Evaluation of PM2.5 Chemical Speciation Samplers Used in the Implementation of a National Trends Monitoring Network

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ABSTRACT

The U.S. Environmental Protection Agency has implemented a multi-tiered chemical speciation monitoring program which provides both prescriptive requirements for national consistency and flexibility to adapt to individual State needs and advances in measurement technologies. To provide national consistency, EPA has begun deploying a 54 site national Speciation Trends monitoring network to produce detailed chemical characterization of PM2.5 at locations within major urban areas across the contiguous U.S. and Puerto Rico. The data from this network are to represent a measure of long term trends in PM2.5 concentrations and compositions as well as a timely, uniform and comprehensive data set which can be used by health studies researchers and regional modeling programs. Populating the network has involved the development of national contracts with three vendors to commercial samplers based on EPA-specified performance requirements. This process has provided flexibility for innovation. Also, the processes of analysis of network samples, data validation, reporting, and national database entry are accomplished through a national laboratory support contract to ensure consistency and uniform quality. Prior to full-scale deployment of the network, a comparative evaluation of the sampling technology and the integrated field and laboratory processes was carried out using a 13 site subset of the final network design. Multiple samplers were located at each site for comparative evaluation along with collocated samplers at selected sites for determining individual sampler precision. All sample modules were prepared and analyzed using standardized SOPs and QA/QC procedures to be used for the full network deployment. Samplers were installed during December, 1999-January, 2000. Sampling was then initiated in February, 2000, and the field sampling phase of the intercomparison was completed on August 1, 2000.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) promulgated a new National Ambient Air Quality Standard (NAAQS) for particulate matter (PM) on July 18, 1997. The new PM regulations consist of a revision to the PM10 standard for fine particles less than 2.5µm in aerodynamic diameter and a new standard for fine particles less than 2.5µm in aerodynamic diameter, identified as PM2.5. A detailed discussion of the regulations is given in 40 CFR Parts 50, 53, and 58, Federal Register.[1,2] The regulations describe a new ambient air Federal Reference

Method (FRM) for the measurement of PM2.5. The PM.5 FRM is based on the size-selective collection of fine particles on a 76 mm diameter Teflon® filter disk through which ambient air is sampled at a volumetric flow rate of 16.7 LPM for a 24 hr period. The filter is weighed before and after sampling, according to standardized procedures, and the calculated PM2.5 concentration is reported in units of $\mu g/m^3$ for a 24hr average. The sampling methodology was based upon detailed design criteria and, beginning in 1998, the PM2.5 FRM was made commercially-available through several vendors. Today, PM2.5 hardware systems exist for:

1. Single 24hr event sampling;
2. Sequential (multi-day) 24hr event sampling; and
3. Portable, single 24hr event audit sampling.

Both single and sequential PM2.5 FRM samplers have been deployed by State and Local Air Monitoring Agencies in a vast network of community-oriented monitoring sites. Today, there are over 1000 PM2.5 FRMs operating across the country. Data from this network are being reported by State and Local Agencies and entered by them into the national Aerometric Information Retrieval System (AIRS). This information is being used by EPA and the States to determine attainment with the 24hr and annual PM2.5 NAAQS.

Development of the PM2.5 Speciation Network

Almost immediately with the inception of the PM2.5 NAAQS and the attendant FRM monitoring requirements which prescribed the 1000+ sampler network, EPA received comments and recommendations regarding PM2.5 monitoring issues from States, the National Academy of Sciences (NAS), and the scientific community. The States felt that data on the chemical composition of PM2.5 would be needed to help identify major local and regional contributors to PM2.5 NAAQS violations. This information would be useful to State agencies who must develop attainment strategies requiring further emissions controls. From a related perspective, the NAS and health studies researchers also strongly communicated the need for speciation of PM2.5 to provide data which could be related with on-going and planned research to identify and quantify causal factors between observed health effects and PM2.5 chemical components. Also, the EPA atmospheric modeling program needed PM2.5 speciation data to assess regional emissions control/attainment strategies. Although the regulatory monitoring requirements for mass concentrations are being met with the existing PM2.5 FRM network, it would be impossible to fully characterize PM2.5 components from the analysis of a single Teflon® filter.

Historically, limited local and regional air monitoring studies have focused on characterization of fine particles and reported principal components to consist of sulfate, nitrate, various forms of carbon, ammonium ion, and a range of elements representing anthropogenic and crustal emission sources. These investigations used a variety of sampling approaches incorporating several types of filter media which were chosen to optimize the collection of the PM species of interest. For example, the analysis of fine particle carbon species is based on the thermal volatilization of particles collected on quartz fiber filter media. Quartz filters are

generally free of carbon and can withstand the high temperatures required by the analytical method. The preferred sampling approach for the measurement of fine particle nitrate species involves the collection of particles on non-Teflon® filter media which have a high affinity for nitrate retention. This is important in that ammonium nitrate is both volatile and is thought to represent a significant component of fine particulate matter on a seasonal basis in many regions of the country.

Given the limitations of the extent of chemical characterization of PM2.5 collected from the single Teflon® filter employed in the FRM and the technical concerns dealing with loss of volatile fine particle species, the NAS and scientific community recommended that EPA complement the existing PM2.5 FRM monitoring network with a routine chemical speciation program which could employ state of the art sampling and analytical technologies to more accurately and completely characterize PM2.5. To meet this need, EPA through its Office of Air Quality Planning and Standards (OAQPS) has initiated a sampling and analytical program[3] that will consist of approximate 250 monitoring sites at which the major chemical components of PM2.5 will be measured in the collected aerosol. Since information from this network will be used for the identification of sources contributing to high PM2.5 mass concentrations, development and evaluation of control strategies, measurement of trends, and support of health studies, it is important that there be national consistency in the ways species concentrations are measured by the monitoring network programs.

The EPA Guidance Document, referenced above, provides an overview and discussion on the specific strategies being implemented to support PM2.5 speciation. Effective program implementation requires that viable and proven sampling systems be available for deployment and routine operation by trained State and local agency staff. Also, there must be provision for consistent chemical analysis, data reduction, validation and reporting. Sampling and analytical methods should be used which can produce data which are to be evaluated and interpreted in association with similar data collected from either historical, limited, regional studies or with data being currently produced within the Interagency Monitoring Program for Protected Visual Environments (IMPROVE). The IMPROVE program represents a major monitoring network focused on the characterization of fine particle composition and their effects on visibility in National Parks and Class 1 Wilderness Areas. Responsible program implementation demands that EPA characterize and qualify any technologies used for PM2.5 speciation with respect to sampler configuration, operational performance, and the quality of data being produced from the monitoring activities.

PM2.5 Speciation Network Components

EPA has implemented a multi-tiered chemical speciation monitoring program which provides both prescriptive requirements for national consistency and flexibility to adapt to individual State needs and advances in measurement technologies. To provide national consistency, EPA has begun deploying a 54 site National Speciation Trends monitoring network to produce detailed chemical characterization of PM2.5 at locations within major urban areas

across the contiguous U.S. and Puerto Rico. The site selection process and development of the sampling schedule matrix using the EPA Data Quality Objectives assessment approach is described in detail in a separate report.[4] The emphasis within the Trends Network is placed on the use of tested sampling and analytical methodologies and consistent data analysis, validation, and timely reporting into AIRS. These data are to represent a measure of long term trends in PM2.5 concentrations and compositions as well as a timely, uniform and comprehensive data set which can be used by health studies researchers and regional modeling programs. In addition to the National Trends Network, State and local agencies have been given the flexibility to operate up to an additional 250 chemical speciation monitoring sites (budgetary planning estimate) which may be outfitted with proven technologies and/or more developmental prototype samplers/monitors. These activities are more relevant to individual States' needs where there may be specific requirements in varying sample site location, sampling frequency, and network operational duration to meet local network design objectives. Although EPA has provided wide flexibility to States in their individual network design, EPA has also encouraged them to seek consistency in PM2.5 filter analyses, data reduction, reporting, and AIRS data entry.

PM2.5 Speciation Network Implementation

During the initial planning phase for the chemical speciation monitoring program, EPA recognized the need to facilitate the commercial availability of viable sampling equipment and provide the national ability for sample analyses. EPA believed that the initial sampling technology that should be implemented in the Trends Network should be largely comparable with those technologies historically used, but commercially unavailable, in the IMPROVE program and several smaller and limited research studies. Therefore, in 1998, EPA provided for the development and commercialization of chemical speciation samplers through a National PM2.5 Sampler Procurement Contract. Contrary to the approach taken with the commercialization of the PM2.5 FRM, EPA based the requirements for speciation samplers on performance rather than design criteria. This has allowed the flexibility for innovation in the development of these samplers and has resulted in the development of three slightly different samplers for meeting the specified performance criteria.

To support the analysis of samples from both the 54-site Trends Network and State/Local agency chemical speciation networks, EPA has implemented a National Chemical Speciation Laboratory Support Contract which has the long term capability and capacity to enable States to consistently collect samples with appropriate filter media and quality control provisions for both field[5] and laboratory[6] operations and receive timely analytical validated data reports for review and approval prior to subsequent AIRS entry by the national laboratory contractor.

As these two (field sampler and laboratory analysis) program components were in final stages of development in late-1998, EPA sought a formal, extramural review of its speciation program implementation from both the Clean Air Science Advisory Committee (CASAC) and a Speciation Expert Panel comprised of recognized experts in fine particle sampling and analysis. Suggestions and recommendations from both review groups were consistent.[7] In their reviews,

the panels recommended an intercomparison among the chemical speciation samplers. Also, the intercomparison should include other historical accepted samplers (e.g., the IMPROVE sampler, the Harvard Sampler, etc) and the PM2.5 FRM. The chemical species to be determined should included those recommended by the expert panel and as specified in the guidance document for chemical speciation.[3]

Four City Study

In order to provide timely response to the CASAC and Speciation Expert Panel recommendations, EPA/OAQPS sought the technical support from the National Environmental Research Laboratory (NERL) within the EPA Office of Research and Development (ORD) for conducting the initial speciation sampler intercomparison**.** The program plan for the initial sampler intercomparison[8] outlines the approach and details the implementation of the testing activities which were conducted at four monitoring sites across the country during January and February of 1999. The primary objective of this study was to determine if there are differences in the measured concentrations of the chemical components of PM2.5 mass as determined by the three PM2.5 chemical speciation samplers available through the National Sampler Contracts. Comparisons were also made to two historical samplers and to the FRM using these samplers as a relative reference. A secondary objective of this study was to evaluate the operational performance or practicality of the samplers in the field in terms of their reliability, ruggedness, ease of use, and maintenance requirements.

A detailed discussion of the study results has recently been reported (Solomon et al, 2000). In general, the performance of the three candidate speciation samplers was reasonable for their first use in the field. All samplers initially had operational problems that increased their variability and most issues were quickly addressed by the manufacturers. The evaluation report discusses the tradeoffs that exist among the samplers for ease of use, flexibility for sampling, and cost. There was good agreement (within 10-15%) among the speciation samplers and the PM2.5 FRM for total mass and sulfate concentrations. Higher variability was noted for nitrate measurements and were ascribed to several factors, including:

1. Positive artifact for the determination of nitrate on pre-fired quartz fiber filters (an atypical sampling configuration used during the assessment);
2. Possible volatilization of nitrate from a nylon filter preceded by a denuder; and
3. Volatilization of particulate nitrate from a Teflon® filter following analysis by vacuum XRF.

In particular Items 2 and 3 represent contemporary issues with chemical speciation sampling and analysis.

Differences also were observed among the samplers for organic carbon and appear to be due to filter face velocity variations among the samplers. Lower sampling flow rates appear to result in higher organic carbon concentrations with elemental carbon levels being consistent among the samplers. Also, differences were reported between elemental carbon values reported

using protocols from the IMPROVE program and the EPA PM2.5 Chemical Speciation Program. Although the fundamental analysis methods are identical, the results reported are operationally-dependent and the protocols deviate to produce elemental carbon values which differ by approximately a factor of two. These differences are currently under investigation by ORD/NERL and OAQPS.

Planning and Development of the Minitrends Study

Preliminary results from the Four City Study were presented and discussed during a second review meeting with the Chemical Speciation Expert Panel.[9] Recommendations given during that panel review included:

1. Further sampler intercomparisons should be conducted on a limited scale prior to full Speciation Trends Network deployment to test the operational reliability of the samplers during extreme cold weather conditions. Experience with deployment of the PM2.5 FRM network revealed major sampler issues with sample pump failure, inadequate electronic data display, and internal sampler contamination which could affect sample integrity.

2. Further field evaluations should focus on investigating carbon sampling issues, particularly in areas of the country where wood smoke contributes to a major portion of the PM2.5 levels (Northwestern U.S., in particular).

3. Develop and test the processes which will be used to prepare filter materials and sample to be used in sampling and the mechanisms to perform sample analysis, validate and report the data.

EPA/OAQPS responded to the Panel's recommendations through an incremental deployment of the Speciation Trends Network. In July, 1999, several States designated to operate a speciation trends site were contacted and asked to participate in a multi-sampler intercomparison to be conducted over a six-month period. This activity has been termed the "*Minitrends Study*" and is the principal subject of this paper. Specific States were identified which represented a diversity in expected PM2.5 concentrations and compositional ranges. Candidate States were identified in the Pacific Northwest to represent sampling conditions expected to collect significant fine particle wood smoke components as well as North Central States where extreme cold winter conditions might prevail. In addition, two sites were chosen which were also used during the Four City Study in order to try to provide some continuity in the data set for comparison.

Study Objectives

A meeting was held between EPA and the participants in August, 1999, to jointly develop the study objectives. The participants agreed to the overriding theme of "*keep it simple*". The goal of the effort was to use the information obtained from the complete evaluation of the field

and laboratory activities to shape the speciation trends network operational procedures. This would be achieved during the study by establishing the processes to address, resolve, and implement changes consistently across the network. Three major objectives regarding sampler performance evaluation were developed. These included:

1. Determine sampler intercomparison (Three samplers available through the National Sampler Contracts and the PM2.5 FRM sampler);
2. Determine sampler precision under different sampling conditions, including::
    a. Ambient temperature;
    b. Elevation;
    c. Aerosol composition; and
    d. Mass Loading.
3. Learn practical operational experiences, including:
    a. User-friendliness; and
    b. Revision/refinement of field sampler standard operating procedures (SOPs).

Sampler Characteristics

The three samplers utilized in this study were the Reference Ambient Air Sampler (RAAS™), Mass Aerosol Speciation Sampler (MASS), and Spiral Ambient Speciation Sampler (SASS™). At a minimum, the speciation monitors used contained PTFE, nylon, and quartz filter media and provided for the collection of the target analytes of interest. The PTFE filter was used for mass and elements; quartz for carbonaceous aerosols; and nylon for the collection of nitrate and other cations and anions. The sampling system had to be capable of collecting a 24-hour $PM_{2.5}$ sample. The speciation monitor designs differed in their approach and were configured either as a multi-channel device operating from a single inlet, or a series of separate inlets or instruments, each with its own particle separation device. Overall, the monitor design had to have the capability of collecting particles in a manner comparable to the FRM and with an aerodynamic diameter equal to or less than 2.5 μm.

The following is a brief description of the chemical speciation monitor configurations. For more detailed information, refer to the manufacturer's operation manual. In addition, a very short description of single channel, continuous, saturation and special purpose monitors also appropriate for use in non-routine SLAMS or special studies is provided. Table 1 provides a comparison of the sampler designs, filter types and target species analyzed.

Table 1. Target Analytes Associated with Filter Media Type and Sampler Design.

Sampler Type	Module	Denuder & Filter Media	Mass	Elements	SO_{4}^{2-}	NO_3^-	Particulate NO_3^-	Volatilized NO_3^-	NH_4^+, Na^+, K^+	TC, OC, EC, CC
IMPROVE	1	PTFE	✔	✔						
	2	Na_2CO_3/Nylon			✔		✔		✔	
	3	Quartz 1								✔
MASS 400	1	MgO /PTFE	✔	✔	✔	✔			✔	
		Backup Nylon						✔		
MASS 450	1	Quartz								✔
RAAS™	1	Quartz								✔
	2	PTFE	✔	✔						
	3	Optional								
	4	MgO/Nylon			✔	✔	✔		✔	
SASS™	1	PTFE	✔	✔						
	2	MgO/Nylon			✔	✔	✔		✔	
	3	Quartz								✔
	4	Optional								
	5	Optional								

Mass Aerosol Speciation Sampler (MASS 400 and MASS 450)

The MASS consists of two stand-alone samplers. These samplers are identical except the MASS 400 has sodium carbonate-coated denuder followed by a two stage Teflon® and nylon filter pack, while the MASS 450 has a single stage quartz filter pack. On the MASS 400 the air stream travels through a sodium carbonated-coated denuder which removes HCl, HNO_2, HNO_3 and SO_2. The remaining particulate passes through a 46.2-mm Teflon® filter which is analyzed for mass, elements, anions and cations. The PTFE filter is followed by a nylon filter which captures volatilized nitrate. The MASS 450 is specifically designed for collection of carbon species. The MASS 450 may be retrofitted with a XAD-4 denuder and a PUF/XAD-4 sorbent trap to collect semi-volatile organic aerosols as the technology is developed for use in more routine applications.

To obtain the fine particulate matter, the sample air inlet particle size separator is identical to the FRM WINS as specified in 40 CFR Part 50 Appendix L. This provides for an identical cut point and efficiency curve to the FRM. These samplers use active volumetric flow rate control which is designed to meet FRM specifications and, therefore, has the same accuracy of flow as an FRM sampler. One modification of the inlet is a high capacity sodium carbonate annular denuder

placed between the PM head and WINS inlet.

Perfluoroalkoxy (PFA) Teflon® coating of the inlet is an option that is available. This allows particles and gases to pass through the inlet with high efficiency. If an accurate measurement of nitric acid is desired, then PFA-Teflon® coating is needed. Coated surfaces can pass nitric acid with 80 percent to 100 percent efficiency. Other materials, such as aluminum, can absorb some gases, particularly nitric acid, that may change the equilibrium between volatile particles on a filter an the surrounding air. Coating also minimizes oxidation of inlet internal and external surfaces, thus extending the life of the sampler. A schematic and photographs of the sampler configuration for both the MASS 400 and MASS 450 can be found at http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pm25pict.pdf.

The MASS 450 sampler configuration for the collection of organic and elemental carbon and semi-volatile organic particles may be accomplished through the use of a XAD-coated denuder; a quartz filter pack downstream of the denuder collects only the condensable organic compounds. The semi-volatile organic species that evaporate from the filter during sampling are collected using a PUF/XAD trap downstream of the filter. The extract of the trap may be analyzed by GC/FID/MS methods to quantify the mass of organic compounds lost during sampling. The XAD-4 denuder can be used to collect gas-phase semi-volatile organic species (SVOC). The XAD annular denuder is needed to differentiate between SVOC's in gas phase and the SVOC's that evaporate (negative artifacts) during sampling. Quartz filters have some affinity for gas phase SVOC's, thus, removing these species from the air stream minimizes their adsorption (positive artifact).

The PUF/XAD-4 trap will quantitatively collect the semi-volatile organic species that evaporate from the particles during collection of the sample. These organic species can be quantified by GC/FID/MS analysis of the XAD/PUF extracts or by evaporating the extract and weighing the residual materials.

Reference Ambient Air Sampler (RAAS™)

The RAAS™ consists of an inert inlet, two size selective cyclones, four sampling channels, filter media for sample collection, critical orifices to provide the proper flow, flow sensing devices and a vacuum pump. Ambient air is pulled through a wind direction and wind speed insensitive inlet and through an inert inlet line that is insulated from direct heating by the sun. The inlet has no size selective function. The air sample is directed via the sample downtube to a primary sample flow splitter into two streams. Each of the two flow streams in turn move through a AIHL-design cyclone separator which removes coarse particles with diameters larger than 2.5 μm. The cyclone requires a precise flow of 24-liters-per-minute to produce the correct cut point for sample collection. Following one side after splitting, the remaining particulate and gases are split again through the sample manifold into one, two or three outlet channels. The flow streams are then directed through the sample filters. The flow rate through each filter holder is controlled by a critical orifice that can be changed if a different sampler configuration flow rate is desired for special studies. The other half of the primary flow stream duplicates this flow path. A

total of six channels are available for various speciation sampling objectives. For the routine chemical speciation program a total of 4 channels are used as shown in the schematic and photographs found at http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pm25pict.pdf
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All inlet, manifold, connector and cyclone parts are fabricated from polytetrafluoroethylene (PTFE)-coated aluminum. Any combination of reactive annular denuders or filter materials can be attached with consideration for the flow requirements and species to be measured. In the normal sampling mode, the combined flow rate to both filter holder assembles is 24-liters-per-minute, which is divided into one 16.7 and one 7.3 liter per minute subdivisions. Two of these sampling lines collect fine particles on standard 46.2-mm diameter PTFE filters for subsequent mass, elements and ion analyses. Two PTFE filters are used because samples intended for X-ray fluorescence analysis may be placed in a vacuum chamber during analysis leading to the expected loss of volatile aerosol components, thereby making it desirable to use a second PTFE filter for analysis of ionic species.

A third filter holder is used to collect particles on a quartz fiber filter from which carbonaceous species can be measured by thermal optical analysis. If semi-volatile species are to be determined, a diffusion denuder coated with XAD to remove gaseous semi-volatile organic compounds from the incoming air stream and a backup trap using polyurethane foam (PUF) or XAD resin to capture any semi-volatile organic components evaporating from the particulate captured on the filter may be used.

The fourth filter is a nylon filter located downstream from a magnesium oxide (MgO)-coated diffusion denuder. The diffusion denuder removes nitric acid vapor from the air stream while allowing fine particulate nitrate to pass through the denuder; then the nylon filter captures the fine particulate nitrate. The nylon filter is used because it has a high affinity for nitric acid. The nitrate content of any particulate ammonium nitrate (NH_4NO_3) that dissociates during sampling will be retained by the nylon filter.

The relative humidity, barometric pressure, orifice pressure, ambient temperature, manifold temperature, meter temperature, and cabinet temperature are measured by the RAAS™ control unit. The control unit uses a microprocessor to control the various aspects of the system operation. An RS-232 serial port is provided to allow for retrieval of sampling data using a personal computer or other data storage device.

Spiral Ambient Speciation Sampler (SASS™)

This sampler provides five parallel sample cassettes. Photographs and a schematic of the sampler design can be found at http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pm25pict.pdf. Each cassette has its own cyclone size-selective $PM_{2.5}$ inlet, denuder (if applicable), and tandem filter holder. The five cassettes are mounted in an aspirated solar shield that maintains the five independent sampling cassettes to less than 3°C over ambient temperature during and after a sample event. The cassette inlets point downward. Each channel is independently flow-controlled to 7.0 liters per minute and

volumetric flow and volume are logged each five minutes. Ambient barometric pressure and temperature are also measured and logged.

The sampler incorporates a $PM_{2.5}$ Sharp Cut Cyclone aerosol separator which operates two weeks without maintenance and requires no grease or oil. The $PM_{2.5}$ cyclone inlet is designed to remove from the cassette which allows either field or laboratory maintenance. The cassette with filter samples can be opened in the field, however it is recommended to be transported to the laboratory for analysis. Sample recovery and cleaning in the laboratory insures the inlet and sampling cassette is free from contamination each sample event. The sampler is designed without a plenum or sample tube which require frequent field maintenance. The Fine Particle sample exits the cyclone and is immediately captured on the FRM filter cassette.

The five sample cassettes are designed to use with one or two stacked 46.2-mm filters. Any cassette can be configured with one or two filters or a denuder followed by one or two filters. The five cassettes provided with the sampler can be used in multiple configurations.

The sampler is designed to be compact and portable using a tripod with the solar radiation shield housing the five cassettes. The sampler microprocessor has a simple one level menu and records all the information as required by a $PM_{2.5}$ FRM sampler. A LCD display informs the operator the status of the sampler. Test data is downloaded through the RS232 port. Software is supplied for data summary, faults, and five minute averages reporting.

The flow from each cassette passes through a critical orifice, a mass flow sensor, a valve and then to a common pumping manifold. The critical orifice controls the sample flow rate. The valve located downstream of the filter can be used to close sample lines not in use. The mass flow sensors are used for flow measurement. The flow rate sensors send a signal to the microprocessor which takes the ambient temperature and barometric pressure readings to calculate and display the current volumetric sample rate of each channel. The pumping manifold pressure is read by a mechanical differential pressure gauge leading to a control valve prior to the vacuum pump. The pump, flow controllers and AC/DC power is mounted in its own separate enclosure to minimize heat, vibration and be accessible for field maintenance.

Sampling Frequencies

To achieve the evaluation objectives, the participants were to operate two samplers of a different type from the three sampler assortment. The samplers would be located at the same site and spaced approximately one meter apart. Thirteen sites were to be included in the Minitrends Study and three of the sites would have collocated speciation samplers of the same design to assess sampler precision. Also existing PM2.5 FRM samplers were to be operated at each of the thirteen sites. All sample recoveries would be completed within 48 hours of collection. Most of the participants agreed that they would recover the samples within 12-24 hours of collection but a few States could not agree to this condition because of State policies or issues dealing with payment of overtime for weekend/holiday labor. After the completion of the Minitrends study, the participants agreed that they would continue to operate one of the speciation samplers on a one in three day basis as part of the 54 site Speciation Trends Network.

Sample Analysis

From a laboratory perspective, all sample modules would be prepared and analyzed using the National Speciation Contract Laboratory SOPs and QA/QC procedures as detailed by Research Triangle Institute.[6] Samples would be analyzed and data reported to the States according to the contract requirements. After State review of the data and completion of any corrections/modifications to the data report, RTI would enter the data into AIRS. These procedures essentially describe the main features developed as blueprint for the full scale implementation of the Speciation Trends Network. The participants also agreed that their field staff should be trained in the hands-on operation of the speciation samplers. EPA provided this training to study participants during November 1999.

Samplers were procured and installed during December, 1999-January 2000. The Minitrends Study was initiated in February, 2000 and was completed on July 31, 2000. The initial sampling frequency used in the study was kept at a one in six day interval for the first three months of testing to allow refinement of logistics such as sample shipping/receiving, preparing accurate field data reports, initial sampler performance issues, and scale up of laboratory operations. The last three months of evaluation was performed on a one in every three day sampling event cycle which is intended for the full scale Speciation Trends Network deployment and operation.

Minitrends Geographic Locations

The 13 sites selected for the Minitrends study were selected from the proposed listing of the 54 Speciation Trends sites which would represent the operational network after full deployment. These locations were selected to correspond with the basic statistical design of the study which required testing each sampler under different chemical atmospheres and varying environmental conditions. Each of the locations is an urban PM2.5 National Air Monitoring Site (NAMS) and was already equipped with a PM2.5 FRM and associated samplers/monitors for other NAAQS pollutants, as appropriate.

Site Parameters

Table 2 lists the sampling locations along with their AIRS site identifications and the speciation samplers installed for the intercomparison study. The site locations in Seattle, WA, Portland, OR, and Salt Lake City, UT were chosen to provide sampler intercomparison data for fine particle collection and analysis for environments which may have significant wood smoke contributions during the winter months. These sites were planned to satisfy the Expert Panel recommendations for further sampler testing following the Four City Study. The Bismark, ND, site was chosen to represent sampler evaluation under extreme cold weather environments which was an additional recommendation from the Expert Panel. The sites in Texas and Florida are urban sites where sampler durability and performance could be assessed under high temperature and humidity levels during the late-spring/early summer period of the study.

Trends sites in St. Louis, MO, Chicago, IL, Philadelphia, PA, New York, NY, and Boston, MA were chosen for the study to provide a cross-section of Midwest and Northeastern urban aerosol environments which historically had been characterized as sulfate-dominated compositions during summer months. These areas were also thought to have aerosols with high carbon content but with low nitrate levels .

In contrast, the Phoenix, AZ, site and three California sites were selected to represent urban environments which historically had been characterized as nitrate-dominated compositions (Pace, 1998). Phoenix, in particular, represents an area with the potential for high crustal components in atmospheric aerosols, which typically is dominant above 2.5µm but has been observed in fine particle samples. The Fresno, CA, trends site is also a Supersite study location and is outfitted with several advanced prototype speciation samplers and continuous monitors. The sites in Phoenix and Philadelphia were the exact locations for the Four City Study and would serve as reference points for data comparisons between the two efforts.

An attempt was made to distribute the three sampler types equally among the sites so that they would all be evaluated collectively under similar environmental conditions. A collocated pair of MetOne, Andersen, and URG samplers were sited in New York City, Boston, and Phoenix for an assessment of sampler precision. These sites also have PM2.5 FRMs and many locations have meteorological stations, samplers and/or monitors for other NAAQS and research equipment.

Table 2. Site Locations, AIRS Identifiers, and Speciation Samplers

Site Location	AIRS Code	URG	Andersen	MetOne
Fresno, CA	060670006		X	X
Phoenix, AZ	040139997	XX		X
Portland, OR	410510080		X	X
Seattle, WA	530330080	X		X
Salt Lake City, UT	490353006		X	X
Bismark, ND	380150003	X		X
St. Louis, MO	295100085		X	X
Chicago, IL	170310050	X	X	
Houston, TX	482011039	X	X	
Tampa, FL	120571075	X		X
Philadelphia, PA	421010004	X	X	
Boston, MA	250250042	X	XX	
New York, NY	360050083		X	XX

Sample Handling, Analytical, and Data Reporting Processes

One of the goals of the Minitrends Study was to assess the operational logistics of all processes which would encompass preparing and shipping filter media/sample modules to the Trends sites, recovering samples and sampler data, shipment back to the laboratory, analysis, validation and reporting. In practice, individual State agencies would request prepared filters and sample analyses for their Trends sites. EPA has made provision for the RTI Speciation Laboratory Support Contract to have the capability and capacity to support both the 54 National Trends sites and up to 250 additional State and local agency speciation monitoring sites.

Each State participating in Minitrends prepared an analytical services request identifying the particular speciation sampler, AIRS site location, number of samples to be analyzed, and supporting information prior to initiation of the actual sampling activities. These one-page requests were consolidated within each EPA Region through a Regional Speciation Coordinator (RSC). The RSC forwarded the consolidated request to one of three EPA Delivery Order Project Officers located in Denver, CO (Western States), Chicago, IL (Midwestern States), or New York, NY(Eastern States). The DOPOs consolidated requests from each of the EPA Regions in their areas and processed them to the EPA Speciation Laboratory Project Officer who contractually placed the orders to RTI. After receiving the consolidated orders, RTI prepared all filter media, loaded them into appropriate sample modules and shipped them on a predetermined schedule via Federal Express to each of the Minitrends sites. After sample collection, the site operators recovered the samples along with sampler data and shipped the materials via Federal Express back to RTI. RTI then performed all sample analyses, performed data validation, and provided an electronic copy report to each State and corresponding DOPO within 30 calendar days after sample receipt. The States had 45 calendar days to review the data and approve the data package for AIRS entry by RTI within 15 additional calendar days. The goal was to facilitate valid data entry into AIRS within 90 days following sample collection.

The implementation of this process is intended to support long term, routine operation of the speciation monitoring program (National Trends Network and State Networks). The critical elements in the process require a focus for all parties to adhere to a prescribed schedule of events to permit the timely flow of samples and data between the site operators, RTI, and EPA contacts. The Trends sites operators began installing samplers in November and December of 1999. From that time through January, 2000, the systems were operated without sample analyses to identify any issues with sampler performance from the standpoint of calibration, sample pump and electronics operation, and field ruggedness. During this period several issues of these types were identified and addressed by the equipment vendors.

Formal startup of the sampler intercomparison occurred in February, 2000. For the first two months of the study, the participants agreed to sample on a one-in-six day frequency to gain experience in all of the sample and data transaction processes and identify issues which needed corrective action by either EPA or RTI, as appropriate. Routine, one-in-three-day sampling began in April, 2000 and continued through the end of July for the intercomparison study. In August, a series of experiments were conducted at the Minitrends sites to investigate the potential for positive or negative artifacts that could contribute to loss of sample integrity because of sampling

environment or sample transport conditions. Beginning in September, 2000, each of the Minitrends sites continued with routine, one–in-three-day sampling with one of the speciation samplers they had selected to operate. Also, EPA began to coordinate the continued deployment of the next 17-20 Trends sites with the goal of having all 54 National Trends Sites operational by the end of calendar 2000.

Speciation Analysis Laboratory Quality Assurance Audits

A study has been conducted as part of the QA oversight for the $PM_{2.5}$ Speciation Trends Network. The purpose of this study was to evaluate performance of the gravimetric and the Ion Chromatography (IC) laboratories located at Research Triangle Institute (RTI). A gravimetric analysis of the sample is needed to determine the mass of very fine Particulate Matter (PM) captured from the sampled air. The IC analysis is needed to determine selected ionic species potentially present in the PM capture.

Gravimetric Analysis

For this study, ten new filters were pre-weighed at RTI in the usual manner but were not shipped directly to a field site. These ten filters were shipped to the National Air and Radiation Environmental Laboratory (NAREL) in Montgomery, AL. All ten filters were immediately placed into the weighing chamber at NAREL for equilibration and determination of a NAREL tare weight. After the NAREL tare weights were determined, seven of the ten filters were loaded with very fine PM captured from the outside air near NAREL. An Andersen air sampler was used to load seven of the filters, and the remaining three filters were utilized as field blanks. Following sample collection, filters were returned to the weighing chamber at NAREL to equilibrate and to determine the loaded mass. Finally, the ten filters were shipped back to RTI for their routine determination of the final filter weights.

Gravimetric Results

The results of this study are summarized in Figure 1. The critical information needed by the program is the mass of PM deposited onto the surface of a collection filter, and therefore, PM capture is plotted in Figure 1 for the seven loaded filters, three travel blanks, and one laboratory chamber blank. Figure 2 presents the inter-laboratory differences. Inter-laboratory differences were calculated by subtracting the PM capture value determined at RTI from the capture value determined at NAREL. Notice that a negative bar on the Figure 2 graph represents a smaller PM capture value determined at NAREL.

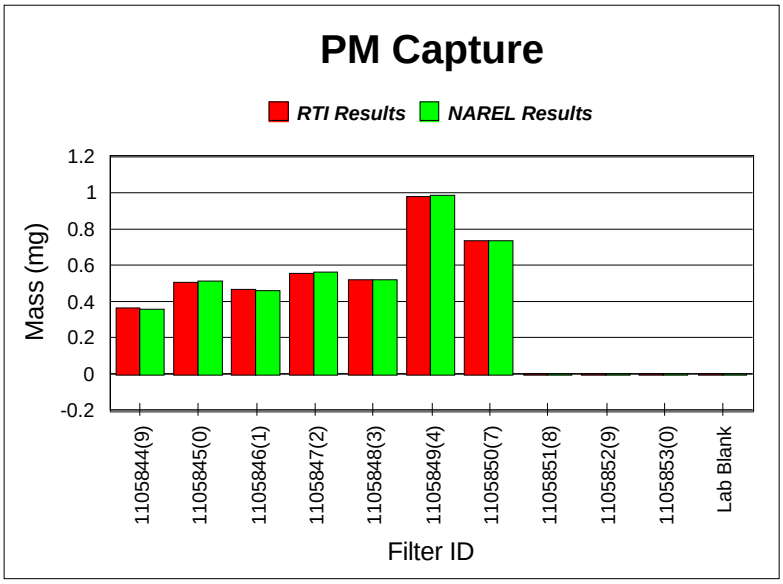

Figure 2

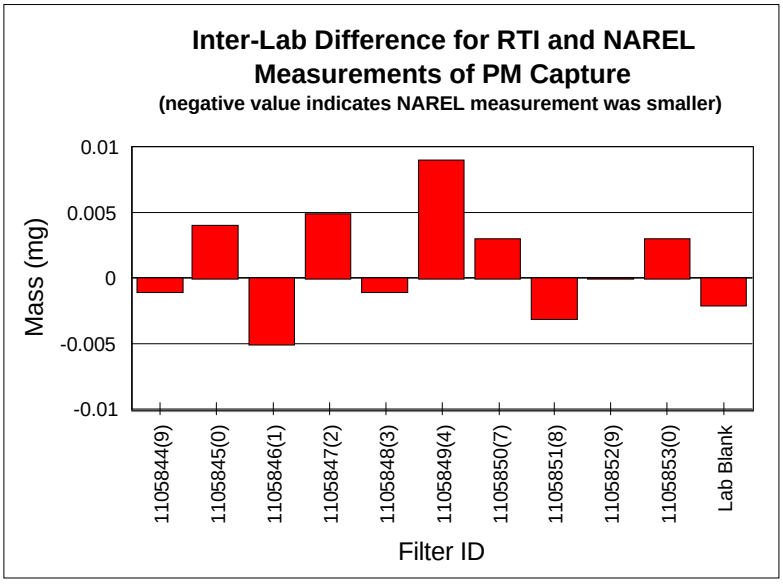

Figure 3

Ion Chromatography Analysis

For this study, six IC spike solutions were carefully prepared at the National Air and Radiation Environmental Laboratory (NAREL) in Montgomery, AL, and shipped to RTI for analysis. Each solution was designed for dilution by a factor of ten using reagent water available at the receiving laboratory. After dilution to full volume, each spike solution was utilized as the

solvent to extract a clean blank collection filter available at the receiving laboratory. The filter extracts were analyzed using an appropriate IC instrument available at the receiving laboratory.

Results were reported for each sample based upon the concentration of analyte present in the final extract. Three solutions were prepared at NAREL for determination of selected anions, and three solutions were prepared for the determination of selected cations. These solutions were designed to offer a mid-level concentration, a low-level concentration, and a blank for each analyte. RTI was told to expect a concentration range of 0-10 mg/L for each analyte in all of the samples. All samples were analyzed at NAREL before they were shipped to RTI

.

IC Results

Results for the mid-level spikes are presented as a bar graph in Figure 3. For each analyte, the mid-level concentration of the fully diluted spike solution was 2 mg/L. Figure 3 presents the expected result, the RTI result, and the NAREL result for each analyte.

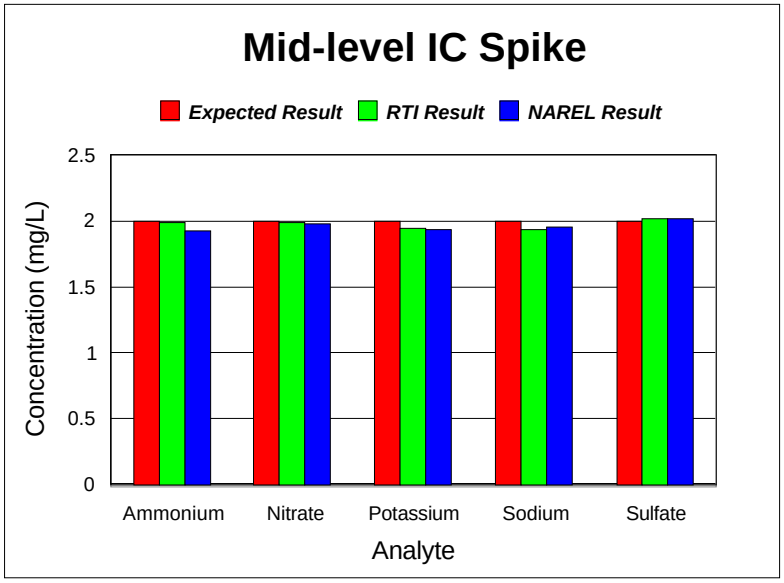

Figure 3

Results for the low-level spikes are presented as a bar graph in Figure 4. For sulfate the low-level spike level was 0.2 mg/L. For all other analytes, the low-level spike level was 0.15 mg/L. Since the concentrations presented in Figure 4 are low, an extra bar was added to this graph showing the Method Detection Limit (MDL) reported by RTI.

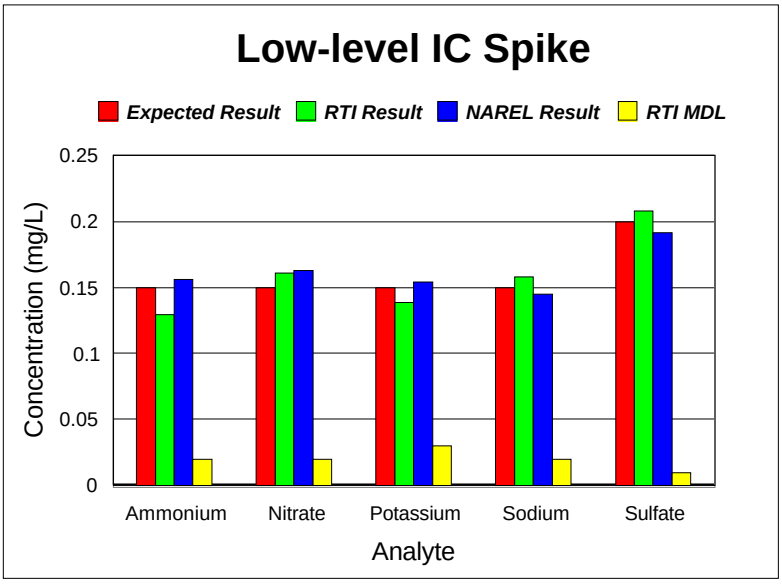

Figure 4

Performance Audit Evaluation Summary

Good agreement was observed for all mass measurements performed at RTI and at NAREL. All three field blanks showed PM capture well below the 0.030-mg failure threshold. The independent chamber blank at both laboratories also showed PM capture well below the program limit of 0.015 mg. The largest inter-laboratory difference for captured PM was 0.009 mg which is smaller than a reasonable warning limit of 0.015 mg and significantly below a reasonable failure limit of 0.030 mg. This study indicates overall good performance by the gravimetric laboratory at RTI. Excellent recoveries (96-101%) were obtained at both laboratories for the mid-level IC spikes. As expected, a slightly wider range of recoveries (87-109%) was observed for the low-level spikes, but in no case did the difference between the expected value and the reported value exceed the MDL expressed by RTI.

Sample spike solutions identified as A-3 and C-3 were actually blank water. These blanks provided a mechanism to measure laboratory contamination from a variety of sources such as (1) the reagent water used to dilute every sample, (2) the "clean" filter extracted by the test solution which is normally provided to the field for PM capture, and (3) containers used to hold and transfer the sample during the extraction and analysis process. No contamination was reported for the cation blank (C-3), but very low levels of nitrate and sulfate were reported for the anion blank (A-3). Nitrate was reported at 0.023 mg/L which is slightly above the 0.02 mg/L MDL, and sulfate was reported at 0.009 mg/L which is slightly below the 0.01 mg/L MDL. If the MDL is defined as the smallest concentration that can be distinguished from a blank, it seems that RTI has done a good job estimating the MDL for nitrate and sulfate.

Assessment of Sampler Operational Performance in the Field

Field performance of the monitoring equipment has a major impact on the monitoring staff's ability to measure accurate readings. In order to assess a sampler's ability to perform, we

needed actual input from the operators. Besides giving us a comparison of the different designs, we also wanted to compare data results to field observations. A survey was e-mailed to all participants and results were compiled. Table 3. contains the actual field survey which was completed by each site operator at the conclusion of the field sampling phase of the study.

Survey Results

All three samplers had both good characteristics as well as design or performance issues. Listed here is a narrative of the advantages and disadvantages in general, for each sampler as reported by the site operators.

Anderson RAAS

Best Features:

38% of the responses felt the Anderson was simple to set up and 25% felt the sampler was easy to use. 12% liked the ability to: store multiple sample records, obtain higher loadings from higher flows, ID an entire run and still ID individual filters, and erase old data. 12% also found the program familiar and thought the data sucker was handy, shipping containers were easy to use (as opposed to the SASS), components were easily accessible, found the large cabinet handy, and liked the fact that no filter modules were needed. 25% also felt the customer support from the vendor was helpful to excellent. 12% felt response was slow.

Operational Issues:

75% of those surveyed did not feel the installation instructions were adequate. Upon operation, their most frequent complaints were torn filters (38%) software lockups along with bad correlations, an inadequate manual, and filter holders that were too small (25%). 12% had problems with each of the following: the accordion hose cracked, firmware, pump too loud, flows were outside acceptable limits, instrument failed checks, data needed to be downloaded too quickly, filter changing and leak checking was awkward, and too much record keeping was reported.

Table 3. Field Operator Sampler Performance Assessment Questionnaire.
Climatic Conditions

Site Operator Name- **Date form completed:**
AIRS Site ID -

Sampler surveyed on this form (please circle one):
Andersen RAAS URG MASS Met1 SASS

1. Installation
Did you find the installation instructions adequate? Yes No
If inadequate, please discuss:

2. Operation
a. What were the most frequent operational issues with the sampler (eg., pump failure, filter tearing, electronics, software malfunction, etc.)?

b. How long (on average) did the collected samples remain in the sampler before it was recovered?
Please circle one:

12 hours or less 24 hours 48 hours 72 hours 96 hours

c. How much time (on average) did you spend on site to recover the samples and sampling data, and reset for the next sampling event?

1 hr 2 hrs 3hrs 4hrs

d. Did local climatic conditions effect the sampler operation? Yes No
If yes, please elaborate:

3. QA and Maintenance
a. What were the 2 most significant maintenance issues with the sampler?

b. Was the sampler calibrated and operated according
to the requirements of the mini-trends draft QAPP? Yes No

If no, please elaborate:

4. Customer Support
How was customer support provided by the vendor (eg., by telephone, e-mail, or on-site visit?)

5. Overall Assessment
a. What are the 3 best features you found in the use of the sampler?

b. What are the 3 most important features in need of design modification or operational improvement?

c. At completion of the overall minitrends study, what issue(s) in item (2) above were not resolved by the vendor?

63% reported no climatic conditions affecting sampler. However, 12% felt that the filter was too hard to loosen, and flows were restricted in freezing weather, leaks occurred in cold weather, and windy conditions affected loading. (Out of the 8 states using this sampler, 63% can be considered states with freezing conditions).

Largest Maintenance Issues

38% of operators reported leaks, 25% reported problems with cleaning inlets and cyclones, and 12% reported problems with: changing filters, recording data, calibrations that didn't hold, flow rate variances, firmware, sampler failing design audits, no internal air filter, and too many airline connections that were prone to leakage.

Features that Need Design Improvements

38% reported the flow control, tubing and flow monitor connection needs improvement. Leakage problems were again identified under this question, including 12% reporting cold weather leak problems and too many connections for leaks to occur. 12% also reported download time too lengthy, Teflon dust found to be coming off of the threads on the sampler filter holders, there was limited blank data, flag software problems, need to reduce the time needed for flow calibrations, sampler required special calibration equipment, samples were collected at different flow rates, should be able to download to a PC, instrument should be able to download to a PC, should filter aspirated air, needs easy access to filters, and the pump was too loud for a neighborhood setting. 25% found dirt filtration and flow rates were a problem.

MET1 SASS

Best Features:

55% found data downloading and general sampler operation easy, while 25% found filter installation and programming easy as well. 11% found the software useful, flow rates reproducible, and found the system portable, reliable, and cyclone inlets easy to clean. 11% also found QC checks easy to run, few parameters to measure, liked the canisters, cyclones and one-button sample run setup with adjustable defaults, and also reported ease with changing filter modules, doing leak checks, maintaining and calibrating.

Operational Issues:

Out of 8 states reporting operational issues, 12% stated the following: They found it difficult to audit temperature probes, device should allow FRM-type flow audits, cyclone was corroding, incomplete documentation, filter edges too sharp which cut filters, flow sensor adjustment difficult, needed access to sample pump, couldn't tell if aspirator was working, and no air filtering found coming from the pump box. 25% found software updates required replacing an EPROM (suggested changing to flash EPROMS).

Climatic Conditions:

There were five cold-weather states in this assessment. North Dakota was the only state that found the display too faint to read in the cold. Utah had not run the instrument in cold weather so this item could not be assessed.

Largest Maintenance Issues:

55% of the states were cold-weather states, however only 1 (or 20% of the cold weather states) reported problems with cold weather, which entailed the display being too faint to read in the cold. One state (Utah) had not run the instrument in cold weather, so this item could not be assessed.

Features that Need Design Improvements:

55% reported the instrument needs improvement in the flow controllers and flow/sensor calibration, and that more storage is needed: capacity for 5 to 10 runs would be ideal. 44% felt that data recovery needed improvement. 12% reported the system needs a reset button, weatherproofed cyclones, filter temperature probe protection and protection of electronics from dirt, needs a device to adjust the flow, better cyclone metallurgy, less bulky shipping containers, better documentation, flow check release pressure valve needed to prevent ruptured filters, should have another method of extracting the data, operate without using all 5 channels, have a filter in the pump housing and display the temperature in the pump housing, and have an LED showing the aspirator fan is working.

URG MASS:

Best Features:

86% responded that installation instructions were adequate. Almost 50% felt the software was very good, well-thought-out, and found programming and data retrieval easy. 43% thought maintenance, filter handling, installation and retrieval were easy. 29% stated the manual and documentation were good and the instrument was an easy setup. About 15% found no leaks, and found that flows were always in +/-4%.

Operational Issues:

In addition to the issues discussed below under "maintenance issues", about 15% of operators found temperature spikes, flow control faulty and pump failures, units that did not work on delivery, board failure, and pump and software problems.

Climatic Conditions:

86% reported that cold weather did not affect sampler. However, the display was found hard to read in North Dakota at temperatures below 0 degrees F, and Arizona operators found it necessary to shield the display from the sun or it would blackout.

Largest Maintenance Issues:

About 43% stated that component replacement and specifically, screwing filter holder into instrument, was difficult; the dry gas meters were not acceptable in cold climates, calibrations were hard to perform and too lengthy in the field, hard to clean inside of the instrument, and the flow control system and pump were unstable. One operator reported the pump/power supply failed once.

Features that Need Design Improvements:

About 57% reported improvement needed in the teflon to stainless connection of

modules/filter holders. Between 15 and 30% of operators felt that the door seals were inadequate, dry gas meter needs replacement with flow controllers,, filter temperature probe should mount inside next to the filter, the flow control system was inadequate, system needs less time-intensive calibration procedures, firmware should include storage pointers, and the shipping procedures/bulky shipping containers need improvement.

Followup by the Sampler Manufacturers

As might be expected with the outcome of independent field performance testing of sampler technologies, each of the vendors have attempted to address most of the critical comments and deficiencies noted above. As issues were uncovered and reported during the study period, frequent communications and corrective actions were taken by the manufacturers in the field to address data display problems, sample pump performance, and other factors which could be remedied without significantly disrupting the sampling activities.

Analysis of Intercomparison Data and Future Field Evaluation Studies

The goals for this analysis are to evaluate how the samplers used in the study compare and what are the major influences of any deviations from one sampler to another (or site to site). Also of concern are the natures of any data values that do not appear to follow the patterns used in making the assessment. The primary species of concern are PM2.5 mass, sulfate, nitrate, total carbon, calcium ammonium, elemental carbon, organic carbon, and the most prevalent metals.

The analyses will be conducted in several stages. Exploratory data analysis (EDA) will be geared to uncovering and understanding what influences the data and what are the relative strengths of those factors. Statistical modeling will be performed which will involve verifying modeling assumptions and appropriately modeling the error structure. The final stage will be to synthesize the results of the various statistical modeling output with the graphical output of the EDA into a "weight of evidence" presentation that addresses the study's primary question, "Are there significant differences among the sampler types?" The target for the primary output will be on a sampler level as a whole, not by species comparison. We anticipate these evaluations will be completed and reported by July, 2001.

As the remaining Trends sites become operational, EPA is planning several additional field evaluation studies. The first study will investigate the performance of sequential speciation samplers. These technologies are largely adaptations of the single event sampler designs and offer the convenience of collecting multi-day samples with reduced field labor resource requirements. However, EPA is concerned about the stability of both unexposed filter media and collected samples under ambient field conditions over time. Specific field experiments will be conducted to evaluated these issues. The schedule projects a six month study to begin in the Spring of 2001.

Recent advances have been made in the commercialization of continuous monitors for nitrate, sulfate, and carbon species. Since these analytes appear to represent the major components

of PM2.5, EPA is interested in evaluating the field viability of these technologies as both enhancements and potentially eventual replacements for the filter-based sampling methods used in the Speciation Trends Network. EPA plans initial field evaluations of these monitors at selected Trends sites in the Summer of 2001.

In an attempt to integrate monitoring networks, EPA is planning to implement an intercomparison of sampling, analysis, and quality assurance approaches between the Speciation Trends Network and the IMPROVE Network. The IMPROVE network employs filter-based samplers for PM2.5 similar to the Speciation Trends designs but sites are deployed in National Parks and remote rural environments. Since the objective of the Trends siting was to focus on major urban populated areas, EPA and IMPROVE staff will conduct a multi-site evaluation of collocated samplers within each network to characterize the quality of how these two independently operated networks produce comparable data.

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Key Words

1. particle speciation
2. air monitoring
3. PM2.5 samplers
4. air quality
5. databases
6. national trends