

**DRAFT**

**Volume I**  
**Quality Assurance Project Plan**  
**Chemical Speciation**  
**of PM<sub>2.5</sub> Filter Samples**

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

**EPA Contract No. 68-D-03-038**

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**A.1 QA Project Plan Identification and Approval**

# Quality Assurance Project Plan Chemical Speciation of PM2.5 Filter Samples

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

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### A.3 Distribution

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 QA Manager will oversee control and update of the QAPP and SOPs.

**Table A.3.1 QAPP Distribution List**

<b>Copy Number</b>	<b>Recipient Name</b>	<b>Position</b>	<b>Organization</b>
1	V. E. Presnell	Project Officer	U.S. EPA/OAQPS
2	J. Homolya	Technical Project Manager	U.S. EPA/OAQPS
3	D. Mikel	Quality Assurance Coordinator	U.S. EPA/OAQPS
4	R. Charles	Delivery Order Project Officer	U.S. EPA
5	K. Wang	Delivery Order Project Officer	U.S. EPA
6	M. E. Kantz	Delivery Order Project Officer	U.S. EPA
7	M. Clark	EPA Quality Assurance Laboratory Director	U.S. EPA/ Montgomery
8	R. K. M. Jayanty	Program Services Manager	RTI/EISD
9	D. M. Haas	Financial Services Program Coordinator	RTI/EISD
10	J. A. O'Rourke*	Sample Custodian, SHAL	RTI/EISD
11	L. C. Greene*	Gravimetric Mass Task Leader	RTI/EISD
12	E. D. Hardison*	Ions Analysis Task Leader	RTI/EISD
13	E. E. Rickman*	Data Management Task Leader	RTI/EISD
14	W.C. Eaton*	Denuder Refurbishment Task Leader	RTI/EISD
15	W. Gutknecht*	Elemental Analysis Task Leader	RTI/EISD
16	M. R. Peterson*	Carbon Analysis Task Leader	RTI/EISD
17	J. B. Flanagan	Quality Assurance Manager	RTI/EISD

\* 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 68-D99-013, with the U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards (OAQPS). Work on this contract in support of the Chemical Speciation Trends Network (STN) program is performed by staff from RTI's Environmental and Industrial Sciences Division (EISD), which is a component of the Sciences and Engineering Group. Chester LabNet, subcontractors 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 IMPROVE method and semivolatile organic compound (SVOC) analysis on selected filters. A schematic of the RTI project organization is shown in Figure A.4.1.

Sound management requires a clear understanding of the roles, functions, and assignments of each position within the project structure. Table A.4.1 highlights the responsibilities and lines of communication for each of the positions.

### **A.4.1 Key Personnel**

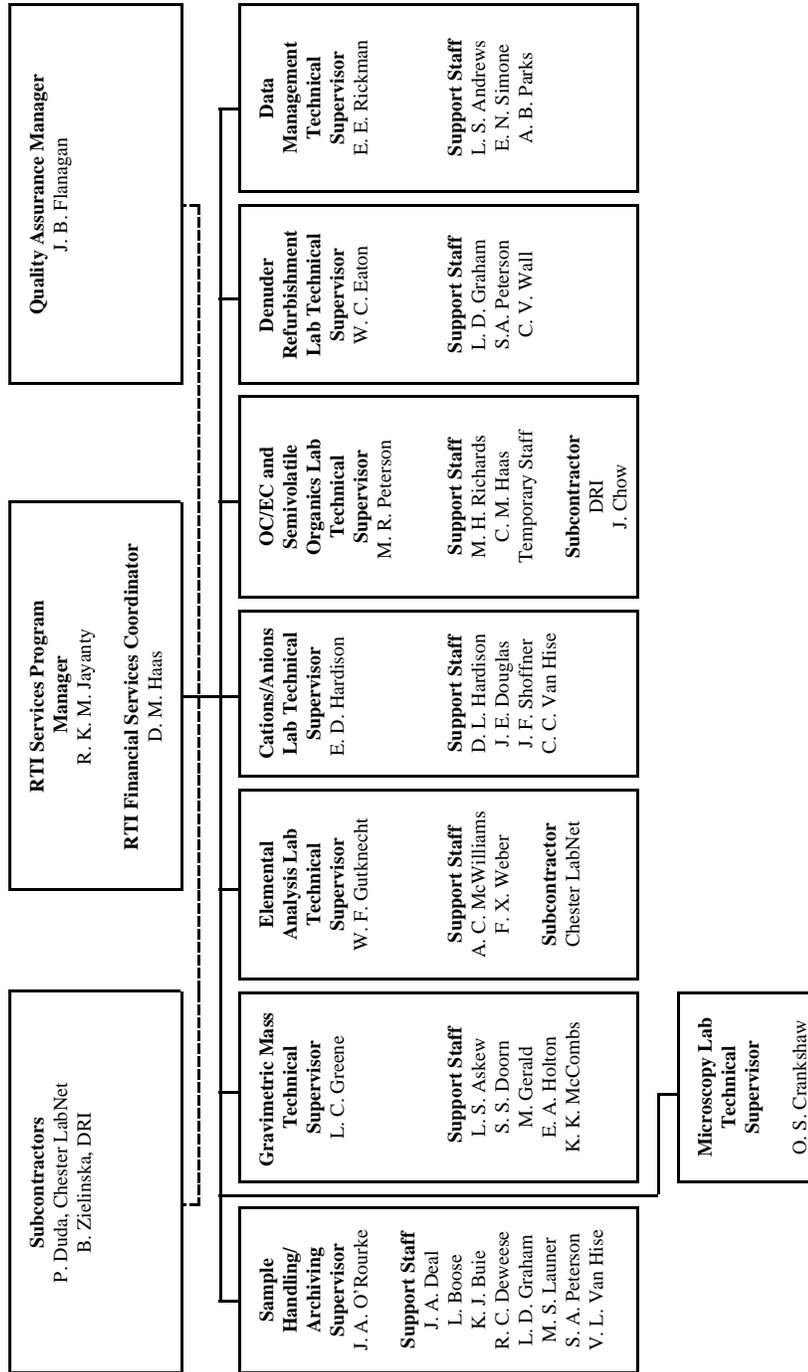
#### **A.4.1.1 Services Program Manager and Program Services Assistant**

The project will be led by Dr. R. K. M. Jayanty who will provide overall supervision to ensure that the technical program is being performed in accordance with the EPA statement of work and according to this QAPP. As Project Manager for many projects, Dr. Jayanty has considerable supervisory experience.

The RTI Services Program Manager's responsibilities include:

- Maintaining liaison 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
- Facilitating interaction among team personnel
- Ensuring that proper techniques and procedures are followed
- Ensuring that reporting requirements are satisfied
- Maintaining cost and schedule control
- Adjusting schedules to meet the needs of the client
- Reviewing and approving deliverables submitted to the client.

Ms. Diane M. Haas will be the Financial Services Program Coordinator and will be responsible for financial and other coordination of activities within RTI.



**Figure A.4.1. Project organizational chart.**  
This chart shows the technical management and support staff for RTI and subcontractors.

**Table A.4.1 Personnel Responsibilities and Lines of Communication**

<b>Position</b>	<b>Responsibilities</b>	<b>Lines of Communication</b>
Services Program Manager <i>R. K. M. Jayanty</i>	Accountable to corporate management for successful accomplishment of the project objectives.	Supervises project. Coordinates project activities with client and subcontractors. Reports to Center Director.
QA Manager <i>James B. Flanagan</i>	Responsible for monitoring all aspects of QA/QC.	Reports to Services Program Manager. Works closely with technical area supervisors and staff. Peer-to-peer coordination with subcontractor QA staff.
Technical Area Supervisors <i>Owen Crankshaw Cary Eaton Lisa Greene William Gutknecht Eva Hardison James O'Rourke Max Peterson Edward Rickman</i>	Responsible for maintaining technical quality, data handling and transfer, and identifying and resolving technical problems. Responsible for staff training and assessment.	Report to Services Program Manager. Work closely with technical staff and QA Manager.
Technical Staff	Perform technical tasks.	Interacts with other team members. Report to Technical Area Supervisors.
Analyst <i>Andrea McWilliams</i>	Responsible for XRF analysis of Teflon filters, maintaining technical quality, data handling and transfer, and identifying and resolving technical problems. Responsible for staff training and instrument maintenance.	Reports to the SPM. Works closely with technical staff and QA Manager.
Chester LabNet <i>Paul Duda Rick Sarver Lisa Ball Emmely Briley Jess Mace</i>	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 SPM.
DRI <i>Judy Chow, OC/EC Barbara Zielinska, SVOC B. G. Cristani D. A. Crow S. D. Kohl N. L. Pennef N. F. Robinson R. J. Tropp J. G. Watson</i>	Responsible for receiving samples from RTI, performing SVOC and OC/EC by IMPROVE method 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 SPM.

#### A.4.1.2 QA Manager

Dr. James B. Flanagan is the RTI QA Manager for this project. As a member of the Quality Systems and Decision Support (QSDS) Department, he is administratively independent from the staff performing the project work and data generation. For the purposes of this project, he will report directly to Dr. Jayanty, the SPM. Dr. Flanagan will monitor quality assurance/quality control (QA/QC) for the project and will perform periodic in-lab and data review audits.

#### A.4.2 Subcontractors

RTI has engaged Chester LabNet as a subcontractor to provide a limited energy dispersive x-ray fluorescence spectroscopy (EDXRF) services for this program. RTI has engaged DRI as a subcontract for SVOC analysis and OC/EC analysis by IMPROVE method on selected filters.

All subcontractor laboratories providing analytical services for this program must provide a project-specific QAPP and the required SOPs for EPA approval and will also be required to analyze EPA-provided PE samples and to undergo a technical systems audit of their facility. RTI will maintain standards and document comparability of laboratories performing the same analyses through an intercomparison program. Calibration check samples from the same source will be analyzed by both laboratories and at least 10 percent of the field samples will be analyzed in duplicate by the participating laboratories.

The capabilities of each subcontractor are briefly outlined below.

##### A.4.2.1 Chester LabNet

RTI will send XRF samples to Chester LabNet as long as Chester LabNet demonstrates 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 the Protocol #6 was 25 samples per day. Chester LabNet has purchased a second KeveX XRF numbered 771. Samples were analyzed on both the 770 XRF and the 771 XRF to test for equivalency. 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 accepted. Therefore, Chester LabNet now has a total capacity of approximately 50 samples per day. Chester LabNet has purchased a third KeveX XRF for serving its other clients.

#### A.4.2.2 Desert Research Institute (DRI)

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

#### **IMPROVE OC/EC Analysis**

RTI has subcontracted with DRI to provide OC/EC analysis by the Interagency Monitoring of Protected Visual Environments (IMPROVE) method based on the technical requirements in DRI's SOP<sup>1</sup>. RTI and DRI have defined data transfer formats and procedures, and developed an SOP for IMPROVE OC/EC analysis. Sample management and transfer SOPs are under development.

The DRI instrument 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<sub>2</sub> in the oxidizer, and the CO<sub>2</sub> is converted to methane (CH<sub>4</sub>) in the methanator before passing into the FID where it is measured. The laser emission 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. The laser-photodiode sensor is used to monitor reflectance of laser light from the filter section during analysis.

#### **Semivolatile Organics Compound Analysis(SVOC)**

RTI has subcontracted with DRI to provide SVOC analysis on selected filter samples.<sup>2</sup>

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<sup>1</sup> DRI Standard Operating Procedure for Thermal/Optical Reflectance Carbon Analysis of Aerosol Filter Samples, 8/21/03, [www.epa.gov/ttn/amtic/files/ambient/pm25/spec/drioceec.pdf](http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/drioceec.pdf).

<sup>2</sup> DRI Standard Operating Procedure for Analysis of Semi-Volatile Organic Compounds by GC/MS, 8/21/03, [www.epa.gov/ttn/amtic/files/ambient/pm25/spec/drisvoc.pdf](http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/drisvoc.pdf).

## **A.5 Problem Definition/Background**

In 1997, the EPA promulgated the new National Ambient Air Quality Standards (NAAQS) for particulate matter. The regulations (given in 40CFR Parts 50, 53, and 58) apply to the mass concentrations ( $\mu\text{g}/\text{cubic meter of air}$ ) of particles with aerodynamic diameters less than 10 micrometers (the PM10 standard) and less than 2.5 micrometers (the PM2.5 standard). Establishment of a 1500-site mass measurements network and a 300-site chemical speciation monitoring network is in process.

The ambient air data from the network which measures solely the mass of particulate matter will be used principally 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 chemical Speciation Trends Network (STN) will consist of a core set of 54 trends analysis sites and some 200 other sites. Chemically speciated data will be used to serve needs associated with development of emission mitigation approaches to reduce ambient PM2.5 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 PM2.5 and its components, and evaluating potential linkages to health effects.

RTI will assist in the PM2.5 STN 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 performing these analyses, as well as in 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. This network was composed of approximately 13 monitoring stations at sites throughout the U.S. Each site had two or more PM2.5 chemical speciation monitors to enable various sampler intercomparisons. The mini-trends network ran from February 2000, to August 2000. RTI is currently supporting 235 sites which includes 54 core STN sites.

## **A.6 Project/Task Description**

The STN laboratory contract involves four broad areas:

1. Supplying each site or state with sample collection media (loaded filter packs, denuders, and, when ordered, absorbent cartridges) and field data documentation forms. RTI will ship the collection media to 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 semi-volatile organic compounds and examination of particles by electron or optical microscopy will not be performed initially; however, these analyses may be included in the full STN program.
3. Assembling validated sets of data from the analyses, preparing data reports for EPA management and the states, and entering data into the AIRS 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 overall contract period extends from July 8, 2003 to July 7, 2008. Additional chemical speciation samplers, up to a total of 250, will be added to the program incrementally. RTI is supporting 235 as of December 31, 2003.

#### **A.6.2 Sample Types and Quantities**

RTI has been awarded a 5-year contract (base period and four options) with EPA/OAQPS. Table A.6.1 shows the number of samples for the base period of the contract.

### **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

**Table A.6.1. Sample Quantities for Base Period  
(July 8, 2003 to July 7, 2004)**

<b>Item</b>	<b>Item Description</b>	<b>Minimum Sample Quantity</b>	<b>Maximum Sample Quantity</b>
0001-1	PM2.5 Gravimetric Mass	2,200	22,000
0001-2	Elemental Analysis by EDXRF	2,200	22,000
0001-3	Sulfate Analysis	2,200	22,000
0001-4	Nitrate Analysis	2,200	22,000
0001-5	Ammonium, and water-soluble sodium and potassium	2,200	22,000
0001-6a	Organic, elemental, and total carbon (STN)	2,200	22,000
0001-6b	Organic, elemental, and total carbon (IMPROVE)	2,200	22,000
0001-7	Semi-volatile organic aerosol analysis	3	30
0001-8a	Microscopic Analysis	1	15
0001-8b	Electron Microscopic Analysis	1	15
0001-9	Organic Denuder Refurbishment	5	50
0001-10	Nitric Acid Denuder Refurbishment	150	1,500
0001-11	Sodium Carbonate Denuder Refurbishment	300	3,000
0001-12	5 Year Archive of Samples	2,360	34,000

overly precise data. The formal DQO process consists of seven steps that allow an experimental design to be developed to meet specific 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 Speciation DQO Workgroup was established to develop and document DQOs for the PM2.5 chemical Speciation Trends Network (STN). The DQO process that the workgroup employed is fully documented in its report (EPA, 1998), which is available online at the EPA's Ambient Monitoring Technology Information Center (AMTIC) Web page for speciation:

<http://www.epa.gov/ttn/amtic/pmspec.html>

#### A.7.1.1 Development of DQOs for the PM2.5 Chemical STN

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:

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

[It should be noted that although the DQO statement says "3 to 5 percent" and "3 to 5 years," the default assumptions in this QAPP will be detection of a **5 percent** trend after **5 years**.]

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

- Model evaluation, verification, and/or validation
- Emission inventory
- Source attribution
- Spatial and seasonal characterization of aerosol distributions.

The desirable data quality characteristics for these secondary uses are probably significantly different from those applicable to trend assessment. This document only considers the needs of the primary objective for trend detection.

Because no STN data had been collected when the DQO process was conducted, PM2.5 chemical speciation data from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network were used for the assessment. Data from the one urban IMPROVE site, Washington, D.C., were used because the STN sites are to be in urban locations. This data set was evaluated using a statistical regression model to refine the experimental design and to define goals for measurement quality.

The chemical species considered in the DQO study were limited to sulfate, nitrate, calcium, and total carbon, all of which are included in both the IMPROVE and STN networks. The analytical methods used in the IMPROVE program are similar to those to be used in the STN. Table A.7.1 summarizes the species considered and compares the measurement methods employed by the two programs.

The four analytes that were studied, along with the modeled error components, are shown in Table A.7.2. The table illustrates that unexplained random error is much larger than the measurement error for all the analytes considered.

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<sup>3</sup> Seasonality refers to periodic differences in the concentration of PM2.5 and its constituents due to seasonal factors such as weather conditions, human activity patterns (traffic, agriculture, manufacturing, etc.), and changes in ground cover. Seasonal differences like these must be accounted for before multi-year trends can be reliably ascertained.

**Table A.7.1 Analytes Included in DQO Study  
(specific analytes shown in parentheses)**

Chemical Species	IMPROVE Method	STN Method	Comment
Elements (calcium)	Proton induced x-ray emission (PIXE)	Energy dispersive x-ray fluorescence (EDXRF)	Relative sensitivity of the two methods needs clarification.
Ions (sulfate and nitrate)	Ion chromatography	Ion chromatography	Same method.
Carbon analysis (total carbon)	Thermal optical reflectance (TOR)	Thermal optical transmittance (TOT)	TOR and TOT are thought to be similar in performance, however studies to confirm this are currently in progress.

Source: U.S. EPA 1998b

**Table A.7.2 Improve Data Summary – Urban Washington, D.C. Site**

Analyte	Geometric Mean Concentration ( $\mu\text{g}/\text{m}^3$ )	Unexplained Error in Model (Average CV)	Measurement Error (Average CV)
Sulfate	4.932	57.4	3.6
Nitrate	1.240	85.0	4.6
Calcium	0.039	57.2	8.3
Total Carbon	4.119	52.4	6.4

Source: U.S. EPA, 1998.

CV = coefficient of variation = (standard deviation / mean)  $\times$  100.

### A.7.2 Quality Objectives for Total Measurement Error

A key conclusion of the DQO study was that the statistical power to detect concentration trends in the chemical speciation data is relatively insensitive to measurement error, up to about twice the level seen in the IMPROVE Washington, D.C., data. This is because the "uncontrollable" error components, which are primarily due to natural day-to-day variation in pollutant levels, dominate the random errors that limit the ability of the statistical analysis to detect a trend. Table A.7.3 shows the number of years worth of data necessary to detect a 5 percent annual trend using the IMPROVE data set in conjunction with the regression model assuming one in three day sampling.

**Table A.7.3 Years Required to Achieve 0.8 Power With 1-in-3-day Sampling**

Species	Measurement Error = IMPROVE Error × 1
Sulfate	4.1 years
Nitrate	6.3 years
Calcium	4.1 years
Total Carbon	3.4 years

Source: EPA 1998.

The DQO study also concluded that with sampling every 3<sup>rd</sup> day for 5 years, trends greater than 5 percent (or less than -5 percent) 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 percent to be detected with a power of 80 percent. The workgroup members concluded that this was not sufficiently different from the 5 percent goal to require adjustment to the sampling design. Sampling daily instead of every 3<sup>rd</sup> day provides little improvement in the ability to detect trends; however, the model showed that cutting the sampling rate to every 6<sup>th</sup> day begins to impair the ability to detect concentrations 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.7.4. 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 bias MQO specified because trend identification is insensitive to bias *as long as the bias is consistent across the 5-year time span of interest*. 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.

**Table A.7.4 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

To calculate the total measurement error corresponding to the values given in Table A.7.4, it is necessary to quantify the individual components of random error using QC data collected by the monitoring program. The individual error components are calculated based on appropriate QC measurements and are combined to determine the total measurement error. A careful statistical assessment of the entire measurement system is necessary to accurately calculate the total measurement error.

### **A.7.3 Measurement Quality Objectives (MQOs)**

There are several components of total data variability included in the model used in the DQO study. Of these, measurement error is the component that can be controlled and/or quantified most readily through the QA/QC program. Quantitative or qualitative goals for particular QA/QC measures are the detailed MQOs. There are several important purposes for the information provided by the QA/QC program:

- detect failures and initiate troubleshooting
- identify observations or groups of observations that must be investigated for data validation (flagging or invalidation)
- assess progress toward attainment of the detailed MQOs, the MQOs for total error, and the DQO for trend detection.

Many different sets of MQOs could be developed that are consistent with meeting the DQO for trend detection. The DQO study recognized that measurement error is a relatively small part of the total uncertainty involved with the evaluation of the trend detection DQO; therefore, other considerations must be taken into account in developing an optimum set of MQOs.

The 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.

Systematic bias and random errors are aggregated into a single figure that was called "measurement error," in the DQO study. Systematic bias is commonly understood as the offset error when comparing a measurement system against a known standard, such as a NIST-traceable material. One justification for combining bias and random errors into a single figure is that over the long time scale 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. When actual monitoring data are available for analysis, the systematic and random components of error can be considered in the ways that are most appropriate.

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 five years.

## A.7.4 References

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.

U.S. EPA (1998). *Data Quality Objectives for the Trends Component of the PM2.5 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>.

U.S. EPA (1999a). *Particulate Matter (PM2.5) 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 (PM2.5) Quality System for the Chemical Speciation Monitoring Trend Sites.*, U.S. EPA, Research Triangle Park, NC, April 16, 1999.

**Table A.7.5. Laboratory MQOs**

Measurement	Measurement Error <sup>a</sup>	Completeness Goal <sup>b</sup>
Cations and Anions	±10% if C > 10×MDL <sup>c</sup> or ±MDL if < 10×MDL	90%
Carbon Species	±15% if C > 10×MDL	90%
Filter Weight	±10% if Wt > 6 µg/m <sup>3</sup>	90%
Elements (EDXRF)	±20% if C > 10×MDL	90%
SVOCs <sup>d</sup>	±10% if C > 10×MDL or ±MDL if < 10×MDL	90%
SEM and Optical Microscopic Examination <sup>d</sup>	N/A	90%

Notes:

- 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.
- c - MDL = Method Detection Limit. Typically determined as 3 times the standard deviation of 7 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.

## **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 PM2.5 program will be required to be experienced with the basic measurement techniques relevant to the analyses that they are to perform. These techniques include operation of an analytical microbalance, X-ray fluorescence (XRF), ion chromatography, gas chromatography/mass spectrometry (GC/MS), and electron and optical microscopy. Determination of organic and elemental carbon (OC/EC) requires an analyst who has been trained to use the apparatus and trained to practice good laboratory techniques to avoid contamination of filters and standards.

With experience in the basic methodology, the analyst to be trained 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 measurement quality objectives for recovery (or bias) and precision. The Task Leader 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 samples. Even then, the analyst will work under the direction of the 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 analyst.

RTI will require gravimetric analysts to pass a test similar to the certification test administered to analysts working on the EPA's PM2.5 Federal Reference Method Performance Evaluation Program (FRM PEP), which RTI helped to develop under another contract.

Permanent RTI employees, including high level personnel and Task Leaders are eligible to attend training courses relevant to the project areas. Both in-house and extramural training opportunities are provided at RTI's expense to its employees. Most employees attend one or more such courses each year. Project staff will be encouraged to attend courses such as manufacturer's 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 a verification by the Task Leader 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 feels 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 also receive copies of the QAPP and the relevant SOPs necessary to performing 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:

- **Mass Determination**
  - Lisa Greene - Seventeen years of relevant experience, including five years of experience in determination of gravimetric mass and technical and fiscal management of PM10 and PM2.5 analytical work for several State air quality agencies and commercial engineering firms.
  - Stacy Doorn - Eight years of relevant experience, including extensive experience in the preparation and analysis of samples by electron microscopy and over three years in the determination of gravimetric mass.
  - Maurice Gerald - Seven years military training in various leadership roles, including records creation, maintenance and accountability; medical experience in sterile and aseptic techniques; and first response experience under high-stress conditions. Currently Mr. Gerald is working as a Laboratory Technician, where he provides key technical support to a variety of projects associated with the nationwide Air Monitoring Network established in response to the National Ambient Air Quality Standards (NAAQS) for fine particulate matter. For the Chemical Speciation program, Mr. Gerald is responsible for routine laboratory maintenance, sample processing and inspection, filter weighing, and transfer of samples to the XRF Laboratory. He has 8 months prior experience working in the Sample Handling and Archiving Laboratory for the National Chemical Speciation Network.
  - Emily Holton - Four years of relevant experience, including over two years of experience in the determination of gravimetric mass.

- Karen McCombs - Sixteen (16) years of laboratory experience. She has worked in cell culture, microbiology quality control, and with laboratory animals. She is currently a Laboratory Technician providing key technical support to a variety of projects associated with the nationwide air monitoring network established in response to the NAAQS for fine particulate matter. For the Chemical Speciation program, Ms. McCombs is responsible for routine laboratory maintenance, sample processing and inspection, filter weighing, and transfer of samples to the XRF Laboratory.
  
- **Ion Analysis**
  - Eva Hardison - Twenty-four (24) years of relevant experience in the technical and fiscal management of ion chromatographic analysis, including 14 years of filter analysis for the National Park Service. Also, extensive experience in sample handling, data reduction/analysis and report preparation.
  
  - David Hardison - Twenty-eight (28) years of relevant analytical experience including nine years 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 - Eleven(11) years of relevant experience in sample handling and preparation, including over three years of experience in air filter extraction.
  
  - Joyce Shoffner - Six years of relevant experience in sample handling and preparation, including over two years of experience in air filter extraction.
  
- **Metal Analysis**
  - William Gutknecht - (RTI) Thirty (30) years of experience in trace metal analysis including four years of experience in proton-induced XRF(PIXE) and thirteen years of experience in portable XRF technology. Technical and fiscal management of principally inorganic analytical programs, extensive experience in data treatment/analysis, QA/QC, and report preparation.
  
  - Andrea McWilliams - (RTI) Nine years of relevant experience, including three years of experience operating, maintaining, and troubleshooting the ThermoNoran QuanX (EDXRF).

- Paul Duda - (Chester) Thirteen(13) years of relevant experience including five years of experience in air filter analysis by EDXRF. Nine years experience as a LIMS administrator.
- Jess Mace - (Chester) Five years analytical experience and three years experience in EDXRF.
- Richard Sarver - (Chester) Twenty-two (22) years of relevant analytical experience, including fifteen years of experience in environmental air quality analysis, specializing in analysis of air particulates by EDXRF.
- **Organic/Elemental Carbon (OC/EC)**
  - Max Peterson - More than thirty-seven (37) years of relevant experience in separation and analysis of volatile and semivolatile organic compounds including fifteen years in source and VOC emission measurements. Five years of experience in OC/EC analysis and data review, validation, and reduction.
  - Melville Richards - More than twenty-seven (27) years of relevant experience including experience in ion chromatography and carbon analysis. Also, four years of experience in OC/EC analysis by the current EPA adaptation of NIOSH Method 5040.
- **OC/EC by IMPROVE Method**
  - Judy Chow - More than twenty-five (25) 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.
  - Brenda Cristani - More than 17 years experience in data processing involving data management, validation, and report preparation utilizing the current state-of-the-art software and hardware. Her laboratory experience includes gravimetric, XRF, and atomic absorption analysis of filter samples. She also loads, unloads, ships, and logs filter packs

according to specified criteria. She calibrates and tests field and laboratory equipment, and when needed, visits air monitoring field sites to conduct checks on chart recorders, data loggers, gas analyzers, high-volume (hivol) and minivol samplers, and various meteorological systems. Ms. Cristani can load and retrieve ambient monitoring data to and from EPA's AIRS/AQS. Ms. Cristani will serve as DRI's Data Technician and will be responsible for processing data in formats designated by clients and/or suitable for uploading to AIRS AQS.

- Dale Crow - More than 18 years experience in ambient air quality measurements and quality assurance. Serves as laboratory Manager for the EAF's Carbon Analysis Laboratory, including data validation, reporting, and analysis of organic and elemental carbon measurements.
  
- Steven Kohl - Six years of experience with scheduling and coordination of laboratory work. His 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. He 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.
  
- Norm Robinson - More than 25 years of experience in model development and database design and implementation. Designs and implements databases and procedures for laboratory information management system and field study and related data.
  
- Richard Tropp - More than 25 years of experience in conducting air quality studies, statistical data analysis, and quality assurance. Project Manager for PM2.5 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 PM2.5 regulatory proposal and promulgation packages. Outside reviewer of Section 2.12 of EPA's QA Handbook.
  
- John Watson - More than 25 years in environmental sciences, including the planning and conduct of major air pollution studies. Serves as Quality Assurance 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 - Sixteen (16) years of relevant experience with scanning electron microscopy (SEM) and transmission electron microscopy. Specifically experienced in analysis of PM10 and PM2.5 samples, including the analysis of Teflon, polycarbonate, and fibrous glass/quartz filters.
  
- **Semivolatile Organic Compound (SVOC) Analysis**
  - Barbara Zielinska - More than 25 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. Her 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. She is currently a member of EPA's Clean Air Scientific Advisory Committee (CASAC) and is a regular reviewer for the professional journals *Environmental Science & Technology*, and *Atmospheric Environment*.
  - Nancy Peneff - Five years of experience managing analytical laboratories. She is currently the laboratory manager of the Organic Analytical Laboratory responsible for coordinating projects: budget review, analysis protocol, and data management. Prior to coming to DRI, she managed an inorganic analytical laboratory for plant, soil, and water analysis. She has a strong analytical background with emphasis in method development and instrument maintenance.
  
- **Sample Handling**
  - James O'Rourke - Fourteen (14) years of related experience in sample handling and preparation. 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 - Four years of relative experience in supporting the PM2.5 chemical speciation project, that includes handling, packaging, and maintaining records for different types of air filters used for air sampling studies. She also serves as assistant supervisor for a number of temporary staff performing this type of work.
- **Data Base Development/Management**
  - Edward Rickman - More than fifteen (15) years of relevant experience in design and implementation of environmental and QA databases including a database for EPA's OAQPS PM2.5 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 - Six years 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 participated in creating database programs to process data for use in risk assessment modeling, for statistical analysis, or for further use by external clients.
- **Quality Assurance**
  - James Flanagan - Nineteen (19) years of relevant experience in data reduction/analysis and QA/QC. Performed numerous QA plan reviews as well as audits of field measurements and laboratory operations. Provided support for a major QA contract for EPA's Air Pollution Protection and Control Division (APPCD).
- **Denuder Refurbishment**
  - W. Cary Eaton - Twenty-four (24) years of relevant experience in measurement of ambient air pollutants. Experience with use of denuders and cascade impactors. Reviewed manufacturer's applications of candidate samplers for FRM designation, edited EPA's comprehensive PM2.5 QA guidance document, and assisted with workshops for EPA's Performance Evaluation Program for the national FRM PM2.5 network and the Speciation Trends Network.

## A.8.2 Summary of Experience and Training

The qualifications of each analyst will be maintained in training folders. Courses taken, special in-house training, and results of performance audits will be documented in the training folder.

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

- Gravimetric Laboratory staff have given instructional workshops and prepared SOPs to train analysts for the PM2.5 Performance Evaluation Program.
- The RTI ion chromatographic team has performed air filter analysis for the National Park Service for the last fifteen years. PM2.5 ion analysis has been performed in support of EPA evaluation of PM2.5 samplers and for the California Air Resources Board.
- Three staff members have trained other personnel in the use of single channel PM2.5 samplers and in the handling and shipment of filters for the FRM PEP.
- At least five 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 chain of custody 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 has 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 needed 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 critically important 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. We will hire new employees for the analytical laboratories in order to maintain analysis schedules.

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

- New personnel will be interviewed, and their credentials carefully assessed with regard to prior experience and aptitude for the assigned task. Candidates will be interviewed by the Task Leader and by at least one other senior-level project participant, such as the Services Program Manager, QA Manager, or a Task Leader 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 two years experience, but individuals will be assessed on a case-by-case basis by the Task Leader. References will be contacted to verify that the applicant has the required laboratory skills and aptitude.
- For individuals hired as permanent RTI employees, a probationary period of six 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 will be on-the-job and will be provided by the Task Leader or by a staffer who has already mastered the task area. The specific SOPs will be 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 Task Leader 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 Task Leader. The individual may work unsupervised only after the Task Leader 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 (Table A.9.1). Consolidated requests from the DOPOs will be received and examined by the SPM, and will be circulated to all the laboratories for advanced planning and materials procurement.

**Table A.9.1 Management Records**

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

### 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**

<b>Document Name</b>	<b>Brief Description</b>	<b>Format</b>	<b>Storage Location</b>
Training Files	Records substantiating the training and proficiency of analysts relevant to this program	Hard copy	Program Office
Audits, Questionnaires, 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 resolution	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**

<b>Document Name</b>	<b>Brief Description</b>	<b>Format</b>	<b>Storage Location</b>
Delivery Order	Instructions from DOPOs for sampling module needs.	Hard copy and electronic	Program Office and SHAL
Chain of Custody (COC) forms	Forms used to track sample module shipments between RTI and the States.	Hard copy, triplicate form (copies: 1 & 3 to RTI, 2 to field site)	SHAL
Laboratory Chain of Custody Forms (LCOC)	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, 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 which 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
Storage Box Form	Lists aliquots in a particular storage box sent to archive.	Hard copy	SHAL

### 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**

<b>Document Name</b>	<b>Brief Description</b>	<b>Format</b>	<b>Location</b>
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 Laboratory Records

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

**Table A.9.5 Gravimetric Laboratory Records**

Document Name	Brief Description	Format	Location
Filter Inventory and Inspection Form	Completed upon receipt of filters lots from the vendor. Indicates the order to use filter boxes, date inspected and number of filters rejected.	Spreadsheet or hard copy	Gravimetric Laboratory
Filter Conditioning Information	Indicates the dates filters were conditioned and stability test results.	Hard copy	Gravimetric Laboratory
Calibration Certificates and Records	Includes certificates of NIST traceability and similar records.	Hard copy	Gravimetric Laboratory
Gravimetric Filter Database	Includes filter ID, initial weighing information (including date, RH, Temperature, cassette number), the date shipped and received, final weighing information (date, RH, temperature, and weight), mass loading of the filter.	Spreadsheet or DBMS	Gravimetric Laboratory
Gravimetric QC Database	Includes all QC information for each weighing session including standard weights, duplicates, field blanks, and laboratory blanks.	Spreadsheet or DBMS	Gravimetric Laboratory
Weighing Room Environmental Data	Data logger is programmed to record "grab samples" at five-minute intervals.	Data logger spool file or spreadsheet	Gravimetric Laboratory
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 Laboratory; original returned to the SHAL
Laboratory Notebooks	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 include acceptance limits that are periodically recomputed.	Hard copy or spreadsheet	Each laboratory

In addition to the records shown in Table A.9.5, the Gravimetric 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 PM2.5 Chemical Speciation 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 the month's sampling and field blank requirements. This projection will be sent to the Gravimetric Laboratory via electronic 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 PM2.5 analyses	Computer files; database files	Instrument PC; database
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 PM2.5 analyses	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**

<b>Document Name</b>	<b>Brief Description</b>	<b>Format</b>	<b>Location</b>
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 and supervisor's office
Raw Data Records	Results of PM2.5 analyses (including supporting data that is not uploaded to the database)	spreadsheets; hard copy; and database	Analyst's PC; supervisor's office; 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**

<b>Document Name</b>	<b>Brief Description</b>	<b>Format</b>	<b>Location</b>
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

## **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 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 STN Field QAPP prepared for OAQPS contains a full description of sample acquisition, including sample chain of custody, 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**

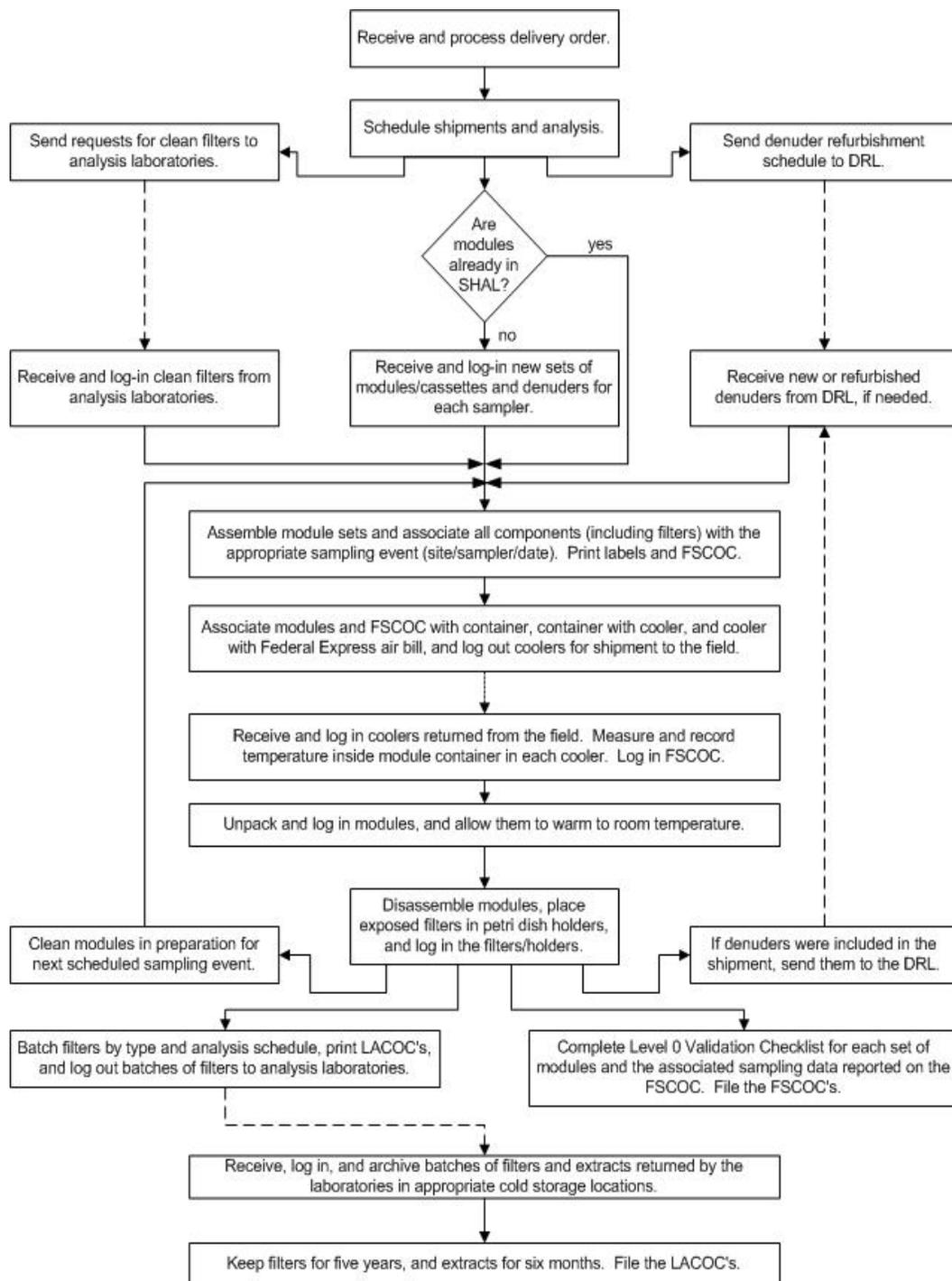
*Note: This section relies heavily on design of RTI's sample handling system, including the SHAL. Please refer to the applicable SOP for more details.*

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 SPM 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



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

validates the data, enters data meeting Level 1 criteria into the Aerometric Information Retrieval System (AIRS), 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 of technical quality issues and contract dispute issues.

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 will be described in more detail in the SHAL SOP.

### **B.3.2 Chain of Custody**

*Note: An example of the field chain of custody (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 3-part carbonless form for sending and receiving samples from the field sites. The COC form will be computer-generated so that they are customized for each type 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 where 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. Hard copy internal tracking forms will be used initially to document the location of individual samples through the RTI laboratories, as described in the following section.

### **B.3.3 Processing System for PM<sub>2.5</sub> Chemical Speciation Modules**

RTI has designated eight laboratories that will be involved in the program, which are described below:

- ***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 six months. COC and field sampling data sheets will be 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.

- ***Denuder Refurbishment Laboratory (DRL)***. Personnel in the DRL will be responsible for refurbishment of all denuders. The DRL must have a hood and sink for work with volatile solvents and cleaning spent denuders. The DRL will coordinate with the SHAL to prepare and track denuders as they are needed.
- ***Gravimetric Mass Laboratory (GML)***. Personnel in the GML will be responsible for all activities associated with PM 2.5 mass determinations on Teflon filters.
- ***Elemental Analysis Laboratory (EAL)***. Personnel in the EAL will be responsible for all elemental (selected elements, sodium through lead, by atomic number) analyses. RTI will analyze the majority of the sample, including all of the URG samples, which require quick turnaround. Chester LabNet will assist with elemental analysis support for the contract and will be responsible for Teflon filter acceptance testing.
- ***Cations/Anions Laboratory (CAL)***. Personnel in the CAL will be responsible for all ion analyses. This will include both anions (sulfate and nitrate) and cations (ammonium, sodium, and potassium) on sample filters. They will also be responsible for acceptance testing and cleaning, if necessary, of nylon and other filters used for collection and measurement of target anions and cations.
- ***RTI Organic Carbon/Elemental Carbon Laboratory (OC/ECL)***. Personnel in the OC/ECL will be responsible for total, elemental, organic, and fractions analyses on quartz filters. They will also be responsible for acceptance testing and cleaning, if necessary, of quartz filters.
- ***DRI OC/EC Laboratory***. Personnel in DRI's OC/EC laboratory will be responsible for carbon analysis by the IMPROVE method.
- ***Semivolatile Organics Laboratory (SVOL)***. Personnel in the DRI SVOL will be responsible for measuring individual SVOCs extracted from PM 2.5 collected on quartz filters and from backup sorbent traps.
- ***Microscopy Laboratory (ML)***. Personnel in the ML will be responsible for all optical and electron microscopy (with or without elemental particle analysis).

- ***X-ray Fluorescence Laboratory (XRFL)***. Personnel in RTI's XRF laboratory will be responsible for trace elemental analysis on Teflon™ filters. They will be responsible for sending excess filters to Chester Labnet for analysis.

Figure B.3.2 shows a flow diagram for filter processing by filter type. Teflon filters will be used for determination of gravimetric mass and element (sodium through lead) concentrations; some Teflon filters will be analyzed for ions; quartz filters will be used for determination of total, organic, elemental, and fractions concentrations; and nylon filters will be used for determination of cations (ammonium, sodium, and potassium) and anions (sulfate and nitrate).

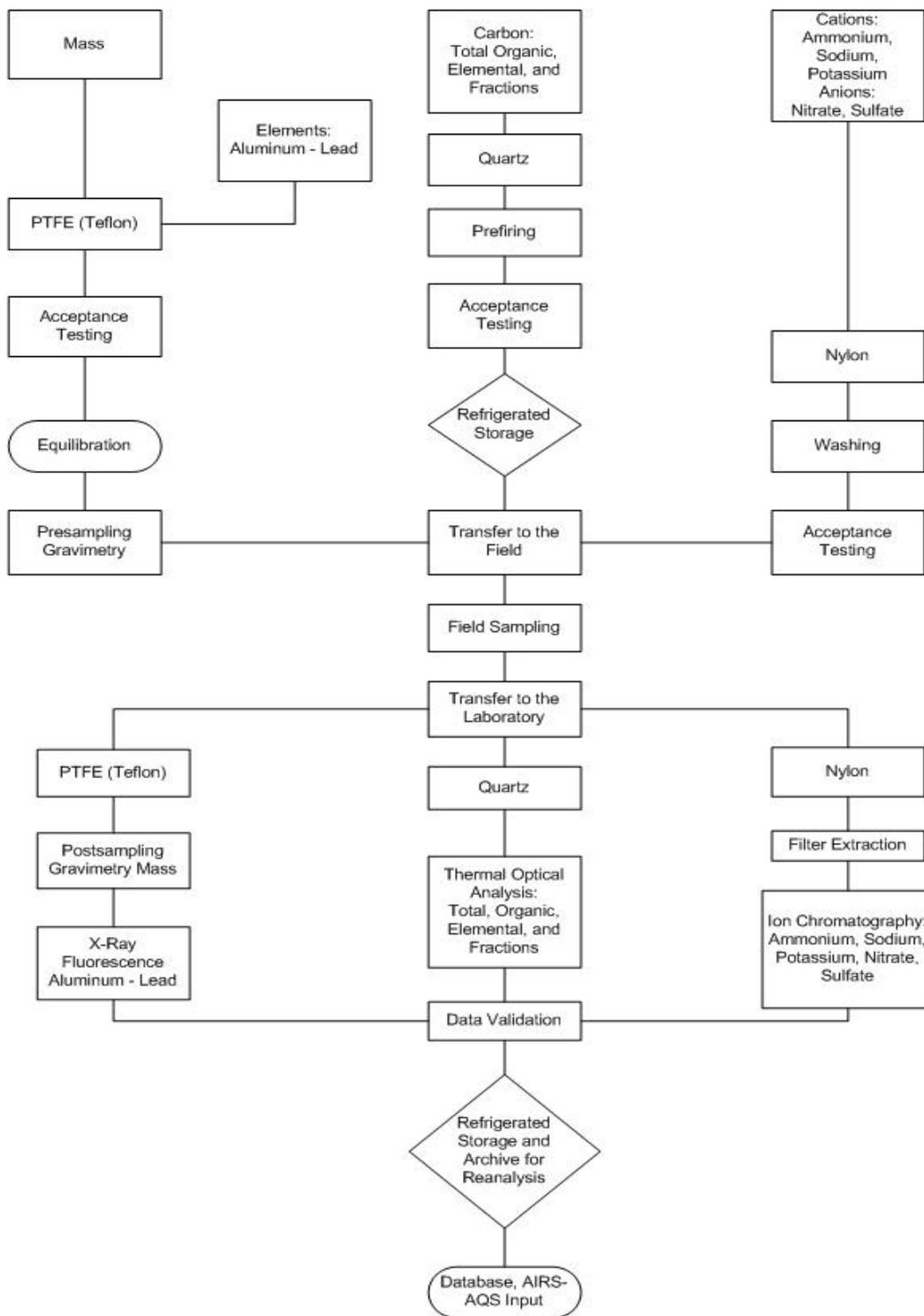
Figure B.3.3 shows the anticipated movement of filters and extracts through RTI laboratories described above. The focal point for shipping and receiving sampling media and for archiving analyzed filters and extracts is the SHAL. The other laboratories, except for the DRL, will be responsible for cleaning 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.

It should be noted that following final weighing in the Gravimetric Mass Laboratory, custody of the exposed Teflon filters is transferred to Ms. Andrea McWilliams (Bldg. 7, Room 212). She will distribute filters to two laboratories, Chester LabNet and RTI. Analyzed filters will be returned to Ms. McWilliams to either archive, or in the case of filters collected with URG instrumentation, send the filters to the Cations/Anions Laboratory.

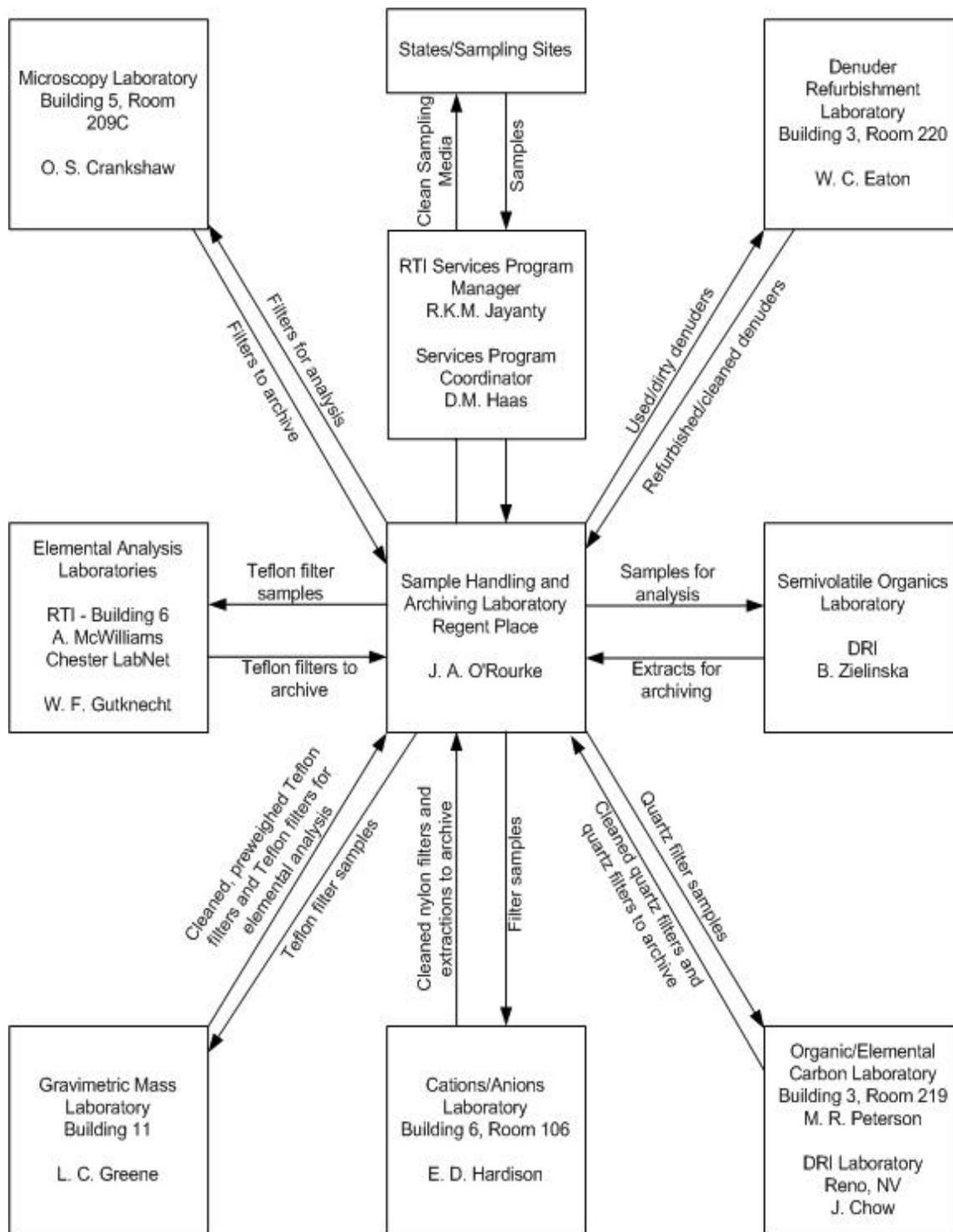
Table B.3.1 shows the sampling media used in each type of PM 2.5 speciation sampler, the species collected on each type of filter, and the RTI laboratory (or laboratories) that will measure those species on that filter. All of the sampler models use at least one each of the three types of filters (Teflon, 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, assembled properly 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 will be 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 will be assembled according to the manufacturer's instructions and with the sampling components requested by the State agencies and approved by the DOPOs. These operations will be fully described in SOPs specific to each model of sampler.



**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. Movement of filters and extracts through RTI and subcontractor laboratories.**

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

SAMPLER		ROUTINE ANALYSIS					
Model	Sampling Module	Component	Gravimetric Mass Laboratory	Elemental Analysis Laboratory	Cations/Anions Laboratory	Volatilized Particulate	OC/EC Laboratory
			Mass	Elements	NO <sub>3</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	TC, OC, EC, and Fractions
					NO <sub>3</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	
					SO <sub>4</sub> <sup>2-</sup>	NH <sub>4</sub> <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup>	
MASS 400*	(single)	MgO Denuder Teflon Filter Nylon Filter (backup)	x	x	x	x	
MASS 450*	(single)	Quartz Filter			x		x
RAAS	Channel 1	Teflon Filter	x	x			
	Channel 2	MgO Denuder Nylon Filter			x	x	
	Channel 3	Quartz Filter					x
SASS	Channel 1	Teflon Filter	x	x			
	Channel 2	MgO Coated Al Denuder Nylon Filter			x	x	
	Channel 3	Quartz Filter					x
R&P speciation sampler	Channel 1	Teflon Filter	x	x			
	Channel 2	Na <sub>2</sub> CO <sub>3</sub> Coated Honeycomb Denuder Nylon Filter				x	
	Channel 3	Quartz Filter			x	x	x
R&P FRM	Unit 1*	Teflon Filter	x	x			
	Unit 2*	Quartz Filter					x

\*Separate FRM samplers for each channel.

### B.3.3.2 Shipping to and From the Field

Filter cassettes, sampling modules, and any additional required components will be shipped in coolers, using the sample transport hardware provided by each sampling site or other location designated by the States through the DOPOs. Special services available from Federal Express, such as "PowerShip" and web-based tracking will be utilized. Federal Express priority overnight delivery will be used for most shipments.

Scheduling of shipping dates to and from the state agencies will be a key part of the SHAL's operation. RTI will 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 will be added to each cooler to maintain a transit temperature  $\leq 4$  °C. Each State agency will be responsible for freezing the ice packs and packaging the shipment so that it maintains a temperature of  $\leq 4$  °C. Shipments will be returned to RTI overnight by Federal Express as described above. The temperature of each shipment will be determined upon delivery at the SHAL using a temperature probe with digital readout. Temperature upon receipt will be recorded on a Level 0 validation form.

### B.3.3.3 Disassembly of Sampling Modules

Upon their return to RTI, sampling modules will be logged into the data base and disassembled by SHAL personnel. Each filter will be sealed in a new, clean, labeled petri dish and sent to the appropriate laboratory for analysis. Any denuders used in the module will be refurbished, 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 will be used to transfer batches of filters removed from the sampling modules in the SHAL to the respective RTI laboratories. Several filters will be 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 will be 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 will be used to transfer samples from RTI to its external analytical subcontractors.

 H10046D		Page 1 of	
		<b>RTI PM 2.5 Laboratory Chain of Custody Form (LCOC)</b> Research Triangle Institute Gravimetric Analysis Lab	
Bar Code	Identification Number	Filter Type	Analysis Requested
<b>Delivery Order: 0002</b>			
	A1003961	Teflon Filter 11003057	GRAV
	A100529W	Teflon Filter 1102349	GRAV
	A100540R	Teflon Filter 11003091	GRAV
	A1005785	Teflon Filter 11002452	GRAV
	A1005854	Teflon Filter 11003080	GRAV
	A1005912	Teflon Filter 11002338	GRAV
	A100603P	Teflon Filter 11002496	GRAV
	A100606S	Teflon Filter 11003079	GRAV
	A100607T	Teflon Filter 11002485	GRAV
<b>Delivery Order: 0003</b>			
	A100538X	Teflon Filter 11002225	GRAV
	A100541S	Teflon Filter 11002463	GRAV
	A100546X	Teflon Filter 11002429	GRAV
	A1005821	Teflon Filter 11003068	GRAV
	A100612Q	Teflon Filter 11002236	GRAV
<b>Delivery Order: 0004</b>			
	A100410I	Teflon Filter 11003046	GRAV
<b>Custody Record (Name, Date)</b>			
1. RTI SHAL, Out		Laboratory, In	
2. Laboratory, Out		RTI SHAL, In	
Comments _____			
_____			
_____			

**Figure B.3.4.** RTI Laboratory Chain of Custody Form used in tracking.

### B.3.3.5 Archiving of Filters and Extracts

See *Standard Operating Procedure for Long-Term Archiving of PM<sub>2.5</sub> 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 analyzed subsequently for ions cannot be archived)
- Teflon filter 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) (SVOC analyses were not performed in the mini-trends program)
- Teflon (or other) filters (following subsampling for microscopic analysis).

Quartz filters will be archived for up to 5.5 years in petri-slide holders, sorted by location into petri-slide trays, and sorted by sampling date within a tray. Full trays of quartz filters will be placed in heavy-duty plastic zippered bags and placed in plastic bins in a freezer maintained at or below -15°C. Individual filters will be located by Archive Bin ID, Tray ID, and Aliquot ID.

Teflon filters will be archived for up to 5.5 years in petri-slide holders, sorted by location into petri-slide trays, and sorted by sampling date within a tray. Full trays of Teflon filters will be 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 will be located by Archive Bin ID, Tray ID, and Aliquot ID.

Filter extracts (nylon or Teflon) will be archived for 6 months in extraction vials, grouped in lab batches, which will be 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 will be 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. The reason for removal of such gases is to preclude their collection on the filter or on the backup absorbent pad 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, and thus the nitrate 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<sub>2.5</sub> collection filter.

RTI will provide support for the operation and use of denuders associated with the four types of speciation samplers to be used in the speciation networks. Denuder specifications for the samplers are provided in Table B.3.2. Only one source of XAD-4 resin (ground to size specifications and cleaned) is presently available.

**Table B.3.2 Denuders Used with Speciation Samplers**

Sampler	Denuder Description
IMPROVE	<ul style="list-style-type: none"> <li>• Magnesium oxide-coated glass. Useable for up to 10 months if in rotation with other denuders.</li> </ul>
MASS 400	Magnesium oxide-coated glass. Annular design. Removes acids including nitric acid.
MASS 450	<ul style="list-style-type: none"> <li>• XAD-4-coated glass. Removes SVOCs.<sup>(a)</sup></li> </ul>
RAAS	<ul style="list-style-type: none"> <li>• Magnesium oxide coated glass. Annular design. Removes acids including nitric acid used for three months (30 exposure sessions).</li> <li>• XAD-4-coated glass. Removes SVOCs.<sup>(a)</sup></li> </ul>
R&P 2300	<ul style="list-style-type: none"> <li>• Glass honeycomb, “ChemComb®” coated with sodium carbonate/glycerol coating solution. Recoated after each 24-hour daily sampling session.</li> </ul>
SASS	<ul style="list-style-type: none"> <li>• Magnesium oxide-coated aluminum honey comb design. Usable for up to 18 months if in rotation with five other denuders.</li> <li>• Activated carbon. Removes SVOCs. Usable up to 12 months; surface can be renewed by heating or a replacement can be purchased.<sup>(a)</sup></li> </ul>

(a) Optional; not currently being used.

The State (or local agency within the state) planning to employ denuders in its PM2.5 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 SPM of the State’s need for denuders (and filters), and details on special filter pack arrangements associated with the denuders. The sampling schedule also will be 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 IMPROVE, MASS, RAAS, and R&P denuder devices according to one or more of the following SOPs:

- *Standard Operating Procedure for the 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 R&P Speciation Sampler Chemcomb™ Denuders with Sodium Carbonate*
- *Standard Operating Procedure for Coating Aluminum Honeycomb Denuders with Magnesium Oxide*

All prepared, or refurbished, or purchased denuders will be 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 and R&P samplers' denuders will be installed in the sampling module prior to shipment to the field.

The denuders to be installed at the site sampler will be shipped by Federal Express to the requesting State or local agency. Denuders will be listed on the COC form that will accompany each shipment to a particular speciation sampler. A record of the number of uses of a particular denuder will be maintained by the laboratory SHAL so that the denuder is refurbished or replaced according to schedule. All MgO denuders are currently replaced after approximately 30 exposures and NaCO<sub>3</sub> denuders are replaced after each sampling event. A conservative limit for number of uses must be established by EPA research.

The denuders, COC forms, and field data sheets will be returned with the filter samples to RTI from the sampling sites by Federal Express. Upon receipt, the denuders will be inspected for damage. The State will be responsible for replacement or repair of denuder components damaged in the field; the shipping company will be 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 denuders will be refurbished. The newly-coated denuders will be 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 PM2.5 Gravimetric Analysis*, describes the procedure to be used for gravimetric mass determination in RTI's laboratory.

#### **B.4.2 EDXRF Analysis for Elements**

SOPs used by RTI and Chester LabNet for EDXRF analysis are listed below:

##### **RTI**

- *Standard Operating Procedures for X-Ray Fluorescence Analysis of PM2.5 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)*
- *Standard Operating Procedures for the Kevex XRF 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 PM2.5 Material*
- *Standard Operating Procedures for PM2.5 Anion Analysis*
- *Standard Operating Procedures for PM2.5 Cation Analysis*

#### **B.4.4 Carbon Analysis**

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

DRI's laboratory facility and procedures for OC/EC analysis by the IMPROVE method are detailed in *Standard Operating Procedure for Thermal/Optical Reflectance Carbon Analysis of Aerosol Filter Samples*.

While the STN Thermal-Optical-Transmittance (TOT) analysis and the IMPROVE Thermal-Optical-Reflectance (TOR) 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 STN/TOT analysis is a timed analysis with fixed times at each temperature in the heating profile, and the

IMPROVE/TOR analysis is an event-driven analysis with the sample remaining at a given temperature until evolution of carbon from the filter drops to near zero. An STN/TOT analysis runs for a total of 12 minutes; and an IMPROVE/TOR analysis may take anywhere from 15 minutes to 70 minutes. The maximum temperatures for the various fractions are also different. The table below describes the carbon fractions measured for both methods and the conditions (non-oxidizing or oxidizing atmosphere, maximum temperature) under which each fraction is measured.

### Carbon Fractions Reported

Atmosphere/Fraction	STN/TOT <sup>†</sup>		IMPROVE/TOR <sup>‡</sup>	
	Analyte Name	Maximum Temperature	Analyte Name	Maximum Temperature
He&He-O <sub>2</sub> /OC	OC	900°C	Regular OC	550°C
He/1st OC	Pk1_OC	310°C	OC Peak #1	120°C
He/2nd OC	Pk2_OC	480°C	OC Peak #2	250°C
He/3rd OC	Pk3_OC	615°C	OC Peak #3	450°C
He/4th OC	Pk4_OC	900°C	OC Peak #4	550°C
He-O <sub>2</sub> /Pyrolyzed C	Pyrol_C	varies	Reg. pyro'd OC	varies
He-O <sub>2</sub> /Elemental	EC	920°C	Regular EC	800°C
He-O <sub>2</sub> /1st EC	Not Calculated	675°C	EC Peak #1	550°C
He-O <sub>2</sub> /2nd EC	Not Calculated	750°C	EC Peak #2	700°C
He-O <sub>2</sub> /3rd EC	Not Calculated	825°C	EC Peak #3	800°C
He-O <sub>2</sub> /4th EC	Not Calculated	920°C	N/A	N/A

<sup>†</sup>Speciation Trends Network/Thermal-Optical-Transmittance Analysis

<sup>‡</sup>Interagency Monitoring of Protected Environments/Thermal-Optical-Reflectance Analysis

#### B.4.5 Semi-volatile Organic Compounds

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

#### B.4.6 Characterization of Particles by Electron and Optical Microscopy

*Note: Scanning Electron and optical microscopy have not been performed in the speciation program as of this date.*

RTI will provide scanning electron microscopy (SEM) and optical microscopy for characterization of particulate samples. RTI has extensive experience in the analysis of airborne particulate matter by both optical and electron microscopy techniques, having analyzed a large number of PM10 filters by optical microscopy for several state air quality agencies and a significant number of air filters for commercial firms.

#### B.4.6.1 SEM

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 particulate matter. 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 purpose of analysis by SEM. The procedures for analysis by particulate material by SEM are described in detail in *Standard Operating Procedure for Samples Preparation and Analysis of PM<sub>10</sub> and PM<sub>2.5</sub> Samples by Scanning Electron Microscopy*.

#### B.4.6.2 Optical Microscopy

The RTI optical microscopy laboratory is fully equipped with both stereobinocular 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  $\mu\text{m}$ . 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<sub>2.5</sub> sampling is not a suitable substrate for analysis by optical microscopy because the thickness and translucent nature of the filter severely limit the transmittal of light and 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 and other criteria applicable to the national gravimetric PM<sub>2.5</sub> monitoring network. Table B.5.1 contains a summary of all the laboratory QC samples for gravimetric measurements and their acceptance criteria.

**Table B.5.1 Gravimetric Analysis QC Sample Requirements and Acceptance Criteria**

<b>Requirement</b>	<b>Frequency</b>	<b>Acceptance Criteria</b>
<b>Blanks</b>		
Lot Blanks	3 per lot	± 15µg difference
Lab Blanks	1 per weigh session	± 15µg difference
<b>Calibration/Verification</b>		
Balance Calibration	1/yr	Manufacturers spec.
Temp. Calibration	1/yr	± 2° C
RH Calibration	1/yr	± 2%
<b>Accuracy</b>		
Balance Audit	1/year	± 15µg for unexposed filters
Balance Check (100 and 200µg standards)	beginning, every 10 <sup>th</sup> sample, end	≤ 3µg
<b>Calibration standards</b>		
Working Mass Stds.	1/yr	25µg
Primary Mass Stds.	1/yr	25 µg
<b>Precision</b>		
Duplicate filter weighings	Every 10 <sup>th</sup> filter	± 15µg difference

- At least two Class 1 working mass reference standards traceable to the National Institute of Standards and Technology (NIST) will be 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 including reweighing of any filters not bracketed by acceptable standard checks.
- At least one working standard will be weighed after every 10th 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.
- Standard weight measurements will be monitored by QC charts throughout the year to determine if any bias has developed in the weights or the balance.
- Replicate weighings will be made of every 10th filter at the end of a particular weighing session; if the weights differ by more than 15 µg, the laboratory supervisor for the project will be consulted and corrective action will be taken.

- At least one laboratory blank will be 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.
- Field blanks will comprise 10 percent of the total filters analyzed, with post-sampling weights 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 will be checked. If the laboratory blanks are within 15 µg, the State agencies will be notified to troubleshoot possible contamination in the field. [Note: Filters are not identified as field blanks to the laboratory staff. If the weight difference of any of the field blanks exceeds 30 µg, followup checks and corrective actions will be initiated by the QA Officer.]
- The microbalance will be calibrated annually or more frequently as needed by a Mettler technician.
- The primary and working mass reference standards will be recertified annually against NIST-traceable mass standards at a State weights and measures laboratory holding a NIST certificate of traceability.
- The accuracy of the temperature and relative humidity (RH) recorders will be verified annually.

#### B.5.1.1 Gravimetric Disaster Recovery Plan

For backup and archiving purposes, the raw Microsoft Excel spreadsheets, including all QC data, and the data logger spool files will be stored on a Microsoft Windows NT server, which is backed up nightly by RTI ITS personnel using Arcadia Backup Exec software and DAT backup tape drive. The backup tapes are stored by ITS at an approved off-site location. In addition, archival copies of the raw data spreadsheets and data logger files are copied to a CD on a monthly basis. Hard copies of raw spreadsheets will be printed for backup purposes.

### **B.5.2 Quality Criteria for Ion Analysis**

The quality criteria applicable to analysis of cations and anions are provided in Table B.5.2.

#### 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 1-GB disk storage partition on an NT file server located in a different 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,

**Table B.5.2 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.	$\pm 10\%$ 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.	$\pm 10\%$ 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 $\geq 10$ 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 percent	Field samples not bracketed by acceptable QC samples must be reanalyzed after corrective actions have been taken.

and reporting and frequent backups to CDR media. At least two archive CD's are burned of any data before it is deleted from either a lab PC or the NT file server (typically done to free up disk storage space), and the two archive CD's are kept in different buildings at RTI.

### B.5.3 Quality Criteria for EDXRF

#### B.5.3.2 RTI

QC elements practiced by RTI are shown in Table B.5.3.

**Table B.5.3 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 1833 and Micromatter QC standards	Within $\pm 5\%$ of certified values	Investigate and recalibrate if necessary
Instrument precision	Every tray of samples	Comparison of measured value and value at time of calibration for 6 elements on Micromatter QC standard	Relative % error of $\leq 5\%$	Batch reanalysis
Recovery (Accuracy)	Monthly	Measure 7 elements on NIST SRM 1832	Within 3 sigma of the certified values	Investigate and recalibrate if necessary
Reproducibility	Every 20 <sup>th</sup> sample	Duplicate analysis of every 20 <sup>th</sup> filter sample	Difference of $\leq 10\%$ for values with original value $\geq 3x$ its uncertainty	Investigate and possible batch reanalysis

#### B.5.3.2.1 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 CD-R media, which are stored in Building 7.

#### B.5.3.2 Chester LabNet

QC elements 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.5.4.

**Table B.5.4 Chester Labnet's QC Procedures Used to Analyze EDXRF Elements**

QC Element	Frequency	Control Limits	Corrective Action
Calibration	as needed	--	--
Calibration verification	weekly	within NIST uncertainties	recalibrate
Instrument precision	once per batch of $\leq 15$	95–105% recovery	batch reanalysis
Excitation condition check	every sample	within analysis uncertainty	sample reanalysis
Sample replicate precision	10%	$\pm 5$ relative percent difference	batch reanalysis

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

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

where,

$B_i$  is the background counts for element  $i$ ,  
 $s_i$  is the sensitivity factor for element  $i$ ,  
and  $t$  is the counting lifetime.

Theoretically, detection limits may be decreased by simply increasing the counting lifetime. 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.

#### **B.5.4 Quality Criteria for OC/EC Analysis**

The QC applicable to the carbon speciation analysis are provided in Table B.5.5.

##### **B.5.4.1 OC/EC Disaster Recovery Plan for Data**

The OC/EC Lab supervisor or analyst copies raw data (txt) and calculated data (csv) files from the hard drives of each lab computer to a 1-GB disk storage partition on an NT file server located in a different RTI building. Data stored on the NT file server is 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 CDR media. At least two archive CD's are burned of any data before it is deleted from either a lab PC or the NT file server (typically done to free up disk storage space), and the two archive CD's are kept in different buildings at RTI.

**Table B.5.5 QC Criteria for OC/EC Analysis by STN Method**

QC Element	Frequency	Acceptance Criteria	Corrective Action
Method Detection Limit	Annually	MDL $\leq 0.5 \mu\text{g C}/\text{cm}^2$	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% to 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 $\leq 0.3 \mu\text{g}/\text{cm}^2$	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 ( $R^2$ ) $\geq 0.99$ [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% to 110% recovery, and (2) calibration peak area 90% to 110% of average for the weekly 3-point calibration.	Initiate corrective action, if necessary, to solve the problem before analyzing samples.
Duplicate Analyses	10% of Samples	(1) TC Values greater than $10 \mu\text{g}/\text{cm}^2$ -- Less than 10% RPD, (2) TC Values 5 - $10 \mu\text{g}/\text{cm}^2$ -- Less than 15% RPD, (3) TC Values less than $5 \mu\text{g}/\text{cm}^2$ -- Within $0.75 \mu\text{g}/\text{cm}^2$ .	Flag analysis results for that filter with non-uniform filter deposit (LFU) flag.

### B.5.5 Quality Criteria for Denuder Refurbishments

Quality control steps applicable to acid gas denuder refurbishment are listed below in Table B.5.6.

**Table B.5.6. 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.	Prepare fresh coating solution if not refrigerated or if MgO slurry has dried.
Reproducibility of MgO coating (applies to RAAS, MASS, and SASS)	After training session of technicians.	For 10 MgO-coated denuders, determine mass applied and strive for 15% RSD.	Inspect quality of application. Repeat coating of denuders that have low mass applied.
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.
Final inspector	After each coating.	As applicable, check each denuder for; <ul style="list-style-type: none"> <li>• broken glass</li> <li>• O-ring quality</li> <li>• Absence of debris affecting proper seating of denuder.</li> </ul>	Remove broken 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.

### B.5.6 Uncertainty Determination

Uncertainty values reported to AQS (formerly AIRS) with each concentration record will include components of both the 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 STN analytes are included in Appendix A.

### B.5.7 Minimum Detection Limits

The minimum detection limits (MDLs) for the STN analytes are included in Appendix B.

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

### B.6.1 Gravimetric Laboratory

Two different relative humidity and temperature recording devices will be used in the Gravimetric 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 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  $\pm 5\%$  and temperature = 20-23°C with a control of  $\pm 2^\circ$ ) for the preceding 24 hours. Critical criteria tables included in March 2000 guidance from OAQPS on the use of data flags for PM2.5 AIRS data offer slightly relaxed acceptance criteria (RH = 30-40% with a control of  $\pm 5\%$  *standard deviation* and temperature = 20-23°C with a control of  $\pm 2^\circ$  *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, since the consequence of each choice is the same: an AIRS 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 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
Polonium strip replacement	6 Months	RTI Laboratory supervisor
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 weight 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 log book.
Calibration verification	Weekly	Percent recovery of seven elements on thin-film NIST standards.	Adjust instrument calibration factors.	Document in instruments log book.
Ongoing calibration verification	Run with every tray of samples.	95-105% recovery using a multi-element sample containing Ti, Fe, Cd, Se, Pb, and SiO deposits of 5-10 $\mu$ g/cm <sup>2</sup> .	Re-check instrument calibration and adjust if necessary; re-analyze samples.	Document in instrument's log book.
Fast Discriminator (FD)	Weekly	FD value is located on the system status. If the FD is set too low, low energy peaks can be lost and if set too high, the dead time readings can be inaccurate and higher than normal.	Adjust rate	Document in instrument's log book.

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

Item	Maintenance Frequency	Responsible Party
Vacuum pump maintenance and check oil level	Monthly	XRF analyst
Stability test	Monthly - This test checks for instability due to changes in the X-ray tube output or peak shift will be detected	XRF analyst
Perform 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 eleven elements on thin-film NIST standards	Instrument recalibration	Document in instrument log book
Ongoing calibration	Every ten 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 check oil level	Weekly	XRF analyst
Chiller maintenance and check coolant level	Weekly	XRF analyst
Replenish liquid nitrogen Dewar	Weekly	XRF analyst

## B.6.4 Organic/Elemental Carbon(OC/EC) Laboratory

### B.6.4.1 RTI OC/EC Laboratory

In the OC/EC laboratory, the three thermal-optical transmittance (TOT) analyzers are routinely tested and maintained. Table B.6.9 details the analyzer maintenance schedule and who will be responsible for performing the maintenance.

**Table B.6.9 OC/EC Laboratory Maintenance Schedule and Responsibility**

Item	Maintenance Frequency	Responsible Party
TOT Analyzer	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.6.4.2 DRI OC/EC Laboratory

In the DRI OC/EC laboratory, the five thermal-optical reflectance (TOR) and five dual reflectance/transmittance (TOR/TOT) analyzers are routinely tested and maintained. Table B.6.10 details the analyzer maintenance schedule and who will be responsible for performing the maintenance.

**Table B.6.10 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 Cotrol Services (routine) or Mettler Toledo, Inc., service representative (as needed)
Muffle Furnace	As required.	DRI OC/EC Analyst

## **B.7 Instrument Calibration and Frequency**

### **B.7.1 Gravimetric Laboratory**

The microbalance will be externally calibrated and serviced, if necessary, at least annually or as needed when problems are detected. Records will be kept by RTI on the service date and the calibration results. NIST-traceable standards will be tracked to determine if any bias is entering into the system. These standards will be recertified annually. Control charts based on a standard weight will be 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 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 ppm are recalculated with the 25.0 ppm standard added to the calibration curve.

### **B.7.3 EDXRF Laboratory**

#### **B.7.3.2 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, or misidentification or failure to detect one or more elements.

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

- Micromatter, Inc. See table below for listing of the elements and compounds on thin Mylar film.

Analyte	Analyte	Analyte	Analyte
Sodium or Chlorine as NaCl	Vanadium as V metal	Bromine or Cesium as CsBr	Antimony as Sb metal
Magnesium as Mg metal	Chromium as Cr metal	Rubidium or Iodine as RbI	Barium as BaF2
Aluminum as Al metal	Manganese as Mn metal	Strontium as SrF2	Lanthanum as LaF3
Silicon as SiO	Iron as Fe metal	Yttrium as YF3	Cerium as CeF3
Gallium or Phosphorus as GaP	Cobalt as Co metal	Niobium as Nb2O3	Samarium as SmF3
Sulfur as CuSx	Nickel as Ni metal	Molybdenum as MoO3	Europium as EuF3
Potassium or Iodine as KI	Copper as Cu metal	Silver or Mercury as Ag-Hg Amalgam	Terbium as TbF3
Calcium as CaF2	Zinc as ZnTe	Cadmium or Selenium as CdSe	Tungsten as WO3
Scandium as ScF3	Arsenic as GaAs	Indium as In metal	Gold as Au metal
Titanium as Ti metal	Selenium as Se metal	Tin as Sn metal	Lead as Pb metal

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

- NIST SRM 1832 multi-elemental XRF thin film standard.

Analyte	Certified Value (% by Wt.)
Aluminum	9.24 ± 0.6
Silicon	21.77 ± 0.7
Calcium	12.34 ± 0.8
Vanadium	2.96 ± 0.3
Manganese	2.83 ± 0.3
Cobalt	0.64 ± 0.04
Copper	1.50 ± 0.1

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<sub>2</sub> line (1.487 KeV) and a high energy line is measured at the Cr K<sub>2</sub> 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:

- Micromatter, Inc., vapor deposit of single or two non-interfering elements onto thin mylar film
- EPA organo-metallic acetate film, usually with two non-interfering elements
- 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, interference factors correction for PM<sub>2.5</sub> particle size are presented in Section b.4 of Appendix A-4.4 of the original proposal.

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.7.1, the TOT analyzer is calibrated daily using an external standard and during every analysis using an internal standard. The external standard is prepared by spiking a clean 1.5-cm<sup>2</sup> section of quartz filter with 10 µL of a standard sucrose solution, which corresponds to a filter loading of about 14 µgC/cm<sup>2</sup>. The internal standard is 5% methane in helium. A set of three concentrations of external standards (10 µL of each, giving a range corresponding to about 3-27 µgC/cm<sup>2</sup> of filter is run weekly.

**Table B.7.1 RTI OC/EC Instrument Calibration and Frequency**

Laboratory	Instrument	Calibration: Frequency
RTI OC/EC Laboratory	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 $\pm 10\%$ since the last three-point calibration.
DRI OC/EC Laboratory	TOR carbon analyzer	Semi-Annual: separate 5-pt cals with 5% CH <sub>4</sub> /He, 5% CO <sub>2</sub> /He, sucrose solution, and KHP solution (average slopes for the four separate calibrations; new slope 90-110% of previous slope if no instrument repairs).  Calibration injections of the two NIST traceable gas standards; reverse two cal gases and the carrier gases (O <sub>2</sub> /He and He) between morning and afternoon injections. (counts should be same)

B.7.4.2 DRI OC/EC Laboratory

As shown in Table B.7.2, the DRI carbon analyzers are calibrated in three ways: an end-of run calibration peak, manual calibration injections of CH<sub>4</sub>/He and CO<sub>2</sub>/He, and instrument calibration using KHP, sucrose and the two calibration gases, daily using an external standard and during every analysis using an internal standard.

**Table B.7.2 DRI OC/EC Instrument Calibration and Frequency**

Laboratory	Instrument	Calibration: Frequency
DRI OC/EC Laboratory	TOR carbon analyzer	Semi-Annual: separate 5-pt cals with 5% CH <sub>4</sub> /He, 5% CO <sub>2</sub> /He, sucrose solution, and KHP solution (average slopes for the four separate calibrations; new slope 90-110% of previous slope if no instrument repairs).  Calibration injections of the two NIST traceable gas standards; reverse two cal gases and the carrier gases (O <sub>2</sub> /He and He) between morning and afternoon injections. (counts should be same)  End-of-run calibration peak with 5% CH <sub>4</sub> /He calibration gas performed as part of routine program (counts > 20,000).

## **B.8 Inspection/Acceptance Requirements for Supplies and Consumables**

Supplies and consumables will be 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 STN 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 (i.e., laboratory blanks and field blanks). Cassettes, if required, will be 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 which 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 which 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, etc.) which 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. 7592-204) 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 (i.e., laboratory blanks and field blanks). Cassettes, if required, will 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 2 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 Andersen Instruments (Cat. No. 7410-204). These filters will be prepared as follows:

- Rinse twice in deionized water, approximately one minute per rinse
- 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
- 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

Quartz filters (Whatman 47 mm diameter) are purchased from Andersen Instruments (Catalog No. 1851-047). These filters are prepared by RTI in-house. The procedure is as follows:

Filters are typically prefired in batches of 100, in a muffle furnace at 900°C for at least 3 hours.

- Once the filters have cooled in the furnace under a low flow of nitrogen, they are acceptance tested.
- Accepted filters are placed in groups of 5 to 10 in clean, sterile petri dishes, which are closed and labeled with the batch number.
- Two randomly selected filters (per 100 cleaned) will be tested for total carbon according to National Institute for Occupational Safety and Health (NIOSH) Method 5040 filters to check for evidence of inadequate cleaning or for

contamination that may have occurred during transport. If the total carbon level exceeds  $1 \mu\text{gC}/\text{cm}^2$ , the filters from that lot will be rejected or recleaned.

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

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 will be 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**

In the 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 data bases, literature files, etc. Any supplemental, non-direct measurement data supplied by the monitoring organizations or subcontractors for inclusion in the data base 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, bar code 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 electronic mail and incorporated into the SQL Server database. An AIRS-ready data file is then prepared for import into AIRS.

### **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. Bar code 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 STN Program.

**Table B.10.1 Label Identifiers for  
Tracking STN Records and Equipment**

<b>Prefix</b>	<b>Label Type</b>
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 can't be deleted while records that depend on that record exist. This prevents creation of orphaned records.

As an example of referential integrity, laboratory results for a laboratory sample (aliquot) can't 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 that have incorrect sample identification would be prevented. Attempts to delete an aliquot that has analytical data would also not be successful, 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 Chain of Custody (COC) form. To prevent data entry errors, information on these forms are double entered and compared by a comparison program and 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 is sent from the laboratory to the DMS as an electronic file through electronic mail. The laboratory data is 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 following is a short summary of backup and restore procedures, which are covered in more detail in RTI's Speciation Data Disaster Recovery Plan.

The information contained in the SQL Server database is written to backup files by an SQL Server Agent job. Two types of files are generated: backup files that contain the entire database contents and transaction files that contain only the changes since the last file generation. The (full) backup files are generated once each week and the transaction files are generated each hour during the business day (8 am to 6 pm, Monday through Friday).

These files are copied daily to the 70 Gbyte backup tape drive by use of the Segate Backup Exec program. All backup tasks are scheduled and run unattended, except for weekly tape changes. Backup tapes are kept for approximately four weeks before being overwritten.

In addition to the daily copy to tape, the backup and transaction log files are copied to a second server (Athena) by an automated SQL Server Agent job. This job checks for any new files on an hourly basis during the business day (on the half-hour from 8:30 to 6:30 Monday through Friday). The second server is located in a different building approximately 1 mile away (800 Park). Files on the second server are kept for 8 days (after which they are automatically deleted by the SQL Server Agent job). This second copy would allow for quicker recovery and less data loss in case of a major disaster (such as fire, etc.).

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

The DMS 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 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<sup>th</sup> percentile.

**Table B.10.2 Statistical Validation Limits for Routine Data**

Percentile	Tail	Analyte(s)	Sample Type	Limit µg/m <sup>3</sup>	Flagged Analytes	Internal Flag
2.0	LOWER	PM25 Mass Conc.	ROUTINE	2.98	PM25 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	ions, XRF	QCR
98.0	UPPER	Sulfur/Sulfate Ratio	ROUTINE	0.45	ions, XRF	QCR

**Table B.10.3 Statistical Validation Limits for Blanks**

Tail	Analyte(s)	Sample Type	Limit µg	Flagged Analytes	Internal Flag
UPPER	PM25 Mass	FIELD BLANK	50.00	PM25 Mass	QL1
UPPER	PM25 Mass	TRIP BLANK	50.00	PM25 Mass	QL1

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

**Table B.10.4 Mapping of Outlier Flags onto AIRS Codes**

Objective Cause Found for Level 1 Outlier	AIRS 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

Notes:

[1] - Use the applicable AIRS validity status code.

[2] - Use the applicable AIRS null value code.

(N/A) - Not Applicable.

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

**Table B.10.5 Automated Checks Based on Fixed Criteria**

Parameter	Limits	AIRS Flag or Action
Exposure Duration, $t_{exp}$	$23 < t_{exp} < 25$ hrs	AN - machine malfunction AQ - collection error AV - power failure or other code as appropriate
Holding Time before removal from sampler, $t_{pick-up}$	$t_{pick-up} < 48$ 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:

- Chain of Custody (COC) form number for each event - field and trip blanks, routine samples, 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 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.
- Total counts of AIRS-deliverable records - each sampler type should generate a specific number of AIRS 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.

- 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.
- Sampled date vs. scheduled date - Any event where these date records do not agree is investigated by examining the FSCOC form, and by contacting the monitoring agency, if necessary. If a sample was actually run on the wrong date the data is transmitted to AIRS with the date actually run. If the date is incorrect due to a typographical or other error, it is corrected.

#### B.10.4.3 Entry and Verification of Data Changes from the States

Changes requested by the state agencies are entered into RTI's data base 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 AIRS 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 AIRS text file is regenerated and transmitted to EPA's AIRS data base as discussed in the next section.

#### B.10.5 AIRS Data Entry

Only routine (actual sampled) data are transmitted to AIRS. Field and Trip Blank data are included in the monthly data reports that go to the state monitoring agencies, and are also provided to EPA/OAQPS for statistical analysis, but are not sent to AIRS.

RTI is entering the data directly into AIRS. Table B.10.6 summarizes all the AIRS parameter codes applicable to the PM2.5 Chemical Speciation analytes. Table B.10.7 presents the AIRS 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.

The validity status of AIRS data is reported in two ways: Data that are qualified in some way but which may be useful for some purposes are assigned Validity Status Codes. These codes, shown in Table B.10.8 do not over-write the data value, so that the data user has the option of including the data item in his or her analysis. On the other hand, data that are judged to be invalid receive an AIRS Null Value Code. In the current AIRS system, the 4-digit Null Value Code over-writes the data value such that the AIRS user cannot access the data. The Null Value Codes applicable to the STN Program are shown in Table B.10.9.

**Table B.10.6 Analytes and AIRS Parameter Codes**

AIRS Parameter Code	Analyte	Symbol	Analysis
88301	Ammonium	NH <sub>4</sub> <sup>+</sup>	Ion Chromatography, Cations
88302	Sodium	Na <sup>+</sup>	Ion Chromatography, Cations
88303	Potassium	K <sup>+</sup>	Ion Chromatography, Cations
88306	Nitrate	NO <sub>3</sub> <sup>-</sup>	Ion Chromatography, Nitrate
88309	Nitrate (MASS/nylon)	NO <sub>3</sub> <sup>-</sup>	Ion Chromatography, Nitrate
88310	Nitrate (MASS/teflon)	NO <sub>3</sub> <sup>-</sup>	Ion Chromatography, Nitrate
88403	Sulfate	SO <sub>4</sub> <sup>-2</sup>	Ion Chromatography, Sulfate
88101	Particulate matter 2.5μ	"PM2.5"	Gravimetric Mass
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)
88121	Europium	Eu	EDXRF (trace elements)
88124	Gallium	Ga	EDXRF (trace elements)
88126	Iron	Fe	EDXRF (trace elements)
88127	Hafnium	Hf	EDXRF (trace elements)
88128	Lead	Pb	EDXRF (trace elements)
88131	Indium	In	EDXRF (trace elements)
88132	Manganese	Mn	EDXRF (trace elements)
88133	Iridium	Ir	EDXRF (trace elements)
88134	Molybdenum	Mo	EDXRF (trace elements)
88136	Nickel	Ni	EDXRF (trace elements)
88140	Magnesium	Mg	EDXRF (trace elements)
88142	Mercury	Hg	EDXRF (trace elements)
88143	Gold	Au	EDXRF (trace elements)
88146	Lanthanum	La	EDXRF (trace elements)
88147	Niobium	Nb	EDXRF (trace elements)
88152	Phosphorus	P	EDXRF (trace elements)
88154	Selenium	Se	EDXRF (trace elements)

**Table B.10.6. (Continued.)**

<b>AIRS Parameter Code</b>	<b>Analyte</b>	<b>Symbol</b>	<b>Analysis</b>
88160	Tin	Sn	EDXRF (trace elements)
88161	Titanium	Ti	EDXRF (trace elements)
88162	Samarium	Sm	EDXRF (trace elements)
88163	Scandium	Sc	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)
88170	Tantalum	Ta	EDXRF (trace elements)
88172	Terbium	Tb	EDXRF (trace elements)
88176	Rubidium	Rb	EDXRF (trace elements)
88180	Potassium	K	EDXRF (trace elements)
88183	Yttrium	Y	EDXRF (trace elements)
88184	Sodium	Na	EDXRF (trace elements)
88185	Zirconium	Zr	EDXRF (trace elements)
88186	Wolfram (Tungsten)	W	EDXRF (trace elements)
88305	Organic Carbon STN	OC_TOT	OC/EC TOT
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
88320	Organic Carbon IMPROVE	OC_TOR	OC/EC TOR
88321	Elemental Carbon IMPROVE	EC_TOR	OC/EC TOR
88322	OH IMPROVE (high temperature OC)	OH	OC/EC TOR
88323	EH IMPROVE (high temperature EC)	EH	OC/EC TOR
88324	O1 IMPROVE	O1	OC/EC TOR
88325	O2 IMPROVE	O2	OC/EC TOR
88326	O3 IMPROVE	O3	OC/EC TOR
88327	O4 IMPROVE	O4	OC/EC TOR
88328	OP IMPROVE	OP	OC/EC TOR
88329	E1 IMPROVE	E1	OC/EC TOR
88330	E2 IMPROVE	E2	OC/EC TOR
88331	E3 IMPROVE	E3	OC/EC TOR

**Table B.10.7 Field Data and AIRS Parameter Codes**

<b>AIRS Parameter Code</b>	<b>Property</b>	<b>Units</b>
68103	Min ambient Temp	°C
68104	Max ambient Temp	°C
68105	Avg ambient Temp	°C
68106	Min Barometric Pressure	torr
68107	Max Barometric Pressure	torr
68108	Avg Barometric Pressure	torr

**Table B.10.8 AIRS Validity Status Codes**

<b>AIRS Validity Status Code</b>	<b>Flag Name</b>
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
D	Sandblasting
E	Forest Fire
F	Structural Fire
H	Chemical Spills & Indust. Accidents
I	Unusual Traffic Congestion
J	Construction/demolition
K	Agricultural Tilling
L	Highway Construction
M	Rerouting of Traffic
N	Sanding/salting of Streets
O	Infrequent Large Gatherings
P	Roofing Operations
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 AIRS Null Value Codes**

AIRS Code		Flag Name
Original AIRS	Re-engineered AIRS	
9964	BI	Sample Lost or Damaged in Shipment
9967	AA	Sample Pressure out of Limits
9968	AB	Technician Unavailable
9969	AC	Construction/repairs in Area
9970	AD	Shelter Storm Damage
9971	AE	Shelter Temperature Outside Limits
9972	AF	Scheduled but Not Collected
9973	AG	Sample Time out of Limits
9974	AH	Sample Flow Rate out of Limits
9975	AI	Insufficient Data (Can't Calculate)
9976	AJ	Filter Damage
9977	AK	Filter Leak
9978	AL	Voided by Operator
9979	AM	Miscellaneous Void
9980	AN	Machine Malfunction
9981	AO	Bad Weather
9982	AP	Vandalism
9983	AQ	Collection Error
9984	AR	Lab Error
9985	AS	Poor Quality Assurance Results
9986	AT	Calibration
9987	AU	Monitoring Waived
9988	AV	Power Failure (Powr)
9989	AW	Wildlife Damage
9990	AX	Precision Check (Prec)
9991	AY	Q C Control Points (Zero/span)
9992	AZ	Q C Audit (Audt)
9993	BA	Maintenance/routine Repairs
9994	BB	Unable to Reach Site
9995	BC	Multi-point Calibration
9996	BD	Auto Calibration
9997	BE	Building/site Repair
9998	BF	Precision/zero/span

**B.10.6 Data Management in the Laboratories**

Prior to entry of data into the STN Program's Data Base, the individual analytical laboratories are responsible for managing their data. The procedures for data management vary significantly between laboratories, and are described in the respective SOPs.

## 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. James Flanagan 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 quarterly during the first year of the contract, and annually thereafter.

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 participates in the following external QA assessments:

- EPA/NAREL:
  - 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](http://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/rtaudit2.pdf](http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/rtaudit2.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](http://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](http://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](http://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](http://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/](http://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 April 10, 2003.

## C.2 Reports to Management

Within 20 business days from receipt of the sample, the laboratory is responsible for forwarding completed Level 0 and 1 data validation checklists and the results of filter analyses to the appropriate EPA DOPO and State or local contact who submitted the delivery order. Upon approval, the final data set will be released from the laboratory in hard copy and electronic format to the EPA DOPOs, the State or local agency contacts, and to the AIRS electronic data base. Draft and final composite semi-annual data summary reports will be issued from the laboratory to the State or local contact, the DOPO, and the EPA Project Officer. Results of resolution of problems with data sets will also be prepared, sent to the concerned parties, and filed for the record.

The SPM will approve data report summaries sent to EPA. These act as monthly summaries of the projects. The SPM and the QA Manager will be notified whenever there is a QA problem and will be apprized 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. Semiannual 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 directed by the EPA regional QA laboratory for the STN.

The reports, summaries, and deliverables required for the proposed program and RTI's plans to produce them are described as follows:

- ***Level 0 Validation Report (Checklist)***. Data entry checking of the Level 0 validation process is performed by double-entry, with comparison done at RTI. This provides better accuracy than manually reviewing sampler forms to catch errors. Comparison between the requested sampling events and sampling data from the field sampling COC forms is performed using a database report.
- ***Level 1 Validation Report (Checklist)***. Data entry checking of the Level 1 validation process will be performed by double-entry, with comparison done at RTI. This will provide better accuracy than manually reviewing laboratory analysis result forms to catch errors. Cation, anion, and ammonia balance reports will be performed from the DBMS. Other statistical reports are done using data from the DBMS. Additional statistical reporting, as necessary, will be developed based on experience with the chemical speciation data.
- ***Traceability Report***. A report to show traceability between components and analytical results for each sampling event is produced using the DBMS. 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. This report is produced monthly.
- ***Monthly Analytical Report (Electronic and Hard copies)***. Data for this report are generated from RTI's DBMS using the calculated data and sampler. RTI has developed SQL queries to produce the report data sets. Electronic copies of this report are made available to the DOPOs, the State agencies submitting the delivery orders, and EPA/OAQPS.
- ***Semiannual Composite Analytical Report***. Composite data reports are being generated from RTI's DBMS and are being delivered to EPA's statistician for review and analysis. The query and reporting software have been developed and verified as part of the initial database development process.

## **D.1 Data Review, Validation, and Verification Requirements**

The following describes RTI's approach to data review, validation, and verification for gravimetric filter analysis. Similar procedures will be developed for the other analyses. The QC criteria given elsewhere in this QAPP will be used as the data validation requirements. Additional data screens will be developed as the STN starts up. Any data that indicates unacceptable levels of bias or precision or a tendency will be flagged and investigated.

Analytical data will be 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 AIRS, 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 valid holding times. Table B.10.8 provides the data validity flags currently available for PM2.5 data in AIRS. RTI will implement any additional or alternative flags that may be defined for PM2.5 chemical speciation data.

## **D.2 Validation and Verification**

RTI will be responsible for validating the gravimetric data and other data produced in its laboratories. Subcontractor laboratories will apply Level 0 and Level 1 screening to data produced in their laboratories. RTI will be responsible for overall, final data review, validation, and verification and for data reporting. Data validation and verification procedures are discussed below and in the following SOPs:

- A-5.5 Review of Data Reports (Chester LabNet Proprietary Methods)
- A-5.7 RTI XRF SOP
- A-11 Data Handling Procedures for the Speciation Analysis Program
- A-12.1 Procedures for Handling Aberrant and Out-of-Specification Data

### **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 filled in, and any problems related to COC, 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 will work 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 SPM 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 will be 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 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 sample or related group of samples.

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 will be 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 will be 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 will be 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 will be 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 based on input from the State monitoring agencies.

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 AIRS along with AIRS codes generated during the data validation process.

### **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 subcontractors EDXRF data, because this would duplicate efforts already expended by the subcontractors. However, data from EDXRF will be included in certain Level 1 checks such as reconstructed mass balance and sulfur/sulfate ratio.

### **D.2.4 Data Corrections**

RTI will investigate and attempt to make corrections of 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 when 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  $K_{\infty}$  from the titanium secondary target, titanium  $K_{\infty}$  from the iron secondary target) are corrected by the instrument software.

Impurities on the Teflon filter media are reported with all blank analyses. These impurities are not subtracted because the level of impurities is not consistent from filter to filter and because the subtraction would overcorrect the analyte signal due to attenuation by the deposit itself.

- Inter-element interference corrections are carried out as described in the XRF SOPs.

#### D.2.4.3 Ions

RTI's experience has indicated that artifacts and interferences pose no problem to the analysis of PM<sub>2.5</sub> 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 STN 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 judgement in applying corrections, and will fully document any such corrections and will discuss them with EPA before the data are submitted to AIRS.

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 (exposed to HCl vapor, which removes carbonate as CO<sub>2</sub>) and takes carbonate carbon as the difference between the pre- and post-acidification results. The second approach estimates carbonate carbon by integrating separately the carbonate peak in the thermogram and using the instrument's software to calculate the mass of carbonate carbon volatilized. Carbonate carbon is not generally present in PM<sub>2.5</sub> on quartz filters at loadings above the absolute error of the measurement; therefore, carbonate carbon was not included in the list of analytes for the current contract.

#### 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 meets 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 important user data characteristics are met. RTI will do the following to ensure that our performance meets contract requirements and client expectations:

- Regular communications between the SPM 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 by the QA Manager to ensure that quality problems are addressed in a systematic way. This system will enable the SPM to allocate 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 STN 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 SPM. The only exceptions to this rule will be dealings on a technical level with EPA personnel (e.g., to define data delivery formats for AIRS), 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 SPM 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 SPM.

## Appendix A Uncertainty Calculations

Uncertainty values reported to AQS (formerly AIRS) 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 STN analytes. A list of symbols is given at the end of the section.

The mass uncertainty (micrograms per filter) will be calculated as shown in eqn. (1) for XRF elements, Ion Chromatography, and OC/EC (mass uncertainties for gravimetric analysis are shown in equations (3) and (4) below). The use of the *max* function simply 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.

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

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

$$\sigma_{C_{i,j}} = \sigma_{M_{i,j}} / V_k \quad (2)$$

### Gravimetric Analysis (PM2.5 Mass)

Determination of gravimetric mass requires two separate weighings, each of which will contribute to the total uncertainty. Assuming that the preweighing uncertainty is equal to the postweighing uncertainty, the following equation would apply:

$$\sigma_{M_{i,j}} = \sqrt{(2\sigma_G^2 + M^2 \sigma_{Vk}^2)} \quad (3)$$

RTI is currently conducting experiments to determine whether or not loaded filters have the same repeatability as blank filters. If these are found to be different, then equation (3) would be modified as follows:

$$\sigma_{M_{i,j}} = \sqrt{(\sigma_{Gp}^2 + \sigma_{Gt}^2 + M^2 \sigma_{vk}^2)} \quad (4)$$

where  $\sigma_{Gp}$  and  $\sigma_{Gt}$  refer to preweighing and postweighing standard deviations, respectively. As with the other analyses, equation (2) is used to convert mass uncertainty to concentration units.

### XRF Elements

For XRF elements, an uncertainty value for each analyte is calculated by the manufacturers' software, using an algorithm based on counting statistics for each sample. The value of  $\sigma_{Aj}$  used in eqn. (1) is calculated as this uncertainty divided by the reported mass. If the mass is reported as zero,  $\sigma_{Mi,j}$  will be set equal to the reported uncertainty value.

### Ion Chromatography and OC/EC

Equation (1) will be used for anions and cations (sulfate, nitrate, sodium, ammonium, and potassium), and OC/EC. Initial analytical uncertainty values ( $\sigma_{Aj}$ ) will be based on replicate analysis of an up-scale QC standard. These results will be intercompared to the results of replicate analysis to be sure that they are similar in magnitude.

For Total Nitrate, which is the sum of nitrate analyzed on a Teflon and a nylon filter, substitute the following for the term under the square root sign in equation (1):

$$\sqrt{\sigma_T^2 M_T^2 + \sigma_N^2 M_N^2 + \sigma_V^2 (M_T + M_N)^2} \quad (5)$$

where,

$\sigma_T, \sigma_N$  - laboratory uncertainties (relative) for the Teflon and nylon filters (dimensionless)

$M_T, M_N$  - mass measured on the Teflon and nylon filters (micrograms per filter)

other symbols are defined below.

### Determination of Volume Uncertainty

The relative uncertainty in the sampled volume is often a significant portion of the overall uncertainty. 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 DRI for the IMPROVE samplers, is probably in the right order of magnitude for most of the STN samplers. More accurate values would require statistical assessment of field audit results.

## Definitions

i - index for analytes

j - index for individual sampling events

k - index for sampler type (SASS, RAAS, etc.)

$\sigma$  - standard deviation

M - analytical mass (micrograms per filter)

V - sampled volume (cubic meters)

$\sigma_{M_{i,j}}$  - std. dev. of mass for analyte i for event j (micrograms per filter)

$\sigma_{C_{i,j}}$  - std. dev. of concentration analyte i for event j (micrograms per cubic meter)

$\sigma_{A_j}$  - relative standard deviation for analyte i from lab QC samples (dimensionless)

$\sigma_{B_j}$  - blank std. dev. from lab QC blanks (micrograms per filter)

$\sigma_G$  - std. dev. for replicate gravimetric analyses (micrograms per filter)

$\sigma_{V_k}$  - relative std. dev. of sampler volume (dimensionless) [initially use 5%]

## Appendix B Minimum Detection Limits

Laboratory method detection limits (MDLs) are reported periodically by the analytical laboratories and are subject to periodic updates, unless noted otherwise. Laboratory MDLs can be converted to concentration units ( $\mu\text{g}/\text{m}^3$ ) by dividing by the sampled volume for the respective sampler type and channel. Note that the resulting MDL in concentration units will not include any allowance for field uncertainties, including uncertainty in the measurement of volume.

### B.1 X-Ray Fluorescence, Chester LabNet

Chester LabNet follows EPA Protocol IO-3.3, Section 12.

Reference: *Compendium Method IO-3.3, Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy*, U.S. EPA Center for Environmental Research Information, Office of Research and Development, Cincinnati, OH, June 1999.

Sampled area for all STN filters is assumed to be 11.3. Two separate instruments are used to analyze STN filters. These are designated "770" and "771" in the tables below.

Analyte	MDL, ug/filter	
	770	771
Aluminum	0.157	0.163
Antimony	0.213	0.158
Arsenic	0.036	0.037
Barium	0.850	0.601
Bromine	0.029	0.031
Cadmium	0.152	0.095
Calcium	0.050	0.044
Cerium	1.242	1.113
Cesium	0.533	0.436
Chlorine	0.084	0.132
Chromium	0.023	0.019
Cobalt	0.020	0.018
Copper	0.019	0.019
Europium	0.162	0.084
Gallium	0.048	0.071
Gold	0.072	0.127
Hafnium	0.378	0.155
Indium	0.163	0.108
Iridium	0.086	0.165
Iron	0.028	0.024
Lanthanum	1.004	0.795

Lead	0.079	0.085
Magnesium	0.266	0.427
Manganese	0.033	0.026
Mercury	0.063	0.065
Molybdenum	0.069	0.085
Nickel	0.018	0.015
Niobium	0.060	0.067
Phosphorus	0.090	0.056
Potassium	0.049	0.062
Rubidium	0.031	0.031
Samarium	0.089	0.068
Scandium	0.035	0.031
Selenium	0.031	0.033
Silicon	0.109	0.098
Silver	0.151	0.091
Sodium	0.738	1.580
Strontium	0.036	0.036
Sulfur	0.095	0.204
Tantalum	0.282	0.255
Terbium	0.109	0.073
Tin	0.258	0.131
Titanium	0.030	0.034
Vanadium	0.022	0.021
Wolfram	0.199	0.208
Yttrium	0.044	0.044
Zinc	0.021	0.017
Zirconium	0.052	0.054

## B.2 X-Ray Fluorescence, Research Triangle Institute

Two separate instruments are used by RTI to analyze STN filters. These are designated "XRF 1" and "XRF 2" in the table below. Sampled area for all STN filters is assumed to be 11.3.

Analyte	MDL, ug/filter	
	XRF 1	XRF 2
Aluminum	0.219	0.219
Antimony	0.267	0.267
Arsenic	0.014	0.014
Barium	0.099	0.099
Bromine	0.011	0.011
Cadmium	0.100	0.100
Calcium	0.071	0.071
Cerium	0.080	0.080
Cesium	0.097	0.097
Chlorine	0.078	0.078

Chromium	0.019	0.019
Cobalt	0.014	0.014
Copper	0.024	0.024
Europium	0.036	0.036
Gallium	0.026	0.026
Gold	0.037	0.037
Hafnium	0.257	0.257
Indium	0.135	0.135
Iridium	0.040	0.040
Iron	0.020	0.020
Lanthanum	0.083	0.083
Lead	0.027	0.027
Magnesium	0.175	0.175
Manganese	0.015	0.015
Mercury	0.033	0.033
Molybdenum	0.082	0.082
Nickel	0.016	0.016
Niobium	0.033	0.033
Phosphorus	0.102	0.102
Potassium	0.106	0.106
Rubidium	0.014	0.014
Samarium	0.041	0.041
Scandium	0.000	0.000
Selenium	0.025	0.025
Silicon	0.178	0.178
Silver	0.082	0.082
Sodium	0.526	0.526
Strontium	0.017	0.017
Sulfur	0.085	0.085
Tantalum	0.074	0.074
Terbium	0.042	0.042
Tin	0.192	0.192
Titanium	0.048	0.048
Vanadium	0.031	0.031
Wolfram	0.059	0.059
Yttrium	0.021	0.021
Zinc	0.025	0.025
Zirconium	0.027	0.027

### B.3 Gravimetry

Gravimetric MDLs have been determined by multiple re-weighings of blank filters. A factor of the square root of two has been included in the calculation to account for the fact that each filter must be weighed twice to produce a net result. The RTI gravimetric laboratory operates two balances, designated "B" and "CET", which are assumed to have the same MDL.

No assumptions regarding filter area are required to calculate the MDLs below; however, these MDLs apply only to the 47 mm Teflon filters used by the STN program.

<b>Instrument</b>	<b>Analyte</b>	<b>MDL, ug/filter</b>
B	Particulate matter	7.200
CET	Particulate matter	7.200

#### **B.4 Anion and Cation Analysis**

RTI operates the Anion and Cation analysis laboratory. Two cation instruments and three anion instruments are currently in operation. These MDLs were determined for the analysis of ions on nylon filters. No assumptions regarding filter area are required to calculate these MDLs.

<b>Instrument</b>	<b>Analyte</b>	<b>MDL, ug/filter</b>
D5C	Ammonium	0.160
D5C	Ammonium	0.160
D5C	Potassium	0.134
D5C	Potassium	0.134
D5C	Sodium	0.290
D5C	Sodium	0.290
D6A	Nitrate	0.084
D6A	Nitrate	0.084
D6A	Sulfate	0.120
D6A	Sulfate	0.120
D6C	Ammonium	0.160
D6C	Ammonium	0.160
D6C	Potassium	0.134
D6C	Potassium	0.134
D6C	Sodium	0.290
D6C	Sodium	0.290
S1A	Nitrate	0.084
S1A	Nitrate	0.084
S1A	Sulfate	0.120
S1A	Sulfate	0.120
S2A	Nitrate	0.084
S2A	Nitrate	0.084
S2A	Sulfate	0.120
S2A	Sulfate	0.120
S3A	Nitrate	0.084
S3A	Nitrate	0.084
S3A	Sulfate	0.120
S3A	Sulfate	0.120

## B.5 Organic and Elemental Carbon by Total Optical Transmission (TOT)

Organic Carbon/Elemental Carbon (OC/EC) analysis by the TOT method is performed by RTI. Three analyzers are operated by the RTI lab, and are designated "R", "S", and "T". Note that the MDLs reported here were determined by the manufacturer. These MDLs are used by the OC/EC laboratory as an upper limit for their periodic redetermination of MDLs. If the MDL determination result exceeds the tabulated value, then corrective action must be taken. Exposed filter area was assumed to be 11.76 cm<sup>2</sup>.

<b>Instrument</b>	<b>Analyte</b>	<b>MDL, ug/filter</b>
R	Elemental carbon	2.352
R	Organic carbon	2.352
R	Pk1_OC	2.352
R	Pk2_OC	2.352
R	Pk3_OC	2.352
R	Pk4_OC	2.352
R	PyroC	2.352
S	Elemental carbon	2.352
S	Organic carbon	2.352
S	Pk1_OC	2.352
S	Pk2_OC	2.352
S	Pk3_OC	2.352
S	Pk4_OC	2.352
S	PyroC	2.352
T	Elemental carbon	2.352
T	Organic carbon	2.352
T	Pk1_OC	2.352
T	Pk2_OC	2.352
T	Pk3_OC	2.352
T	Pk4_OC	2.352
T	PyroC	2.352

## B.6 Organic and Elemental Carbon by Total Optical Reflectance (TOR)

Organic Carbon/Elemental Carbon (OC/EC) analysis by the TOR method is performed by DRI. Multiple analyzers are operated by the DRI lab, and are not distinguished in the table below. Exposed filter areas were assumed to be 3.53 and 11.76 cm<sup>2</sup> for the IMPROVE and STN filters, respectively.

Analyte	MDL, ug/filter	
	IMPROVE(a)	STN(b)
OC	2.895	9.643
EC	0.671	2.234
OH	2.859	9.526
EH	0.424	1.411
TC	3.283	10.937
O1	0.318	1.058
O2	0.600	1.999
O3	1.977	6.586
O4	0.777	2.587
OP	0.565	1.882
E1	0.424	1.411
E2	0.530	1.764
E3	0.177	0.588

Notes:

- (a) IMPROVE filter area = 3.53 cm<sup>2</sup>
- (b) STN filter area = 11.76 cm<sup>2</sup>