

# PM<sub>2.5</sub> Chemical Speciation Network and Its Challenges

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## ABSTRACT

Particulate matter (PM) with particle aerodynamic diameters of 2.5  $\mu\text{m}$  and smaller (PM<sub>2.5</sub>) in ambient air has been associated with respiratory and other health-related problems in addition to contributing to atmospheric visibility impairment and regional haze. Negative health effects have been statistically correlated to total mass concentration ( $\mu\text{g}/\text{m}^3$ ) of PM<sub>2.5</sub> in ambient air, but whether the correlation is actually to total mass concentration or to concentrations of specific chemical species comprising PM<sub>2.5</sub> has not yet been determined.

The deployment of a new PM<sub>2.5</sub> monitoring network by EPA is a critical component in the national implementation of the PM<sub>2.5</sub> National Ambient Air Quality Standards (NAAQS). The compliance (mass) monitoring portion of the network was established first. Data from the compliance network is used to determine attainment with the NAAQS. EPA has supplemented the network with a chemical speciation monitoring program to provide complementary data on the chemical composition of PM<sub>2.5</sub> for the purposes of identifying sources, developing implementation plans, and supporting ongoing health effects research. The program has grown significantly over the last three years and currently RTI is providing chemical speciation support to over 225 PM<sub>2.5</sub> monitoring sites established throughout the United States and Puerto Rico.

Several challenges encountered in the operation of this program include sample handling, high blank levels for gravimetric mass on Teflon filters, high background levels for quartz and nylon filters, data validation, and reporting. For example, RTI has shown that the outgassing from the white Delrin® rings originally used in the MetOne sampler are a cause of high blank levels for the gravimetric mass on Teflon® filters. Subsequent research performed at EPA/Montgomery confirmed RTI's findings. Other challenges and their solutions implemented in the nationwide network, as well as a general overview of the PM<sub>2.5</sub> Chemical Speciation Program, are described in this paper.

## INTRODUCTION

On July 18, 1997, the U.S. Environmental Protection Agency (EPA) promulgated new National Ambient Air Quality Standards (NAAQS) for PM. The NAAQS applies to the mass

concentration of particles with aerodynamic diameters of 2.5 $\mu$ m or less (PM<sub>2.5</sub>) and 10 $\mu$ m or less (PM<sub>10</sub>). The standards are detailed in 40CFR, Parts 50, 53, and 58.<sup>1</sup> The deployment of a PM<sub>2.5</sub> monitoring network by the U.S. Environmental Protection Agency is a critical component in the national implementation of the new PM<sub>2.5</sub> NAAQS. Data derived from this PM<sub>2.5</sub> monitoring network include both aerosol mass measurements and chemically resolved or speciated data.

The initiation of a PM<sub>2.5</sub> chemical speciation network of approximately 54 core sites within the National Air Monitoring Stations (NAMS) for routine speciation monitoring by EPA is described in the Federal Register.<sup>2</sup> Speciation samples are collected over a 24-hour period every third day at NAMS sites. In addition to the 54 required sites, EPA set-up another 200 sites specifically for speciated data collection. The sampling frequency at these sites vary, depending on the specific data application requirements developed by the individual states where the sampling is performed.

The PM<sub>2.5</sub> chemical speciation program involves both sampling and analysis components. Sampling is performed by non-RTI personnel. These are typically state or local government agencies. In July 1999, in order to obtain consistent data, the monitoring and data validation branch of the EPA Office of Air Quality Planning and Standards located in Research Triangle Park, NC, awarded a four-year, simple laboratory support contract (EPA contract no. 68-D-99-013) to Research Triangle Institute (RTI). The purpose of this contract, titled, "Chemical Speciation of PM<sub>2.5</sub> Filter Samples," is to assist state and local agencies with the operation of PM<sub>2.5</sub> chemical speciation monitoring networks by providing filter media and analytical support for the analysis of sampler filters for mass, selected elements (Al through Pb), organic and elemental carbon, anions (sulfate and nitrate), and cations (ammonium, sodium, and potassium), as well as analysis of semivolatile organics and microscopic analysis of selected filters. The program has grown significantly over the last three years, and RTI is currently providing chemical speciation support to over 225 PM<sub>2.5</sub> monitoring sites established throughout the U.S. and Puerto Rico.

Several challenges thus far encountered in the operation of this program include sampling handling, high blank levels for gravimetric mass on Teflon filters, high background levels for quartz and nylon filters, data validation, and reporting. A general overview of PM<sub>2.5</sub> chemical speciation program and the challenges and their solutions implemented in the nationwide network are described in this paper.

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<sup>1</sup> U.S. Environmental Protection Agency, "National Ambient Air Quality Standards for Particulate Matter Final Rule, 40 CFR, Part 50." Federal Register, 62(138), 8651-8760, 1997.

<sup>2</sup> Committee on Research Priorities for Airborne Particulate Matter, National Research Council, "Research Priorities for Airborne Particulate Matter: 1-Immediate Priorities and a Long Range Research Portfolio." National Academy of Sciences, 1998. (Report may be read on-line at <http://books.nap.edu/books030906094x/html/index.html>.)

## OVERVIEW OF LABORATORY SUPPORT ACTIVITIES

A detailed description of the laboratory support activities for chemical speciation of PM<sub>2.5</sub> are presented elsewhere.<sup>3</sup> A brief overview of laboratory support activities and the challenges and their solutions implemented are as follows.

EPA began the national PM<sub>2.5</sub> chemical speciation laboratory program in February 2000 with its Mini-Trends Program, which included approximately 30 PM<sub>2.5</sub> speciation samplers at 13 sites across the continental U.S. Sampling for Mini-Trends, so-called because the sites represent a subset of the 54 Trend sites, ended in July 2000. The program has grown significantly over the last three years and currently RTI is providing support for over 225 PM<sub>2.5</sub> monitoring sites established throughout the U.S. and Puerto Rico. SASS samplers (MetOne) are predominantly used (69%) for sample collection in the network. The samplers used at the remaining sites include MASS (URG), RAAS (Anderson), and R&P speciation samplers.

PM<sub>2.5</sub> speciation samplers typically have from two to five (or more) flow channels that can be used to collect PM<sub>2.5</sub> on various types of filters. A Teflon filter is used to collect PM<sub>2.5</sub> for measurement of total mass by gravimetry, elements by x-ray fluorescence, and in some cases, anions and cations by ion chromatography; a nylon filter is used to collect PM<sub>2.5</sub> for measurement of anions and cations by ion chromatography; and a quartz filter is used to collect PM<sub>2.5</sub> for measurement of organic, elemental, carbonate, and total carbon. A nylon filter is typically preceded by a denuder coated with magnesium oxide or sodium carbonate to remove acid gas molecules from the sampled air before they are absorbed by the nylon filter.

Figure 1 summarizes the approach used to support EPA's national PM<sub>2.5</sub> Chemical Speciation Laboratory Program. Less common speciation analyses, such as semivolatile organic analysis and microscopic analysis, are not included in this discussion.

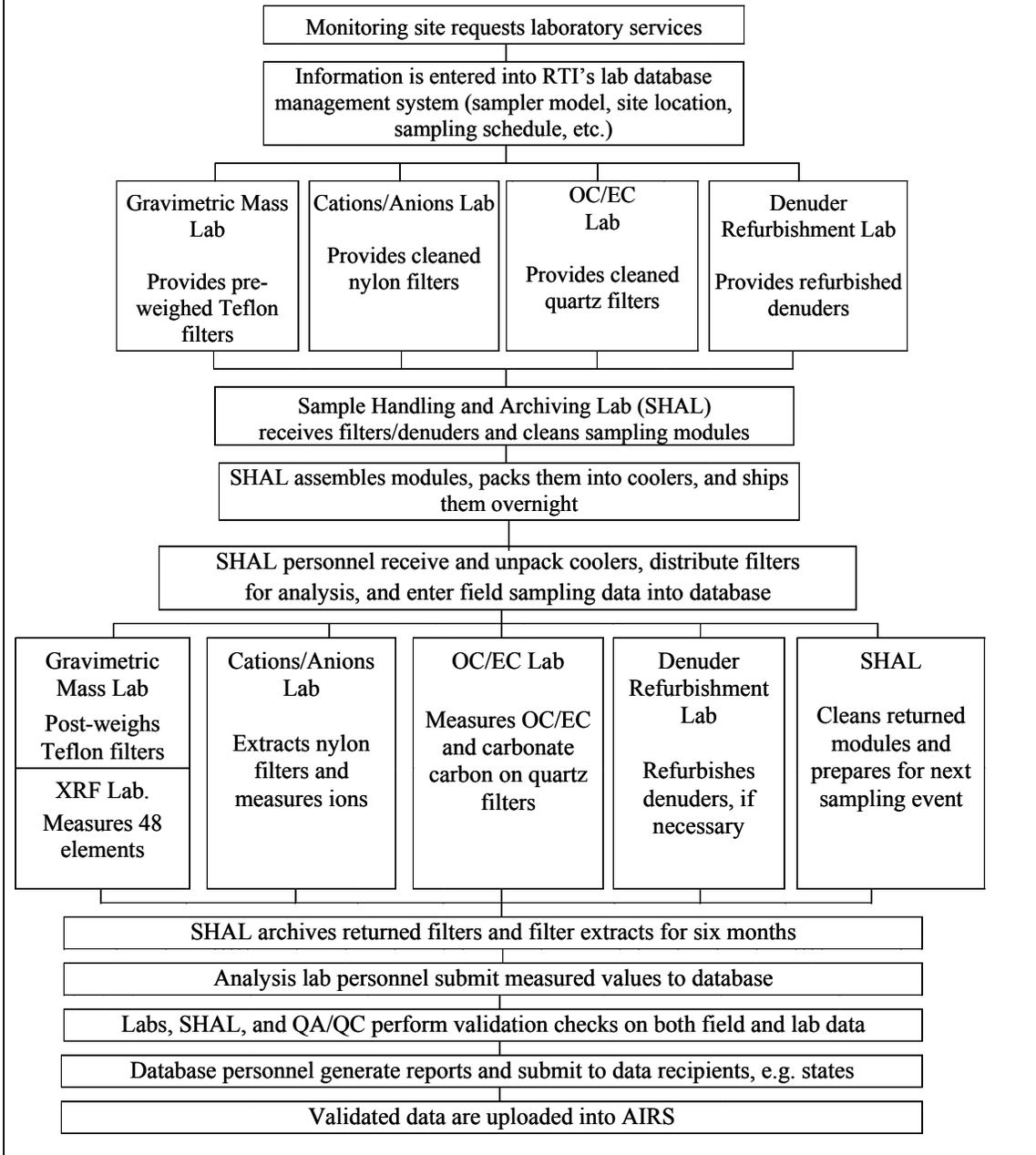
Laboratory support for chemical speciation of PM<sub>2.5</sub> begins with a request for service from the sponsoring agency or client, for example a state. The request must include information about the sampler model, the configuration of sampling media to be used and the analyses to be performed on each filter, the sampling schedule, a contact name and shipping address for the site, and a contact name and address for the data report.

The Sample Handling and Archiving Laboratory (SHAL) established at RTI is a critical component of the laboratory operations and its functions are shown in Figure 2. Scheduling includes associating specific speciation samplers at specific locations for sampling on specified days. Sampling schedules implemented in the speciation network include 1 in every 3 days, 1 in every 6 days, EPA alternate 1 in every 3 days, EPA alternate 1 in every 6 days, and a separate schedule for the Texas sampling programs. EPA alternate schedules were implemented about one year ago for the convenience of some sites, which may not be able to perform weekend sampling or shipping. The operation of five types of sampling schedules is

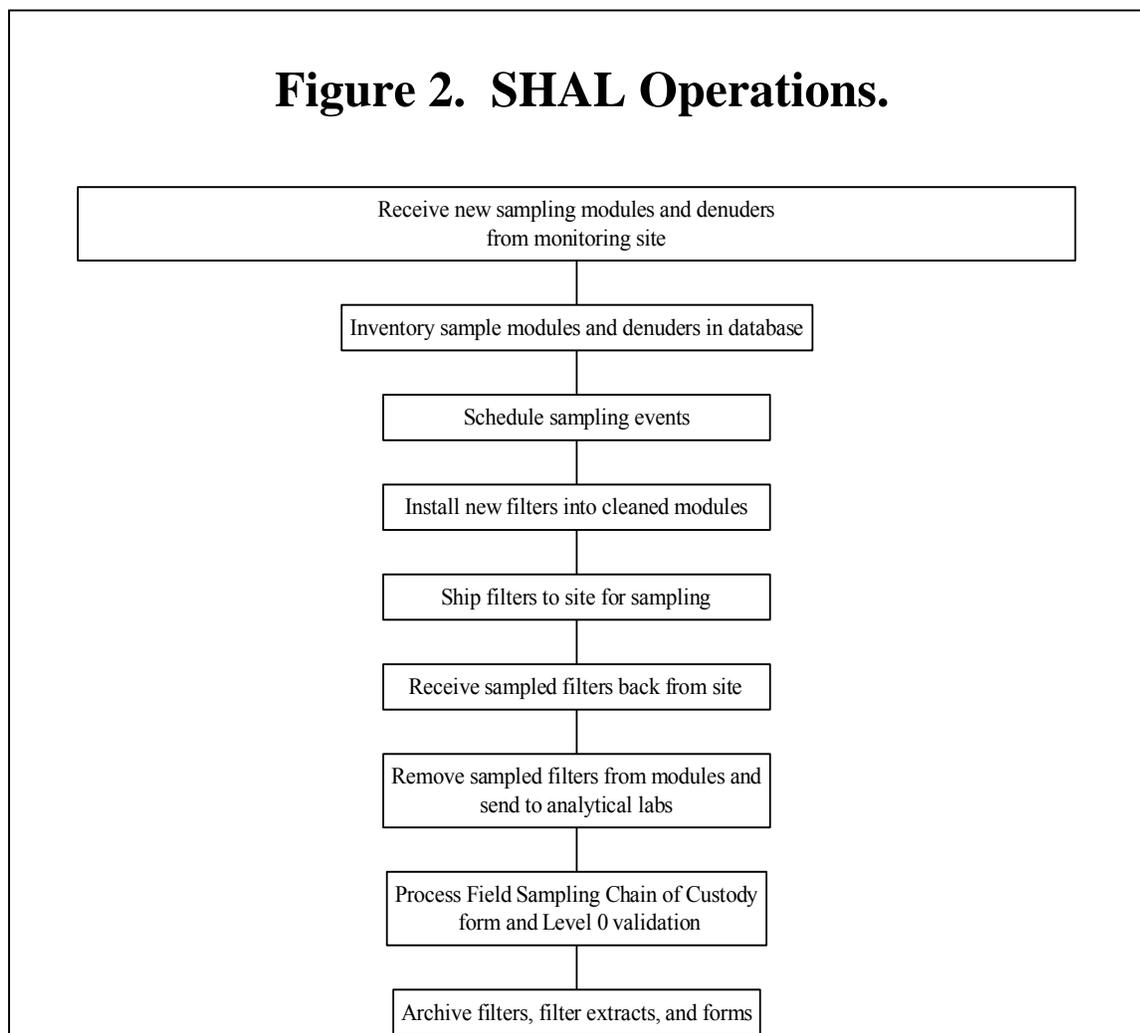
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<sup>3</sup> Peterson, M. R., W. F. Gutknecht, R. L. Perkins, R.K.M. Jayanty, and E. D. Hardison. "Laboratory Support for Chemical Speciation of PM<sub>2.5</sub>," *Environmental Manager*, pp. 17-22, August 2000.

**Figure 1. Overview of Laboratory Activities**



## Figure 2. SHAL Operations.



a great challenge to the speciation program. A shipping and receiving schedule is created to ensure that sets of sampling modules arrive at the sampling sites in time for installation before a scheduled sampling event and also that module sets used for sampling are returned to the laboratory in time to be prepared for a subsequent sampling event. All parties involved in a monitoring program are given copies of the shipping and receiving schedule and asked to ship only on the specified dates.

SHAL staff prepare a set of sampling modules for each sampler in each sampling event. Clean sampling modules are fitted with clean, acceptance-tested filters and shipped to the field. The laboratory is also responsible for providing denuders coated with magnesium oxide or sodium carbonate as needed. Non-RTI field personnel place the modules, and any required denuder, in the designated sampler before the beginning of the sampling event and retrieve the modules from the sampler after the sampling event. Modules are cooled to 4°C (or below), placed in a bin inside a high-efficiency cooler, and shipped back to the RTI laboratory. Approximately 1600 coolers are shipped back and forth to the laboratory and field sites every month.

SHAL staff measure and record the temperature of the modules in each cooler upon receipt. Trained personnel distribute the filters to the appropriate speciation laboratories for analysis. The components of the disassembled sampling modules are cleaned by SHAL staff, and the modules are reassembled with clean filters and shipped back to the field sites according to schedule for a subsequent sampling event.

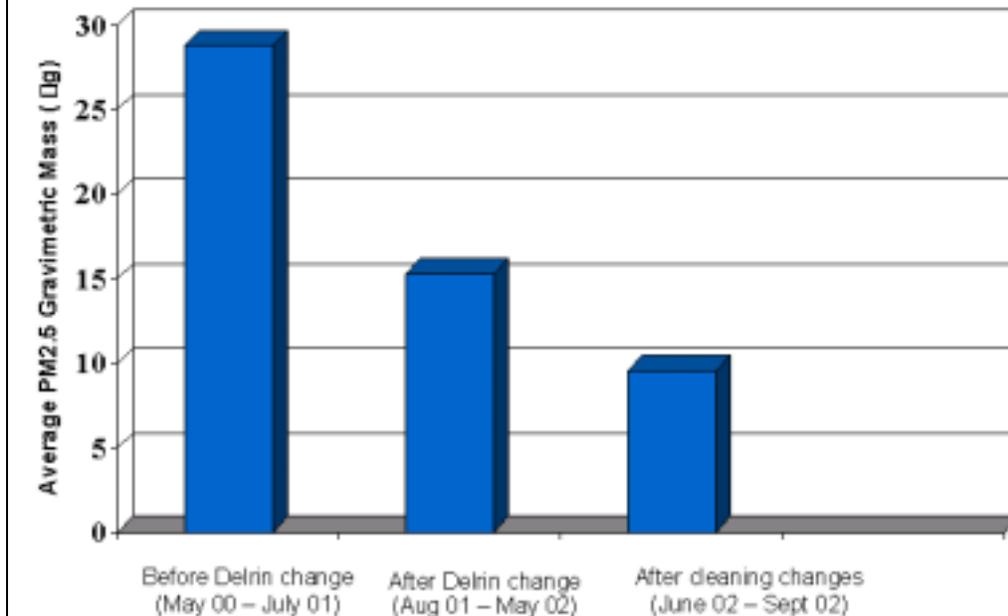
## **CHALLENGES IN THE SPECIATION ANALYSIS**

### **Determination of Gravimetric Mass**

The gravimetric analysis of PM<sub>2.5</sub> filters is performed according to guidelines specified in 40 CFR, Parts 50, 53, and 58, and the EPA *Quality Assurance Guidance Document 2.12*, “Monitoring PM<sub>2.5</sub> in Ambient Air Using Designated Reference or Class I Equivalent Methods.” New Teflon filters received from the manufacturer are checked for defects and defect-free filters are placed in the walk-in weighing chamber for conditioning and determination of lot stability. The chamber is maintained at a temperature of 20 to 23°C and a relative humidity of 30 to 40%. Weighing is performed with a microbalance having a readability of ≤1µg. Laboratory quality control checks include lot stability blanks, replicate weighing of laboratory blanks and working mass standards, and replicate filter weighing.

In May 2000, PM<sub>2.5</sub> speciation sampling sites reported higher masses for field blanks from speciation samplers when compared to FRM samplers. The average PM<sub>2.5</sub> trip and field blank masses were 30µg during January through July 2001 compared to 9µg for the FRM sampler field blank mass. Laboratory personnel investigated the reasons for high mass blanks from the speciation samplers. They observed oily material on a number of Teflon filters and subsequently this contamination was traced to cassette filter holder rings made of Delrin, a plastic based on polyformaldehyde. Heating experiments performed at RTI determined the extent of transfer of materials from the Delrin cassette to the Teflon filter. RTI results were later confirmed by the EPA Quality Assurance Laboratory at Montgomery, AL. The Delrin filter holder rings in all the MetOne samplers (Teflon filter holder only) were replaced with blue plastic rings. RTI personnel also observed potential contamination from the Kimwipes and plastic trays used during cleaning of filter holders; these were subsequently eliminated to further reduce the PM<sub>2.5</sub> mass blanks. The replacement of Delrin rings in all MetOne samplers and the elimination of the Kimwipes and plastic trays have considerably reduced the mass blank levels as shown in Figure 3.

**Figure 3. Effects of Delrin Rings and Cleaning Procedures on MetOne Samplers (Includes all trip and field blanks)**



### **Analysis of Elements by Energy Dispersive X-Ray Fluorescence**

The method of choice for the determination of trace metals collected on PM<sub>2.5</sub> filter samples is energy dispersive X-ray fluorescence (EDXRF). The analysis is typically performed using EPA Method IO-33.<sup>4</sup> Currently the national EPA M<sub>2.5</sub> Chemical Speciation Program requires the analysis of 48 metals and non-metals in a single scan. The detection limit achieved varies with each element (0.04 to 0.40µg/filter).

Instrument calibration is typically performed using commercial thin film vapor-deposited standards. It is common to notice a calibration drift in the XRF analysis. In September 2002, RTI Quality Assurance staff discovered an excessive number of outliers during the check of sulfur/sulfate ratios and subsequently attributed a drift of 20% for sulfur in one of the XRF instruments used in the analysis. The XRF laboratory was notified and all XRF data for the drifting instrument were corrected before data were reported. A new reference standard for sulfur was located, purchased, and is now being analyzed weekly to monitor for any unacceptable drift.

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<sup>4</sup> U.S. Environmental Protection Agency, Office of Research and Development. "Method IO-33, Determination of Metals on Ambient Particulate Matter Using X-ray Fluorescence, Compendium Methods for the Determination of Inorganic Compounds in Ambient Air; Atmospheric Acidic Constituents." EPA/625/R-93-010a, Washington, D.C., September 1997.

## **Ion Analysis**

Water-extractable ions are measured using ion chromatography, a precise and accurate instrumental method of analysis. The standard operating procedures followed for the EPA PM<sub>2.5</sub> speciation efforts were developed by RTI over 14 years ago. In the current EPA PM<sub>2.5</sub> Speciation Program, the anions sulfate and nitrate, and the cations ammonium, sodium, and potassium, are being measured. The detection limits are generally low (~0.1 µg/filter).

Each ion chromatograph is calibrated daily with a 6- or 7-point calibration curve. Data treatment is performed with typical chromatographic software; peak location identifies the species and peak height or area provides quantification. Calibration checks are performed daily before analysis of field samples and every 10 samples using standards prepared from alternate sources; NIST-traceable standards from commercial sources are run daily before field samples analysis. The acceptance level for these check samples is ±10% of nominal values. Reagent blanks are run daily before analysis of field samples; values measured are to be less than the method detection limit (MDL) for each ion. Duplicates and matrix spikes are typically analyzed every 20 samples. Relative percent differences of less than 10% for duplicates at concentrations ≥10 times the MDL and recoveries for matrix spikes of 90 to 110% are typical quality control goals. Field blanks are also analyzed; ion levels above 1 µg/ filter are cause for corrective action.

The samples are collected on Teflon or nylon filters. Teflon filters from commercial sources have been found to have acceptable blank levels (set by EPA at <1 µg/filter) for each species of interest. Nylon filter blank contamination (sodium and sulfate) is a potential problem. Nylon filters directly from the supplier have been found to be loaded with more than 10µg sodium per filter; this loading varies with the manufacturers lot number. The washing procedure has been modified several times in response to increasing levels of contamination. Currently, the filters are reused briefly in deionized water twice, and then washed three times in fresh aliquots of deionized water. These three washing times are respectively, 7-8, 12-14, and about 24 hours. The washing is done in 2-L polypropylene bottles. The bottles with fifty filters in each bottle are rotated on a TCLP apparatus.

## **Organic, Elemental, Carbonate, and Total Carbon by Thermal-Optical Analysis**

The EPA-approved method for carbon analysis is National Institute of Occupational Safety and Health (NIOSH) Methods 5040, *Elemental Carbon (Diesel Particulate)*, with some specific conditions. Organic, elemental, carbonate, and total carbon in PM<sub>2.5</sub> are determined by thermal-optical analysis of a portion of the sample collected on a quartz fiber filter.

A rectangular portion (area ~1.5 cm<sup>2</sup>) of the quartz filter sample is removed with a punch and placed on a quartz boat in the front (or desorption) oven of the analyzer. The boat is positioned in the furnace so that a small laser beam passes directly through the quartz filter portion. Carbon analysis by NIOSH Method 5040 requires two heating stages, and the EPA method adds specific ramp temperatures and residence times for both stages. In the first stage, organic and carbonate carbon are thermally desorbed from the filter under a flow of helium with a controlled temperature ramp. The oven is then partially cooled, and the original flow of helium is switched

to an oxidizing carrier gas (He/O<sub>2</sub>). In the second stage, the original elemental carbon component, plus pyrolyzed organic carbon formed during the first heating stage, are oxidized/desorbed from the filter with another controlled temperature ramp. In both heating stages, all carbon evolved from the sample is converted to CO<sub>2</sub> in a second oxidizing oven, and the CO<sub>2</sub> is converted to methane (CH<sub>4</sub>) by a methanator oven before being measured with a flame-ionization detector (FID). The split point between the organic and inorganic carbon is taken as the point where the filter darkness (as monitored with the laser) returns to its original level after an amount of elemental carbon equal to the pyrolyzed organic carbon has oxidized and removed as CO<sub>2</sub>.

In preparation for sampling, batches of quartz fiber filters (typically 100 filters per batch) are cleaned by heating them in a muffle furnace at 900°C for at least three hours. Filters are blank-checked by analyzing either two or 2%, whichever is more, of the filters from a batch. The acceptance criterion for a batch of filters to be used is a total carbon measurement of no more than 1 µg C/cm<sup>2</sup> of filter.

Both internal and external calibration standards are used for the analysis. External standards, which are typically prepared from sucrose (although NIOSH Method 5040 lists several alternatives), are used for a weekly 3-point calibration and for a daily calibration check sample. The internal standard is a gaseous mixture of 5% methane in helium, which is injected through a fixed-volume loop at the end of each analysis.

Several ongoing issues in the organic carbon/elemental carbon analysis include: filter contamination by ambient volatile organic compounds (VOCs) and definition of the split point between organic and elemental carbon. Researchers both at RTI and others are reporting some of these issues.<sup>5,6</sup>

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<sup>5</sup> Flanagan, J.B., M.R. Peterson, R.K.M. Jayanty, and E.E. Rickman. "Analysis of PM2.5 Speciation Network Carbon Blank Data." Presentation at the Symposium on Air Quality Measurements Methods and Technology, San Francisco, CA, November 2002.

<sup>6</sup> Peterson, M.R. and M.H. Richards. "Thermal-Optical Transmittance Analysis of Organic, Elemental, Carbonate, Total Carbon, and OCX<sub>2</sub> in PM2.5 by the EPA/NIOSH Method." Presentation at the at the Symposium on Air Quality Measurements Methods and Technology, San Francisco, CA, November 2002.

## Data Validation

A custom database management system (DBMS) has been developed for the PM<sub>2.5</sub> Speciation Program. A versatile DBMS is essential for quality control validation checks. Currently more than 100 data items are being reported for each sample. Because of the complexity of the multi-channel speciation samplers and the number of data items reported, a system for flagging suspect or invalid data was developed that flows downward through the hierarchy: sample > channel > filter > analysis > analyte. For example, if an entire sample was found to be invalid, any validity flag assigned to the sample would flow down the hierarchy so that each analyte reported for that sample would be flagged. If only a single filter is found to be invalid, any flag assigned to that filter would flow down to each analyte reported for that filter. Some typical validation checks are given in Table 1.

**Table 1.** Typical validation checks.

Type	Validation Check
Field data checks	Total volume Elapsed time Operator observations and validation flags from sampler
Disassembly checks	Shipper received intact, with all components? Temperature in container <4°C? All forms received, numbers checked against original? Module end caps in place? Evidence of filter damage (ripped, contaminated, creased, etc.)?
Analysis laboratory checks	Laboratory validation flags are assigned by the analysts based on laboratory quality control results and are entered into the database along with the analytical data (mass per filter). Laboratory validation procedures vary widely and are determined primarily by the respective standard operating procedures.
Data Screening and Review: Internal consistency checks	Correct number and type of samples by date and site Verification of scheduled vs. actual exposure information
Outlier tests based on prescribed acceptance ranges	Flow rate Elapsed sampling time Holding time(s)
Temperatures	Filter-ambient Shipping
Other within-sample tests	Cation/anion ratios Mass conservation Visual and statistical screening

Flags for data uploaded to EPA's Aerometric Information Retrieval System (AIRS) are assigned based on more detailed flags that have been entered into RTI's database. There are two kinds of validation codes in AIRS: (a) *null-value codes*, which overwrite data that are considered completely invalid; and (b) *AIRS validation codes*, which indicate when a data item is suspicious, but do not overwrite the data value.

## Reporting

The DBMS removes much of the reporting burden from the individual laboratories, which simply log in batches of filters in barcoded Petri slide holders, analyze the filters, report the results to the DBMS, and log out the filters, filter portions, or extracts that remain after analysis before they are archived. Analysis laboratory personnel are not required to associate filters with any particular sampler, sampling event, or field data. The DBMS is used to combine all sampling and analysis data and quality control validation checks for each sampling event into a series of reports. Some of the data reporting challenges are shown in Figure 4.

### Figure 4. Data Reporting Challenges

- **Project size** (over 200 sites, 1,800 samples, 200,000 values reported each month).
- **Multiple analysis per event** - Filters from one sample event must be sent to multiple labs and results combined back to one result set.
- **Matching field and laboratory data** from same event to produce results.
- **Extensive QA/QC Needs.**
- **Reporting schedule** – Need rapid turnaround to sites and then rapid delivery of site changes to AIRS.

Participants in the program can download any or all of the reports for their sites from a secure Web page. Access to data is restricted by means of an assigned username and password. The fully validated data are loaded into AIRS within 60 days of the initial data report to the monitoring agencies.

## **SUMMARY AND CONCLUSIONS**

Laboratory support for the PM<sub>2.5</sub> Chemical Speciation Program requires a complex network of activities that must be performed in a well-choreographed fashion that: keeps sampling modules cycling on a rigid schedule between laboratory and field; keeps filters moving from acceptance testing, to sampling, to analysis, and to archiving; and keeps data flowing from the field and from the chemical speciation analyses through validation and reporting.

RTI has implemented a successful laboratory analysis and sample processing program to support 225 sites in the nationwide network. Several complex challenges involving scheduling, filter blanks, and filter contamination have been identified and addressed to improve data quality.