i

For $PM_{2.5}$, the attenuation uncertainty is estimated using the homogeneous layer model for all elements. The calibration uncertainty is assumed to be 5%, and is consistent with the estimated uncertainty of the calibration standards. The field sampling and handling uncertainty accounts for the uncertainties in the flowrate, filter deposit area, and losses and/or contamination during shipping and handling steps. Based on analysis of prior data, the field sampling and handling uncertainty is assumed to be 5%.

1.4 Ion Chromatography

Equation 1 is used for anions and cations (sulfate, nitrate, sodium, ammonium, and potassium), with the analytical uncertainty assumed to be a linear function of concentration, as shown. The intercept at low concentrations, σ_B, is determined from a replicate set of reanalyses of a low-level standard. We attempted to base our initial analytical uncertainty values (σ_{Ai}) on replicate analysis of an up-scale QC standard; however, large and difficult-to-reproduce variability was found, so that we assumed a multiplier, σ_{REL}, of 5% for all analytes and all instruments.

1.5 OC/EC

Original NIOSH TOT Analysis - Sunset Labs, which manufactures the OC/EC instrument that was used by RTI for TOT measurements, provides the formulas used by their software to calculate uncertainties, which include constant uncertainty components of ±0.20µgC/cm² for OC and EC and ±0.30µgC/cm² for TC, and a proportional uncertainty component of 5% for all three species. Assuming a filter area of 11.76 cm^2, the constant loadings are 2.35µgC/filter for OC and EC, and ±3.53µgC/filter for TC. See **Appendix 2** to this QAPP for more details. Equation 4 is used for calculating analytical uncertainty for OC/EC.

$$\delta_{Ai} = (\delta_{CONST} + M \bullet \delta_{PROP}) / M \qquad (5)$$

where:

δ_{Ai} = estimated uncertainty of measurement[1] (use in Eqn. 1), micrograms
δ_{CONST} = [constant uncertainty][11.76], micrograms
δ_{PROP} = proportional uncertainty multiplier [5% for OC, EC, and TC]

RTI independently extended the Sunset Laboratory uncertainty estimates to include the OC Peaks. For all reported carbon fractions, the constant and proportional components of uncertainty defined for each fraction below include at least 95% of replicate measurements across three analyzers for 127 filters analyzed over a three-year period in RTI's OC/EC Laboratory.

Carbon Fraction	Constant Uncertainty Component (δ_{CONST}, µgC/filter)	Proportional Uncertainty Component (δ_{PROP},%)
OC	2.35	5%*OC
EC	2.35	5%*EC
TC	3.53	5%*TC
Pk1 C	2.35	5%*Pk1 C
Pk2 C	2.35	5%*Pk2 C
Pk3 C	3.53	5%*Pk3 C
Pk4 C	3.53	10%*Pk4 C
Pyrol C	2.35	140%*Pyrol C

IMPROVE A Analysis – The equations to be used to calculate total uncertainties for the IMPROVE_A results have not been provided to RTI. This section will be updated when that guidance becomes available.

1.6 Determination of Volume Uncertainty

The relative uncertainty associated with sampled volume and other shipping and handling components of sampling error is often the predominant part of the total measurement uncertainty.

[1] Values are consistent with the Expanded Uncertainty concept used for measurements related to health or safety as described in Taylor, B.N.; Kuyatt, C.E. NIST Technical Note 1297: Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results. Expanded Uncertainty section. Available at http://physics.nist.gov/Document/tn1297.pdf (accessed April 2008).

However, RTI has no way to determine these, based on any of the field data that we routinely receive. A nominal value of 5%, which is used by the IMPROVE program (see IMPROVE SOP 351, *Data Processing and Validation*), is probably in the right order of magnitude for most of the CSN samplers. More accurate values for relative volume uncertainty would require statistical assessment of field audit results, which have not been consistently available for the CSN in previous years. Studies using data from collocated samplers and other means for assessing whole system variability for both the CSN and IMPROVE networks have shown that the value of 5% is probably an underestimate for the majority of chemical species, though it is reasonably accurate for high-level species that are relatively immune from contamination, such as sulfate and sulfur by XRF.

1.7 Definitions

I = Index for analytes
j = Index for individual sampling events
k = Index for sampler type (SASS, IMPROVE, FRM, etc.)
σ = Standard deviation
M = Analytical mass (micrograms per filter)
V = Sampled volume (cubic meters)
$\sigma_{Mi,j}$ = Std. dev. of mass for analyte I for event j (micrograms per filter)
$\sigma_{Ci,j}$ = Relative standard deviation for analyte I from lab QC samples (dimensionless)
σ_{Ai} = Analytical uncertainty
σ_{Bj} = Blank std. dev. from lab QC blanks (micrograms per filter)
σ_{G} = Std. dev. for replicate gravimetric analyses (micrograms per filter)
σ_{Vk} = Relative std. dev. of sampler volume (dimensionless) [typically 5%]

Appendix 2: Method Detection Limits

Laboratory method detection limits (MDLs) are reported annually and are subject to periodic updates by each of the analytical laboratories. The MDLs shown in this Appendix are from the 2010 CSN Annual Data Report. Laboratory MDLs are converted to concentration units by dividing the sampled volume for the respective sampler type and channel. Note that the resulting MDL in concentration units will not include any allowance for uncertainties related to field operations, including uncertainty in the measurement of volume, contamination, or other field-related issues. Because AQS does not distinguish the instrument used to analyze a particular filter sample, the tables in the sections below only include the maximum reported MDL during calendar 2012 for all instruments used to analyze CSN filters.

2.1 X-Ray Fluorescence

RTI operates three ThermoNoran XRF instruments that have been approved for used on the CSN program. Chester Labnet operates two Kevex XRF instruments that have been approved for analysis of CSN filters. As noted above, the maximum MDL value over calendar year 2012 is shown in the table.

2.2 Gravimetry

Gravimetric MDLs are determined by multiple re-weighings of blank filters. A factor of the square root of two is included in the calculation to account for the fact that each filter must be weighed twice to produce a net weight. The RTI laboratory typically operates 3-4 balances during the course of a year. The value shown in the table is the maximum reported MDL over all balances for calendar year 2012. The MDLs shown in the table apply to 47 mm Teflon filters.

2.3 Anion and Cation Analysis

RTI operates the anion and cation analysis laboratory. MDLs shown in the table below were determined for the analysis of ions on 47 mm nylon filters.

2.4 Organic and Elemental Carbon by Thermal Optical Analysis

The great majority of CSN OC/EC samples are analyzed by Desert Research Institute (DRI) using the IMPROVE_A analysis protocol. EPA has not provided the formulas to be used for calculating uncertainties and artifact corrections for the IMPROVE_A data as of this writing. The MDLs listed below are "typical" since MDLs can vary between instruments and over time. In addition, the MDLs in concentration units (micrograms per cubic meter) can vary slightly according to the sampled volume for each filter.

Analysis	Analyte	Mass (µg)	Concentration (µg/m^3) by sampler type	
			SASS	URG 3000N
Gravimetry	Particulate matter 2.5µm	7.5	0.84	
Anions and Cations	Ammonium	0.24	0.026	
	Potassium	0.23	0.025	
	Sodium	0.29	0.032	
	Nitrate	0.21	0.023	
	Sulfate	0.16	0.018	
Organic and Elemental Carbon	E1 IMPROVE	11		0.097
	E2 IMPROVE	7.1		0.065
	E3 IMPROVE	7.1		0.065
	EC IMPROVE TOR	7.1		0.064
	EC IMPROVE TOT	7.1		0.064
	O1 IMPROVE	7.1		0.065
	O2 IMPROVE	7.1		0.065
	O3 IMPROVE	11		0.097
	O4 IMPROVE	11		0.097
	OC IMPROVE TOR	7.1		0.064
	OC IMPROVE TOT	7.1		0.064
	OP IMPROVE TOR	11		0.096
	OP IMPROVE TOT	7.1		0.064
	TC IMPROVE	11		0.097
Trace Elements	Aluminum	0.24	0.027	
	Antimony	0.5	0.056	
	Arsenic	0.026	0.0028	
	Barium	0.57	0.06	
	Bromine	0.022	0.0025	
	Cadmium	0.22	0.024	
	Calcium	0.073	0.0083	
	Cerium	0.84	0.088	
	Cesium	0.44	0.047	
	Chlorine	0.11	0.011	
	Chromium	0.025	0.0028	
	Cobalt	0.019	0.002	
	Copper	0.024	0.0026	
	Indium	0.32	0.035	
	Iron	0.032	0.0034	
	Lead	0.061	0.0064	
	Magnesium	0.18	0.019	
	Manganese	0.028	0.0029	
	Nickel	0.018	0.0019	
	Phosphorus	0.15	0.018	
	Potassium	0.11	0.011	
	Rubidium	0.025	0.0028	
	Selenium	0.025	0.0027	

Analysis	Analyte	Mass (µg)	Concentration (µg/m^3) by sampler type	
			SASS	URG 3000N
	Silicon	0.18	0.019	
	Silver	0.36	0.04	
	Sodium	0.53	0.057	
	Strontium	0.034	0.0038	
	Sulfur	0.095	0.011	
	Tin	0.35	0.039	
	Titanium	0.051	0.0058	
	Vanadium	0.037	0.0042	
	Zinc	0.034	0.0038	
	Zirconium	0.22	0.025	