PARTICULATE MATTER ($PM_{2.5}$) SPECIATION GUIDANCE DOCUMENT

DRAFT

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PREFACE

This document contains information on the objectives for collecting speciated data, selection of target analytes, samplers, quality assurance, and network operations. The guidance provided gives a program overview to managers, site operators, laboratory services support personnel, and regulatory compliance data analysts. Comments on this draft version are invited. Please address comments to:

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1.0 INTRODUCTION

1.1 Purpose

Due to the flexibility afforded by the 300 site $PM_{2.5}$ chemical speciation monitoring network, there will be some variability in the design and operation of the network at the State level; therefore, the Environmental Protection Agency (EPA) is providing guidance on the implementation of a $PM_{2.5}$ speciation monitoring program. The guidance provided in this document provides some introductory material and a basic overview of the principles and procedures necessary for developing and implementing a chemical speciation network. The target audience includes managers, site operators, laboratory services support personnel, and regulatory compliance data analysts involved in $PM_{2.5}$ program implementation. The guidance provides the following:

- A description of data uses - NAAQS support and implementation plan development (trends, control strategies, model validation, source apportionment, and visibility);
- Technical guidance for network design and the collection and measurement of chemical species;
- Identification of useful aerosol properties that can be measured on filter deposits;
- A description of the principles, procedures, and equipment used to sample and analyze filter deposits for particle species; and
- A specific strategy and procedures for aerosol sampling and laboratory analysis.

1.2 Background

Chemical speciation is included in the monitoring requirements and principles set forth by the 40 CFR Part 58 Regulations, specifically those promulgated as part of the $PM_{2.5}$ National Ambient Air Quality Standard (NAAQS) review completed in 1997. A chemical speciation network of 50 sites to provide a first order characterization of the metals, ions, and carbon constituents of $PM_{2.5}$ is a requirement of this rule. These sites will be part of the National Air Monitoring Stations (NAMS) network and will provide nationally consistent data for assessment of trends. This network will serve as a model for other chemical speciation efforts and represents a small fraction of the chemical speciation work that the EPA expects to support with Federal funds.

The EPA anticipates that approximately 300 sites will participate in the full chemical speciation network. The additional 250 sites will be used to enhance the required network and provide information for developing effective State Implementation Plans (SIPs). These sites will allow flexibility in terms of sampling frequency, site selection, site mobility, and the addition of target species. For example, some areas may choose to focus on episodes or specific seasons, such as a winter time wood smoke problem. Retaining a minimum of 50 core sites for consistency across space and time for long-term trends allows other sites to address regional and local issues. The EPA does not believe that a single nationwide approach to speciation sampling and analysis is the best approach in all locations. The EPA expects that most sites will follow a sampling and analysis program similar to the 50 core NAMS sites; however, alternative speciation approaches will be considered on a case-by-case basis through negotiation with appropriate EPA Regional Offices and Headquarters. Since EPA is working toward a single set of data quality objectives for the 50 required sites, States may choose to adopt these objectives as a basic set of guidelines for additional sites. At a minimum, the chemical speciation network will quantify mass concentrations and significant $PM_{2.5}$ constituents which include trace elements, sulfate, nitrate, ammonium, and carbon. This series of analytes is very similar to those measured within the Interagency Monitoring of Protected Visual Environments (IMPROVE) program.

On July 18, 1997, the U.S. EPA promulgated a new NAAQS for particulate matter (PM) in 40 CFR Parts 50, 53, and 58, ***Federal Register*** (U.S.EPA, 1997a, 1997b). The suite of PM standards is revised to include an annual (long-term) primary $PM_{2.5}$ and a 24-hour (short-term) $PM_{2.5}$ standard. The NAAQS applies to the mass concentration of particles with aerodynamic diameters less than 2.5 μm ($PM_{2.5}$) and 10μm (PM_{10}). The NAAQS for $PM_{2.5}$ specifies the following:

- The three-year average of the annual mean of $PM_{2.5}$ concentrations is not to exceed 15$\mu g/m^3$. The average may be based on a single community-oriented monitoring site or the spatial average of community-oriented monitoring sites in a community monitoring zone (CMZ).

- The 3-year average of the annual 98th percentiles of twenty-four hour $PM_{2.5}$ concentrations is not to exceed 65$\mu g/m^3$ at any population-oriented monitoring site in a Metropolitan Planning Area (MPA).

The deployment of the national $PM_{2.5}$ monitoring network is a critical component in the implementation of the new NAAQS. Substantial resources are being provided to support the national monitoring network of 1,500 $PM_{2.5}$ sites. This network will comply with the information provided in President Clinton's Directive of July 16, 1997 and regulations provided in the ***Federal***

Register. The ambient data from this network will drive an array of regulatory decisions, ranging from designating areas as attainment or nonattainment, to developing and tracking cost-effective control programs. There is an urgent need to establish the network as soon as practical so that other programmatic efforts relying on the use of $PM_{2.5}$ environmental data are not delayed.

The ***Federal Register*** describes the initiation of a $PM_{2.5}$ chemical speciation network of approximately 50 core sites within the NAMS for routine speciation monitoring. About twenty-five of the monitors are to be collocated as part of the Photochemical Air Monitoring Stations (PAMS) component of NAMS, with the remaining sites to be selected in coordination among the EPA, Regional Office Administrators, and the States. Speciation samples will be collected every 3 days at the NAMS sites.

Data derived from the $PM_{2.5}$ monitoring network include both aerosol mass measurements and chemically-resolved or speciated data. Mass measurements are used principally for identifying areas of attainment or nonattainment. Chemically-resolved data serve the needs associated with assessing trends and developing mitigation approaches to reduce ambient aerosol emissions in relation to SIPs. These needs include emission inventory and air quality model evaluation, source attribution analysis, and tracking the success of emission control programs. These chemical measurements will also provide support for regional haze assessments, which is the primary objective of IMPROVE.

The overall data gathering needs for the $PM_{2.5}$ program are being addressed by the following objectives and schedules:

- Designation of Federal Reference or Equivalent Method (FRM/FEM) samplers to collect data for $PM_{2.5}$ NAAQS comparison purposes. As of April 30, 1998, a number of samplers have been designated and the process is continuing for additional samplers.

- Establishment of a 1,500 site $PM_{2.5}$ gravimetric monitoring network by December 31, 1999, with 1,100 $PM_{2.5}$ sites established by December 31, 1998.

- Collection, measurement, and storage of quality-assured data beginning on January 1, 1999, to support NAAQS comparisons, $PM_{2.5}$ program implementation needs, and regional haze assessments.

- Development of a national chemical speciation sampling and analysis program by May 8, 1999.

1.1 Programmatic Requirements

The routine speciation program incorporates a balance of prescribed requirements, particularly for the NAMS, and the allowance for alternative sampling and analysis protocols for other sites within the program. It is not possible to anticipate the range of sampling/analysis approaches State and local agencies may consider, especially in light of both emerging technologies and forthcoming aerosol characterizations across different locations. This guidance largely provides "support/background" information that can be utilized in formulating sampling and analysis plans. A description of required sampling and analysis plan elements and procedures for submitting monitoring network descriptions for EPA approval follows in Section 1.1.2.

State and local agencies should submit preliminary speciation sampling and analysis plans as part of all network description submissions to appropriate Regional Offices. The due date for final network descriptions is July 1, 1998. Recognizing that little lead time exists between availability of guidance and the implementation dates, EPA expects final submittal of the speciation network plans by October 15, 1998. Furthermore, subsequent annual updates are required to be submitted by States as part of their annual State monitoring report due July 1, or an alternative date negotiated by the State and the EPA Regional Administrator, per 40 CFR58.26.

1.1.1 National Air Monitoring Stations (NAMS)

The NAMS sites are dedicated to providing air quality trends over time and therefore, require consistent sampling and analysis protocols. The EPA expects that sites not designated as NAMS may conform to similar protocols. Recognizing that a national protocol for trends does not meet the specific needs for every location, the EPA will allow deviations from NAMS protocols at non-NAMS sites when adequate network descriptions and justification are provided in the plans described below (Section 1.1.2). The major requirements for each NAMS protocol include:

- **Sampler type** - The EPA, through consultation with the speciation workgroup, will determine the sampler type(s) utilized at each NAMS for consistency. The sampler will be a multiple filter device capable of collecting the target species of interest.

- **Sampling Frequency** - One 24-hour sample will be collected at each site every 3 days.

- **Analytes** - Elements will be determined using x-ray fluorescence spectroscopy (XRF); major ions [sodium, potassium, sulfate, nitrate, ammonium] will be determined using ion chromatography (IC); and total, elemental, organic and carbonate carbon will be determined by thermal optical analysis (TOA).

1.1.2 Monitoring network descriptions and plan elements

The monitoring network descriptions should describe the chemical speciation monitoring strategy and document any deviations from approaches used in the NAMS. Additional guidance is provided in the ***Guidance for Network Design and Optimum Site Exposure for $PM_{2.5}$ and PM_{10}*** (U.S.EPA, 1997c). At a minimum, the following elements must be included and be reviewed each year as part of the annual network review.

- **Program Objectives** - A description of the basic technical objectives to be addressed through the speciation program. These objectives should go beyond very generic categories such as "develop control strategies" and address the specific technical needs/issues relevant to a particular area.

- **Sampling Network Design** - Location of sampling platforms, including (where applicable) additional collocated instrumentation.

- **Sampler Type** - Plans should provide the vendor name and instrument model selected, if such information is available. Preliminary plans may have to reflect intent with generic descriptions of sampler types.

- **Sampling Frequency** - In many cases, sampling will be conducted with 24-hour sampling periods on an every 3-day basis with exceptions for episodic coverage. These sampling schedules may be analyte or instrument dependent (e.g., use of continuous analyzers).

- **Target Analytes** - Describe what components will be analyzed and include associated sampling frequencies if analyte specific.

- **Sample Handling** - Sample (filter) collection, transportation, laboratory identification and archiving. Provide a detailed description (life history) of the sequence of filter collection, transportation to analysis laboratory, and subsequent storage for future analysis.

- **Data Analysis** - This description should include initial data assessments at the sample level; spatial and temporal aggregation techniques; and more refined and exploratory analyses addressing stated program objectives.

- **Program accountability** - A description of the program organizational structure which defines the persons responsible for management, implementation, and quality assurance for the network. Describe the management plan and accountability measures used for the program.

1.2 Program Goals and Objectives

The goal of the $PM_{2.5}$ monitoring program is to provide ambient data that support the Nation's air quality program objectives. In prioritized order, the programmatic objectives for $PM_{2.5}$ chemical speciation include:

Objective # 1 - Annual and Seasonal Spatial Characterizations of U.S. Aerosols

The analytes, sampling periods and frequency, spatial resolution, and data accuracy affect the utility of the data. Accordingly, the primary use of these data will be to develop general characterizations of aerosols across the major urban areas of the country depicting seasonal and annual patterns. To the extent that networks include sites located in transport and/or "background" locations, similar characterizations of rural/regional environments, especially in combination with the IMPROVE program, are an expected product. This objective serves an important need to gain an understanding of characterization of the aerosol nationwide. The following objectives all require this initial characterization step, which in practice translates into developing common spatial and seasonal/annual displays of aerosol components. Accordingly, this objective is the highest priority. An analysis of the speciation data may lead to the classification of air sheds into groups with similar particulate composition and concentration. This would allow the results of intensive studies to be more broadly applied to appropriate locations, and reduce excessive redundancy of efforts on a national level.

Objective # 2 - Air Quality Trends Analysis and Tracking Progress of Control Programs

The use of observational data to play a central role in ongoing SIP improvement has been encouraged by the scientific community through the 1991 National Academy of Sciences Report on Tropospheric Ozone (NRC, 1991) and the forthcoming North American Research Strategy for Tropospheric Ozone (NARSTO) assessment. The ability to detect trends in ambient concentrations that are associated with planned air quality control efforts must be incorporated in SIP assessments.

Objective # 3 - Developing Emission Control Strategies

The major difference between this and the preceding objective is the fixed time frame associated with "development." A combination of prospective air quality modeling and semi-quantitative source attribution analyses will generate objective information for decision makers

underlying emission control decisions. Accordingly, speciated data will be used in evaluating air quality model performance and the requisite emission fields. A variety of source attribution techniques will be exercised. Recognizing the uncertainties and limitations in models, inventories and sampling/analysis methods, this objective is of lower priority.

There exists a constant need to develop information that may lead to more definitive associations between adverse health impacts and specific aerosol properties. The speciation program provides greater chemical resolution than standard mass measurements and therefore, should provide value to health studies. Nevertheless, this routine speciation program must enlist input from health scientists to optimize overall value. For example, emissions from combustion processes include fine particles containing trace elements of varying toxicity. Information is needed which relate emissions characteristics from processes such as fossil fuel combustion, prescribed burning, and wild land fires, to urban and nonurban $PM_{2.5}$ concentrations and the magnitude of toxicity relative to the exposure of populations to such particles. In contrast, some $PM_{2.5}$ may not be harmful, such as the $PM_{2.5}$ transported from North Africa, which is thought to be primarily very finely ground limestone or calcium carbonate.

1.2.1 Data Use and Analysis

The expectations for data emerging from the routine program should be put in context. In communicating the need for gaining a gross understanding of aerosols across the United States, the inherent limitations of such a program are not obvious. As one proceeds down the list of priorities, important limitations arise. For example, the lack of time resolved measurements constrains the ability to diagnose air quality models and emission estimates, both of which incorporate strong diurnal trends. One might argue that a national program focused on an annual standard does not require time resolved measurements; a debatable subject. Clearly, the effectiveness of assessment tools increases with more resolved information (space, time, composition, size, phase, etc.). Similarly, the aggregate approach (24-hour sampling, 1 size fraction, 1 vertical plane) across all aerosol properties is an acknowledged shortcoming. This program must reflect a reasonable balance that considers available resources, technological limitations, and other efforts. The EPA recognizes that, in future years, there may be a need to adjust the objectives and requirements for speciation sampling and analysis. Just as control programs need to be assessed periodically, a major data acquisition program should undergo periodic assessments as well. However, there must be a careful balance between having a flexible monitoring network which is able to adjust to new technologies as they arise, with the problematic issue of wide scale implementation of rapid innovation with little cohesion between data gathering activities.

The EPA will provide guidance on how to organize and analyze the data (Section 2.0). For example, software applications are needed to organize and display the data in meaningful ways which might be of great use in identifying and understanding significant $PM_{2.5}$ characteristics, trends, etc. Personnel resources will have to be identified in order to properly analyze the data.

Within the current network design framework, data collected every third day will have limited use for epidemiological studies. A majority of the sites would have to be located in highly populated areas greater than 500,000 inhabitants, which are more appropriate for health assessment studies. For the longer term, when continuous methods that provide equivalent data become available, the network can be upgraded. As these methods are implemented, they will also provide valuable diurnal information while reducing sampling and analysis costs.

1.2.2 $PM_{2.5}$ Speciation Data Quality Objectives

An important concern in the collection and evaluation of ambient air monitoring data is the level of uncertainty of the data. Uncertainty arises due to temporal and spatial variability in the ambient air, variability in the samplers, and variability in the laboratory analyses. The data quality objective (DQO) process, a strategic planning approach, will be used to prepare for the $PM_{2.5}$ speciation data collection activity. The DQO process provides a systematic procedure for defining the criteria that the $PM_{2.5}$ speciation data collection design should satisfy, including when to collect samples, where to collect samples, how many samples to collect, and the tolerable level of decision errors. By using the DQO process, EPA will assure that the type, quantity, and quality of the data will be appropriate for the intended application, while guarding against committing resources to data collection efforts that do not support a defensible decision.

For the $PM_{2.5}$ speciation monitoring network, the DQO process will proceed down two tracks due to differing primary objectives. For the NAMS sites, the primary objective is to determine trends on the national level. For the remaining 250 sites, objectives may vary, depending on the Regional and/or local data needs. For example, a State with high concentrations of $PM_{2.5}$ might consider the primary objective to be the characterization of the fine particulate aerosol to assist with the development of control strategies, whereas a State with Class I areas might consider the primary objective to be measuring trends in visibility. For each objective, the DQO process might result in different optimal monitoring designs and tolerable errors.

The Monitoring and Quality Assurance Group (MQAG) within the Emissions, Monitoring, and Analysis Division (EMAD) of the OAQPS has recently initiated an effort to

ensure that the data collected by the ambient $PM_{2.5}$ speciation network is of a sufficient quantity and quality to support the intended uses of the data. This effort includes developing DQOs for the 50 NAMS sites dedicated to measuring national trends in the $PM_{2.5}$ species (available approximately August, 1998) and a blueprint for the DQO process for the remaining 250 sites (available approximately October, 1998).

1.5 Related National Program Efforts

Other regulatory activities that constitute the national $PM_{2.5}$ monitoring program directed by EPA include the additional efforts discussed briefly below.

1.5.1 IMPROVE

The 40 CFR 51 Regional Haze Regulation, proposed in the ***Federal Register*** (U.S. EPA, 1997d), includes visibility monitoring requirements. The technical connections between visibility and fine aerosols are solid and logically point to a comprehensive monitoring program that services both $PM_{2.5}$ and visibility assessments. The technical connections are given below:

- Fine particles are responsible for nearly all visibility degradation.
- Visibility extinction budgets are calculated through speciated aerosol measurements; the measurement and analysis approaches are virtually the same.
- Spatial scales associated with visibility measurements (regional) are frequently the same as spatial scales associated with background and transport $PM_{2.5}$ measurements (regional, urban). It is important to consider data collected in the regional haze program as part of the $PM_{2.5}$ data analysis activities.
- Sources that affect visibility are the same sources that affect $PM_{2.5}$, and control programs that influence visibility also influence $PM_{2.5}$ levels.

Clearly, the technical justification exists for merging these monitoring efforts. Similarly, there is pragmatic value to combining resource planning and network deployment efforts simultaneously as combined planning is far less burdensome to state and local agencies and the EPA than separate efforts. The IMPROVE chemically speciated data will also be useful in the overall $PM_{2.5}$ program. In fact, the Nation is currently in the unusual position where aerosols are better characterized in rural/remote environments relative to urban and populated areas due to the effectiveness of the IMPROVE.

1.5.2 Quality Assurance for FRM Sampling Sites

The QA program includes three major elements: 1) standard instrumentation and weighing lab quality control checks on flow rates, other miscellaneous parameters (e.g., temperature, pressure), microbalance calibration; 2) collocation of samplers at 25 percent of the $PM_{2.5}$ sites for precision estimates; and 3) independent FRM audits conducted at 25 percent of the sites, four times per year to estimate measurement system bias (sampler through lab). A host of training workshops, videos, satellite broadcasts, and other venues developed jointly by EPA and State and local agencies are underway to explain instrument and lab operations, and monitoring requirements. Every State has (or soon will have) access to prototype instruments to gain operational experience.

1.5.3 Special Chemical Speciation Studies

The EPA anticipates special study activities, beyond the routine program described above, that will enhance the information base for control strategy development (emission inventory and air quality model evaluation) and health related studies. As part of this initiative, EPA anticipates establishment and operation of "Super Sites" that provide resolved characterizations (time, space, composition) of aerosols as well as related precursor, intermediate, and sink species that lead to greater understanding of $PM_{2.5}$ (and ozone) formation and loss processes. These studies are intended to foster collaborative relationships among State/local agencies, academia and industry. The mechanisms for conducting these projects may include any combination of public/private partnerships, State/local partnerships with EPA, or partnerships with universities. Certain projects may consist of a series of special field studies aimed at supporting ongoing epidemiological studies, and others may be specific to a single area. Depending upon the study location, the EPA may be able to expand upon existing contractual and grant agreements as vehicles for this work.

1.6 Related Documents and References

The ***Guideline on Speciated Particulate Monitoring*** is forthcoming and will be included as an addendum to this guidance document. It includes a detailed discussion on the physics and chemistry of atmospheric particles, particulate samplers, laboratory analysis methods, and measurement artifacts and interferences. Other documents related to chemical speciation sampling and analysis are listed in the references given at the end of this document.

Guidance for Network Design and Optimum Site Exposure for $PM_{2.5}$ and PM_{10} (U.S. EPA, 1997c).

Quality Assurance Guidance Document 2.12: Monitoring $PM_{2.5}$ in Ambient Air Using Designated Reference or Class I Equivalent Methods (U.S. EPA, 1998a).

Guidance for Using Continuous Monitors in $PM_{2.5}$ Monitoring Networks (U.S. EPA, 1998b).

EPA Air Monitoring Technical Information Center (AMTIC) $PM_{2.5}$ bulletin board is also accessible via the Internet at: **http://www.epa.gov/ttn/amtic/amticpm.html**

2.0 DATA ANALYSIS

The program goals and objectives addressed in Section 1.2 are supported through various data analysis and interpretation activities. Specific examples of data analysis applications are available in the published literature and will be addressed through a series of forthcoming data analysis workshops and guidance documents. The purpose of this section is to present a framework for data interpretation and use.

Physical and chemical speciation data can be used to support several areas of need which include:

- Source attribution analyses, trends, and providing data to assess the effectiveness of control and attainment strategies.
- Correlating data with mass concentrations at sites where $PM_{2.5}$ mass and speciation monitors are collocated to obtain additional information about species that contribute to total mass measurements.
- Air quality modeling and emissions inventories evaluations.
- Monitoring network design and siting adjustment.
- Understanding the effects of atmospheric constituents on visibility impairment and regional haze.
- Assessing the relative contributions of primary emissions and secondary particle formation to $PM_{2.5}$ mass loadings.
- The interpretation of health studies by evaluating the potential linkage of health effects to $PM_{2.5}$ constituents.

Increasingly greater reliance is placed on observational data for air quality planning needs beyond NAAQS comparisons. Many of the recommendations from the National Academy of Sciences Report on Tropospheric Ozone (NRC, 1991) reflected the need to better integrate observations into air quality planning rather than relying completely on emissions based air quality modeling approaches. That message is being reinforced through the current ozone science assessment conducted through NARSTO and a report is scheduled to be released in 1998. A new approach for integrating observations in air quality planning through continuous iterative assessments which revisit program objectives and adjust, where practical, the implementation

strategies is described (U.S. EPA, 1995a). The important messages in this approach are that observations represent our best attempt at defining truth and must be a critical component of planning; and due to current and even more substantial future system uncertainties, planning must be an iterative process. Although these reflections are based on ozone planning experiences, they are relevant for $PM_{2.5}$ given the newness of this program and underling system uncertainties.

Common data processing steps for speciated aerosol data are depicted in Figure 2-1. Following laboratory analyses of filter samples, the total mass is reconstructed by aggregating individually measured components. Typically, this initial reconstruction for a particular sample reflects sampled atmospheric composition for a single 24-hour period in one location. The result often is simply tabulated or presented graphically to illustrate the fractional contributions of individual components. This step incorporates some internal quality control. First, reasonable comparisons (acknowledging sampling and filter artifacts) to gravimetric mass should be expected, ideally resulting in greater confidence that the laboratory analyses and associated filter handling have acceptable system accuracy. Subsequent steps could include spatial and temporal aggregation presentations to address time and spacial scales of interest and lead to more refined applications for model and emissions evaluation. In parallel, more refined analyses can be conducted on single samples, particularly when diagnosing episodic events.

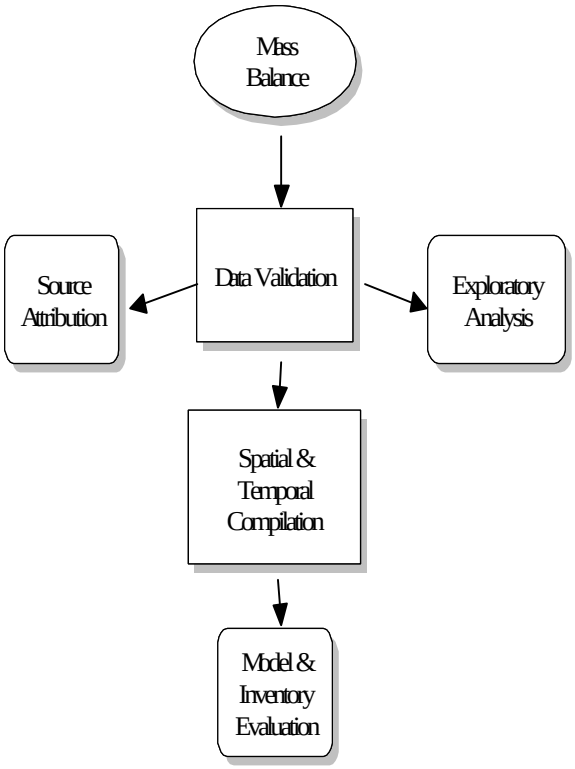

Figure 2-1. Data analysis flow diagram

Secondly, more than one analytical technique often is applied to measure the same chemical component. For example, the use of redundant techniques with resulting agreement leads to further confidence in the analysis methods. Depending on the application of this initial level of processing, the data stands as an end product to answer questions related to data objectives; is expanded over greater spatial and temporal frames for further analysis; or supplies input to more refined emissions testing or source attribution analysis on a single day or point specific basis. The time and spatial scales of interest partially dictate the degree of aggregation.

The annual $PM_{2.5}$ standard suggests that yearly aggregation of data might drive many analyses. Relatedly, the expansive regional domains of air quality models, and the recognition of interacting spatial scales, suggests that many analyses consider multiple monitoring locations. The use of day and location specific data provides value beyond time aggregation and spatial analyses, as diagnostic tests of emission estimates and air quality behavior are conducted on a compartmentalized or bottom-up basis.

A description of the potential uses for speciation data are discussed below.

- **$PM_{2.5}$ Physical Characterization:** Little is known about the physical characterization of the $PM_{2.5}$ mass data. Size distribution data will not be determined routinely, however, this information will enhance our understanding of the particle size and morphology comprising the fine particulate matter. Such understanding might lead to improved source apportionment techniques which might aid in the development of attainment strategies.

- **$PM_{2.5}$ Chemical Characterization:** Little is known about the chemical characterization of the $PM_{2.5}$ mass data. Exploratory data analyses will enhance our understanding of the various chemical components of fine particulate matter. Such understanding might lead to improved source apportionment techniques which might aid in the development of attainment strategies.

- **Trends:** The annual trend in $PM_{2.5}$ constituents will be analyzed to track progress in solving $PM_{2.5}$ air quality problems. Initially, a baseline will be established from which progress can be evaluated. Additionally, it is possible to construct estimates of visibility from the constituents monitored at the $PM_{2.5}$ speciation sites, thus, trends in visibility can be analyzed.

- **Source Apportionment:** The $PM_{2.5}$ mass monitors will identify the regions of the country with high $PM_{2.5}$ concentrations. The speciation network will be used to determine which constituents contribute to the high mass concentrations. Such information might aid in the development of strategies for controlling $PM_{2.5}$.

- **Develop/Verify Attainment Strategies:** Identifying the species that contribute to the high $PM_{2.5}$ mass concentrations will aid in the development of attainment strategies. After implementing the strategies, the speciation network will provide the information necessary for verifying the efficacy of those strategies.

- **Air Quality Model Evaluation:** The speciation network will provide the data necessary to compare the concentrations predicted by the air quality models to the ambient concentrations at a species level. Such comparisons will be useful for identifying ways to

improve the air quality models and will aid in evaluating the emissions inventories that are integral to the modeling process. Speciated data play an especially important role as the deterministic models predict exact chemical components which can be compared to some of the specific measured analytes. The PM mass measurements from FRM/FEM samplers reflect a "health indicator" that is difficult to describe in deterministic physicochemical terms. Of course, all surface point sampling systems, whether measuring exact "gases" or complex aerosols, reflect space and time frames that may not be compatible with averaging schemes used in models. The sampling complexity of aerosols adds greater complexity to model-observation comparisons.

- **Correlation with FRM Mass Concentrations:** Where $PM_{2.5}$ mass and speciation monitors are collocated, it will be useful to develop an empirical relationship between the $PM_{2.5}$ mass observations and the mass concentration obtained from the speciation monitors. Such an analysis will provide information about the comparability of the measurements from the FRM's and from the speciation monitors.

- **Health Studies:** Speciated $PM_{2.5}$ data will be important to continued epidemiological studies into the health effects of $PM_{2.5}$ and its constituents.

- **Synthesis with Oxidant Data:** At the sites with both $PM_{2.5}$ speciation monitoring and monitoring for oxidant precursors and sinks, it will be possible to perform analyses to investigate the relationships between $PM_{2.5}$ constituents and other important atmospheric constituents to gain better process understanding of both $PM_{2.5}$ and ozone formation, maintenance, and removal.

- **Integration with Other Databases:** There are several other databases containing speciated $PM_{2.5}$ data, for example, the data collected through the IMPROVE network, Clean Air Status and Trends Network (CASTNET) and the data used in the numerous health effects studies. It will be important to integrate the data from these various databases to increase the amount of information in one of the networks using the information in these other networks.

3.0 PARTICLE CHARACTERISTICS AND TARGET SPECIES

The following section discusses particle size distribution, the major constituents of $PM_{2.5}$, potential source contributions relative to the chemical speciation program, and the target species and their characteristics. For clarification, a table is included in Section 3.3 that provides a matrix of filter type, the target chemical species measured on that filter type, and the analytical technique used to determine the species concentration.

3.1 Particle Size Distributions

The $PM_{2.5}$, PM_{10}, and total suspended particulate (TSP) size fractions ideally measured by air quality monitoring devices are identified in Figure 3-1 by range of size distribution. The mass collected is proportional to the area under the distribution curve within each range. The TSP fraction ranges from 0 to about 40 μm in aerodynamic diameter, the PM_{10} fraction ranges from 0 to 10 μm, and the $PM_{2.5}$ fraction ranges from 0 to 2.5μm. No monitoring device operates as a discrete step function passing 100 percent of the particles below a certain size and excluding 100 percent of the particles above that size. When particulate sampling occurs, each of these size ranges contains a certain abundance of particles above the upper size designation of each range.

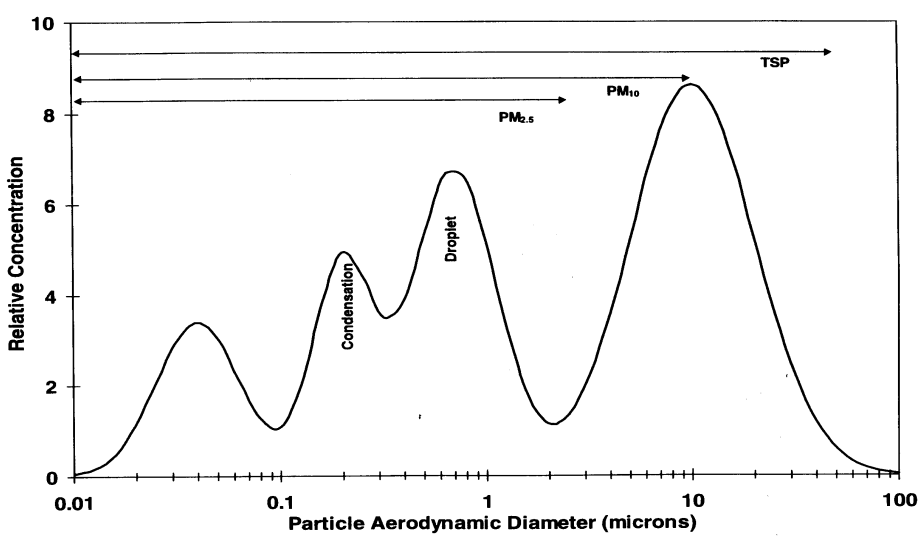

Figure 3-1. Idealized sized distribution of particles in ambient air

The "nucleation" range, also termed "ultra fine particles," consists of particles with diameters less than ~ 0.08 μm that are emitted directly from combustion sources or that condense from cooled gases soon after emission. Nucleation particle lifetimes are usually less than one hour because they rapidly coagulate with larger particles or serve as nuclei for cloud or fog droplets. The nucleation range is detected only when fresh emissions are closest to a measurement site or when new particles have been recently formed in the atmosphere (Lundgren and Burton, 1995). However, ultra-fine particles can persist in the atmosphere if removal mechanisms are weak.

The "accumulation" range consists of particles with diameters between ~ 0.08 and 2μm. These particles result from the coagulation of smaller particles emitted from combustion sources, gas-to-particle conversion, condensation of volatile species, and finely ground dust. Nucleation and accumulation ranges primarily constitute the $PM_{2.5}$ particle size fraction, and the majority of sulfuric acid, ammonium bisulfate, ammonium sulfate, ammonium nitrate, and organic and elemental carbon is found in this size range. The $PM_{2.5}$ accumulation range shows two sub-modes, the condensation mode (containing gas phase reaction products), and the droplet mode (resulting from growth by nucleation and reactions that take place in water droplets). When these modes contain water soluble particles, their peak will shift toward larger aerodynamic diameters as the humidity increases. Particles larger than ~2 or 3 μm are called "coarse particles" that result from grinding activities and are dominated by material of selective biological, geological, and man-made origins (pollen and spores, ground up trash, leaves, and tire abrasion). There are certain conditions under which coarse particles are created from secondary reactions in the atmosphere. For example, the coarse nitrate particle fraction in Los Angeles, California, is believed to occur from a reaction of NO_x with sea salt.

Figure 3-2 shows the size distribution of suspended particles measured from common emissions sources (Ahuja et al. 1989; Houck et al. 1989). The data present here are meant to illustrate "rough" average concentrations of individual components. Windblown dust from soil, unpaved roads, construction, evaporation of sea spray, pollen, mold spores, and dusts formed from the grinding of larger particles are predominantly in the coarse particle size range, with minor or moderate quantities in the $PM_{2.5}$ fraction. Fine particulate can be secondarily formed from gases or by chemical reaction or vaporization. Sources of fine particulate include the combustion of coal, oil, gasoline, diesel fuel, and wood, and high temperature processes such as steel mills, etc. It is important for network operators and data analysts to understand that at various places and times, any one of the three or four major components can dominate the mass in a 24-hour sample.

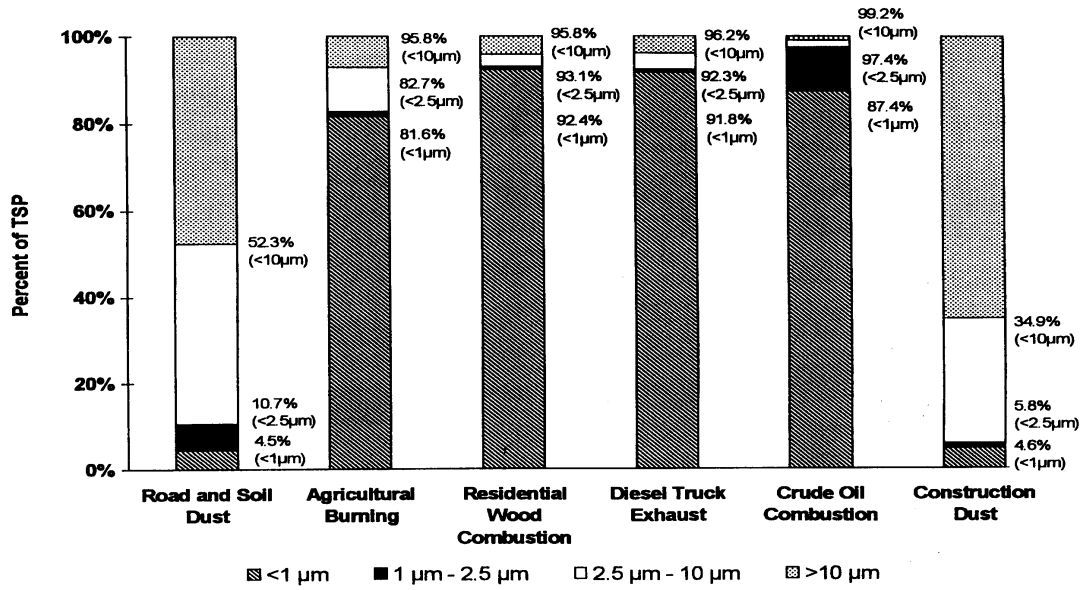

Figure 3-2. Size distributions of several particulate source emissions

3.2 Major Chemical Components and Potential Source Contributions

A variety of suspended particles can be found in the atmosphere; however, there is surprising consistency regarding the major components of suspended particles. $PM_{2.5}$ is composed of a mixture of particles emitted directly into the air (primary aerosols) and particles formed by chemical transformation of gaseous pollutants (secondary aerosols). The primary types of particles emitted directly include soil-related and organic carbon particles from the combustion of fossil fuels and biomass materials. The main sources of soil-related particles are road dusts, construction, and agriculture. The main sources of combustion-related particles are diesel and gasoline motor vehicles, managed and open burning, residential wood combustion, and utility and commercial boilers. Combustion processes also emit primary fine particles consisting of mixtures of many trace metal compounds and sulfuric acid mists. The principal types of secondary aerosols are organics and ammonium sulfate and nitrate formed from gaseous emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) which react with ammonia. Gaseous organics from internal combustion engines as well as other combustion sources such as cooking are precursors to secondary organics. The main sources of SO_2 are combustion of fossil fuels in boilers and the main sources of NO_x are mobile sources and combustion of fossil fuels in boilers. Sulfur dioxide, nitrogen oxides, and ammonia (NH_3) are important precursors to secondary aerosols (ammonium sulfate, ammonium bisulfate, ammonium nitrate) and their chemical abundances are useful at

source and receptor locations to determine causes of high $PM_{2.5}$ levels.

Sulfate, nitrate, particulate organic carbon, and ammonium are quite often the major constituents of $PM_{2.5}$. Most of the $PM_{2.5}$ and PM_{10} mass in urban and nonurban areas can be defined by a combination of the following components that are both primary and secondary aerosols:

- **Geological Material:** Suspended dusts consisting mainly of oxides of aluminum, silicon, calcium, titanium, iron, and other metal oxides. The precise combination of these components depends on the geology and industrial processes of the area. Geological material typically consists of 5 to 15 percent $PM_{2.5}$ particles and could be as high as 30 to 40 percent in central California during summer months.

- **Sulfate:** Ammonium sulfate, ammonium bisulfate, and sulfuric acid are the most common forms of sulfate in atmospheric particles. These compounds are water soluble and reside almost exclusively in the $PM_{2.5}$ fraction. Most fine sulfates are produced by oxidation of SO_2 gas to sulfate particles. Sources of SO_2 emissions include coal-burning power plants and copper smelters. The eastern United States has a concentration of coal-burning power plants that emit significant amounts of SO_2, while the western U.S. has relatively low SO_2 emission densities (Malm, 1994).

- **Nitrate:** Ammonium nitrate is the most abundant nitrate compound resulting from a reversible gas-to-particle equilibrium between ammonia gas and nitric acid gas, and particulate ammonium nitrate. Sampling for particulate nitrate is subject to both positive and negative artifacts due to the reversible gas-to-particle equilibrium. Because the equilibrium is reversible, ammonium nitrate particles can evaporate into the atmosphere or after collection on a filter, due to changes in temperature and relative humidity. Sodium nitrate is found in the $PM_{2.5}$ and coarse fractions near sea coasts and salt playas where nitric acid vapor irreversibly reacts with sea salt (NaCl). The main source of NO_x emissions are from the combustion of various fuels. Nationwide, about one-half of the NO_x is from stationary sources, while the remainder is from mobile sources such as spark-ignition and compression-ignition engines in automobiles and trucks.

- **Ammonium:** Ammonium sulfate, ammonium bisulfate, and ammonium nitrate are the most common compounds containing ammonium. Ammonium sulfate and ammonium bisulfate result from the irreversible reaction between sulfuric acid and ammonia gas. Ammonium sulfate is primarily present as neutralized ammonium sulfate while ammonium bisulfate and sulfuric acid are not present in great abundance. Atmospheric ammonia (NH_3) results from biological decay at the earth's surface and can absorb on wet surfaces or react with nitric acid to form ammonium nitrate.

- **Organic Carbon:** Particulate organic matter is an aggregate of hundreds, possibly thousands of separate compounds that usually contain more than 20 carbon atoms. No single analytical technique can characterize the organic compounds present. Particulate organic carbon originates from combustion, geological processes, road dusts, and photochemistry as well. The chemical composition of particulate organic carbon depends on the strength of the sources. Identification of "organic carbon" is operationally defined by the sampling and analysis methods chosen. Quantification of semi-volatile components of organic carbon depends on the sampling method because the partitioning of semi-volatile compounds can change between the gas and particulate phases during sampling. In addition, accurate differentiation of high molecular weight organic compounds from the elemental carbon depends on the analysis method as described below.

- **Elemental Carbon:** Particles emitted from combustion sources contain light absorbing elemental carbon, often called "soot" or "black carbon". Particulate elemental carbon is a tracer for combustion-derived particles, whereas soil- and marine-derived aerosols contains negligible amounts of elemental carbon. Geological material contains variable abundances. Elemental carbon occurs with organic carbon, and discrimination of particulate elemental from organic carbon depends on the analytical method used. For example, the thermal optical analysis method can incorrectly estimate some of the high molecular weight organic compounds as elemental carbon, because the high molecular weight compounds require a high temperature for volatilization of combustion, and they are sometimes converted to soot before they are quantitated.

- **Sodium Chloride:** Salt is found in suspended particles near sea coasts, open playas, and after de-icing materials are applied. In its raw form, salt is usually in the coarse particle fraction and is classified as a geological material. When sodium chloride-containing water of fog droplets evaporate, many of the "dry" core particles are below 2.5 μm in diameter. Particles that originally contain sodium chloride may be neutralized by nitric or sulfuric acid; the chloride is driven off and replaced by equivalent amounts of nitrate or sulfate. Such particles will be classified as nitrate or sulfate and will be deficient in chloride. Sodium chloride can constitute over 50 percent of the PM_{10} and 30 percent of the $PM_{2.5}$ at the California coast, which is 5 to 10 times higher than is usually found inland.

- **Liquid Water:** Soluble nitrates, sulfates, ammonium, sodium, other inorganic ions, and some organic material absorb water vapor from the atmosphere, especially when the humidity exceeds 70 percent. Sulfuric acid absorbs some water at all humidity levels. Particles containing these compounds grow into the droplet mode as they take on water. Some of this water is retained as the particles are sampled and weighed. The precise amount of water quantified in the $PM_{2.5}$ mass will depend on the ionic composition and the equilibration relative humidity applied prior to laboratory weighing. Highly acidic aerosols containing sulfuric acid would not give up water, even when the particles are equilibrated

at lower relative humidity.

The value of many of the chemical species is, in part, in their use to identify the origins of different air masses. The relative abundance of chemical components in an ambient $PM_{2.5}$ can indicate the chemical composition of the source emissions in the monitored environment. Chemical source profiles are fractional mass abundances of the measured chemical species relative to the primary $PM_{2.5}$ mass from source emissions.

Previous chemical profile compilations include chemical abundances of elements, ions, and carbon for geological material (e.g., paved and unpaved road dust, soil dust, storage pile); motor vehicle exhaust (e.g., diesel-, leaded-gasoline-, and unleaded-gasoline-fueled vehicles); vegetative burning (e.g., wood stoves, fireplaces, forest fires, and prescribed burning); industrial boiler emissions; and other aerosol sources. More modern, research-oriented profiles include specific organic compounds or functional groups, elemental isotopes, and microscopic characteristics of single particles.

As fuels, technologies, and use patterns have changed from 1970 to the present, so have the chemical profiles for many emissions sources. Lead has been phased out of U.S. and Canadian fuels, but it is still used in some Mexican gasolines that might affect $PM_{2.5}$ at border areas. Catalytic converters on spark-ignition vehicles, improved compression-ignition engines, and newly-designed wood combustion appliances have substantially reduced carbon abundances in emissions from these small but numerous sources. Similarly, process improvements and new source performance standards have resulted in changes in chemical component emissions from large industrial emitters. Source profiles must be paired in time with ambient $PM_{2.5}$ chemical species measurements to establish a reasonable estimate of what is expected in ambient air.

The spatial and temporal variability of $PM_{2.5}$ profiles are influenced by many factors, including:

- Source emissions of precursor gaseous and primary particles that are highly variable due to differences in fuel use and process operating conditions.

- Measurements of the major components discussed above for the $PM_{2.5}$ speciated monitoring network can only provide a first-order source attribution of ambient $PM_{2.5}$ concentrations to major source types. Additional measurements of precursor gases, isotopes, particle morphology, and organics need to be acquired to quantitatively assess the associated source sub-types.

- Trace metals acquired from elemental analysis of Teflon®-membrane filters may be found to be abundant in both anthropogenic and geological source signature profiles. Identifying

and quantifying major source contributions are not solely sufficient for source characterization; chemical speciation of ammonium, sulfate, nitrate, organic carbon, and elemental carbon are also essential.

3.3 Targeted Chemical Species

Most of the $PM_{2.5}$ mass in urban and nonurban areas can be attributed to a combination of materials as discussed above. The target species of interest for the $PM_{2.5}$ chemical speciation program are similar to those currently measured within the IMPROVE program. Their selection is based on the chemical speciation program data use objectives, known primary constituents of $PM_{2.5}$, capability of current analytical methods, availability of filter types, and known method performance characteristics.

The target species for this program consist of:

- anions (particulate sulfate, nitrate) and cations (particulate ammonium, ionic sodium, and potassium);
- trace elements (about 20 elements from aluminum through lead);
- particulate organic carbon which includes total carbon (for the purposes of this document is defined as the sum of organic, elemental, and carbonate carbon) and semi-volatile organic aerosol constituents; and
- chemical mass.

Although the target list contains chemical species that have been measured in previous studies, particulate carbon and semi-volatile organic species are considered to be research-oriented or nonroutine in nature. Aerosols include many carbon-containing species with a wide variety of properties; however, most measurement methods identify these as either organic or elemental carbon. The measurement of organic and elemental carbon is an operational one based on the specific analytical technique used. There are currently no reference standards or standardized method for distinguishing between organic and elemental carbon; therefore, differing results can be obtained for the same sample depending on the sampling and analytical method used. Due to this issue, it is extremely important that the same method be used to determine carbon at the NAMS trends sites to maintain consistency. Although no standards are currently available for the organic and elemental carbon content of a filter sample of particulate carbon, good interlaboratory agreement (Birch, 1998) was obtained between six laboratories using the thermal-optical instrumentation on which the NIOSH method 5040 is based. In previous studies, laboratories used different analytical methodologies and variable results were indeed obtained, but this can be expected with an operational method. The fact that a method is operational does not mean that it is not well-characterized or reasonably accurate. When one defines an analyte based

solely on optical and thermal properties, the analysis is by definition an operational one. In this case, the carbon in widely different types of carbon-containing materials is collectively measured as either "organic" or "elemental" depending on these properties. A single standard is not appropriate when analytes are defined as such. Instead, the relative accuracy of different thermal methods is better addressed by examining the accuracy of total carbon measurements and ensuring that pyrolyzable organic materials (e.g., sucrose and cigarette smoke) have no or little elemental carbon content.

Semi-volatile organic aerosols are included in the target list; however, their determination is outside the current scope of the speciation program and should not be considered on a routine basis due to the research-oriented nature of measuring these species. Promising novel approaches for reduction of artifacts due to sampling of semi-volatile compounds are not yet ready for routine deployment; however, research directions suggest that current and future technological developments will permit both extensive quantification of individual compounds and accurate differentiation of semi-volatile gas and particulate phase organic carbon. Therefore, speciation of individual organics and differentiation of the semi-volatile fraction from total carbon is optional. Semi-volatile organic aerosols may be considered for special studies and later added to the routine $PM_{2.5}$ speciation program as the methodology is further developed. Volatilization of semi-volatile compounds is a known source of error for species such as ammonium nitrate and many organics. Evaporative losses of semi-volatile organic compounds can be significant.

Each series of target species requires sample collection on the appropriate filter medium and chemical analysis by methods of adequate selectivity, sensitivity and reliability. For clarity it is beneficial to think in terms of filter type, the chemical species measured on that filter type, and the analytical technique used to quantify the species. Table 3-1 provides a matrix of filter types, target species, and analytical methods.

Table 3-1
$PM_{2.5}$ Chemical Speciation Filter Medium, Target Species and Methods

Filter Medium	Target Species	Analytical Technique
PTFE (Teflon®) filter	Elements: Al through Pb; and mass	EDXRF (IO-3.3) and Gravimetry

Nylon filter with nitric acid denuder	Anions: nitrate and sulfate	IC (IMPROVE Method)
	Cations: ammonium, sodium, and potassium	IC (IMPROVE Method)
Pre-fired quartz fiber filter with gaseous organic denuder	Total carbon (including organic, elemental, carbonate carbon)	TOA (NIOSH 5040)

EDXRF - Energy Dispersive X-ray Fluorescence
IC - Ion Chromatography
TOA - Thermal Optical Analysis

3.3.1 Ions

Ionic species (sulfate, nitrate, ammonium, sodium, and potassium) can represent a large fraction of fine particulate matter, thus their determination is critical in order to meet the data analysis objectives for this program as given in Section 1.2. These ions will be measured at all NAMS speciation sites. The analysis of other important ions such as hydrogen, chloride, potassium, and sodium are optional and may be included at non-NAMS depending upon the specific network and data use objectives and availability of resources.

- **Sulfate:** Sulfate is one of the most robust particulate matter species because it remains stable during and after sampling. Sulfate will be collected on nylon filters and aqueous extracts of these filters analyzed using ion chromatography (IC). This analytical method is both sensitive and accurate. Particulate sulfur is also routinely analyzed using X-Ray fluorescence (XRF). Measurements of collocated samples by ion chromatography and XRF are usually highly correlated. The typical mass ratio of [(sulfate by IC)/(sulfur by XRF)] is about 3, which indicates that almost all of the fine particle sulfur is in the form of sulfate. Therefore, for QC purposes routine comparisons may be made between the sulfate concentrations determined using ion chromatography and sulfur concentrations obtained from XRF if available.

- **Nitrate:** Accurate measurement of particulate nitrate requires the removal of gas phase nitric acid prior to particle collection. It also requires the collection of nitrate on a nylon filter, which binds the nitric acid molecules produced during the volatilization of the collected particulate ammonium nitrate. Nylon filters are slightly alkaline and can collect nitrate quantitatively. Aqueous extracts of the nylon filters will be analyzed using ion

chromatography to determine the nitrate concentration. Removal of the gaseous nitric acid is achieved by using diffusion denuders coated with alkaline substances (e.g., sodium carbonate) or (unanodized) aluminum inlets.

Previous methods which have used Teflon® or glass fiber filters are negatively biased due to the ammonium nitrate loss during and after sampling. Loss of ammonium nitrate can be caused by the presence of ammonium bisulfate and similar incompletely neutralized forms of sulfuric acid collected on the filter media (Koutrakis et al., 1992). The equilibrium between particle ammonium nitrate, gaseous ammonia, and nitric acid can also be perturbed by changes in relative humidity and temperature. In addition, nitrate can be lost after sampling during sample transport and storage. To date, there is no agreement among different studies regarding the extent of nitrate loss. This disagreement stems from the fact that these results correspond to a variety of locations, meteorological conditions, and sampling methods. If the speciation sampler relies upon metallic denuders which may be used for long periods of time (e.g., more than a couple of weeks, as with the IMPROVE network), the capacity of these denuders should be determined through laboratory and field studies.

- **Ammonium:** Aqueous extracts of nylon filters will be analyzed using ion chromatography to determine ammonium concentrations. Ammonium sulfate salts are very stable, so ammonium losses during sampling and storage are negligible. However, ammonium nitrate, which is an important constituent of fine particle mass, is unstable and can volatilize during both sample collection and storage. The extent of dissociation of ammonium nitrate depends on many parameters, including temperature, relative humidity, and face velocity of the collecting filter. It is anticipated that current sampling techniques underestimate ammonium concentrations due to the volatilization of ammonium nitrate, but fine particle mass contains many acidic compounds. Consequently, a fraction of volatilized ammonium (in the form of ammonia) can be retained on a Teflon filter by reacting with the acid compounds. Therefore, it is reasonable to assume that ammonium loss is less than the nitrate loss.

- **Sodium and Potassium:** These two cations can be used to trace wood burning and ocean sources, respectively. Similarly, as for the rest of the ions, aqueous extracts of nylon filters will be analyzed using ion chromatography to determine the concentrations of potassium and sodium. Many precautions must be taken during the filter preparation, sampling, transport, and analysis to minimize sodium contamination of the samples. Otherwise, both laboratory and field blanks will be highly variable, and sampling precision poor.

3.3.2 Elements

Elemental analysis of aerosol samples is very important because it can be very helpful in identifying particle sources, and in determining the contribution of the soil and ocean sources to fine particle mass. The contribution of trace metal salts (oxides, nitrates, and sulfates) may also be determined, but typically they are expected to be negligible. To date, several analytical methods have been used to determine the elemental composition of particulate matter. X-Ray Fluorescence (Dzubay and Stevens, 1975; Jaklevic et al., 1977) and Proton Induced X-Ray Emission (Cahill et al., 1990) have been used extensively in the analysis of ambient aerosols because they are non-destructive, have multi-element capabilities, and are relatively low cost. X-Ray Fluorescence (XRF) is the analytical method of choice. This technique is performed on Teflon® filters to determine the concentration of approximately forty elements (from sodium to uranium); however, for typical atmospheres, the analysis is meaningful only for half of these elements, including aluminum, silicon, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, nickel, copper, zinc, arsenic, selenium, bromine, cadmium, and lead.

3.3.3 Organic Carbon

Accurate mass balance and quality assurance require determination of particulate (total) carbon, C_t, because of its abundance. Differentiation of organic, C_o, elemental, C_e, and carbonate carbon, C_c, provides more useful characterization for trends analysis and source attribution. As mentioned previously, for the purposes of this guidance document, we define total carbon as $C_t = C_o + C_e + C_c$. Semi-volatile species (C_{sv}) compose a fraction of the organic carbon which exists in the atmosphere in an equilibrium between particle and gas phases. This equilibrium depends on temperature, vapor pressures of individual species, and the amounts and types of adsorbing particle surfaces. The amount of the these species in the particulate phase collected on the filter depends on sampling conditions (e.g., filter face velocity). In this guidance, C_{sv} is defined as the semi-volatile carbon that is collected on sorbent traps placed downstream of the collection filter on conventional samplers. At present the differentiation of C_o, from C_e and C_e from C_c are method dependent. In spite of the limitations, the first and fundamental step of carbon speciation is the semi-quantitative assessment of C_o, C_e and C_c from a quartz filter analyzed by thermal optical analysis (NIOSH 5040).

Organic compounds can represent a large fraction of fine particle mass. Organic compound speciation can provide a great deal of information regarding the sources and formation processes of carbonaceous particles. Identification of individual organic compounds is the subject of many ongoing research efforts, yet this goal is beyond the scope of the speciation program. Similarly, promising novel approaches for reduction of artifacts due to sampling of semi-volatile compounds (C_{sv}) are not yet ready for routine deployment; however, research directions suggest that current and future technological developments will permit both extensive quantification of

individual compounds and accurate differentiation of semi-volatile gas and particulate phase organic carbon. Therefore, speciation of individual organics and accurate differentiation of C_{sv} from C_t is optional and may be done depending upon the sampling objectives, and availability of funding and resources. Although organic speciation is desirable, it is not simple to perform because there is no single analytical method that can be used to analyze all classes of organics. It may be more cost-effective to develop inexpensive methods that allow for the measurement of specific characteristic groups of organic compounds. Similar "lumping" approaches have been used successfully in ozone modeling. Attempting to obtain comprehensive spatial and temporal patterns for hundreds of organic compounds is not a cost-effective strategy. "Lumping" approaches have not yet been fully developed, therefore, their implementation to the speciation network is not yet possible.

Some species can be analyzed from more than one media and using other analytical instrumental methods. For example, Teflon® filters can be extracted and analyzed for many of the same analytes as the quartz media. Also, inductively-coupled argon plasma (ICP) spectroscopy can be used to determine several trace metals, but the method is a destructive method of analysis and requires complete digestion of the filter particle sample. For national consistency, the EPA will prescribe the use of the filter media, target species, and analytical methods identified in Table 3-1 for the 50 NAMS sites. If different target species, filter types and methods are used throughout the other 250 sites, implementation of an augmented quality control program with equivalency determinations is necessary in order to validate and evaluate the data for comparability.

4.0 NETWORK DESIGN

This section provides the recommended sites for the NAMS speciation network in Table 4-1, as well as outlines the general concepts to be applied when planning a $PM_{2.5}$ measurement network outside the scope of the 50 core NAMS speciation sites. It also important to emphasize the integration of field and laboratory operations at the very early stages of program design. For example, the analytical laboratory personnel should be involved in target species selection and sampler procurement or design to ensure compatibility among sampling and analysis methods, filter media, and practical quantifiable limits. A representative flow diagram of the steps involved in network design is shown in Figure 4-1, while Table 4-2 in Section 4.4 contains an example of typical components to incorporate in a program plan. Such a plan is essential for ensuring that all participants understand the roles and responsibilities defined for the program.

The network of stations should be designed to meet the monitoring program objectives. At a minimum, the elements outlined below should be addressed in designing a chemical speciation network and developing a program plan. For additional information on the concepts of network design, methodology for planning areas and selecting and evaluating monitoring sites, and usage of existing resources for network design refer to ***Guidance for Network Design and Optimum Site Exposure for $PM_{2.5}$ and PM_{10}***, (U.S. EPA, 1997). This reference builds upon the guidance specified for PM_{10} monitoring associated with the previous NAAQS.

4.1 Establish Monitoring Objectives

The first step in network design is to determine the specific monitoring program goals and objectives and subsequent data quality objectives. The general characterization of the atmospheric aerosol, air quality trends analysis, source attribution, and control strategy development and evaluation are primary objectives of the $PM_{2.5}$ speciation monitoring program. The $PM_{2.5}$ monitoring networks producing mass concentrations for attainment determinations do not provide samples amenable to chemical analyses for all species due to the limitations of a single-filter media. Source attribution, control strategy development, and aerosol characterization require chemical speciation; therefore, additional measures must be taken to address these objectives. In addition, data from the speciation monitoring networks may be augmented for determination of metals, organics, and particle morphology for non-NAMS sites in order to meet specified data use objectives.

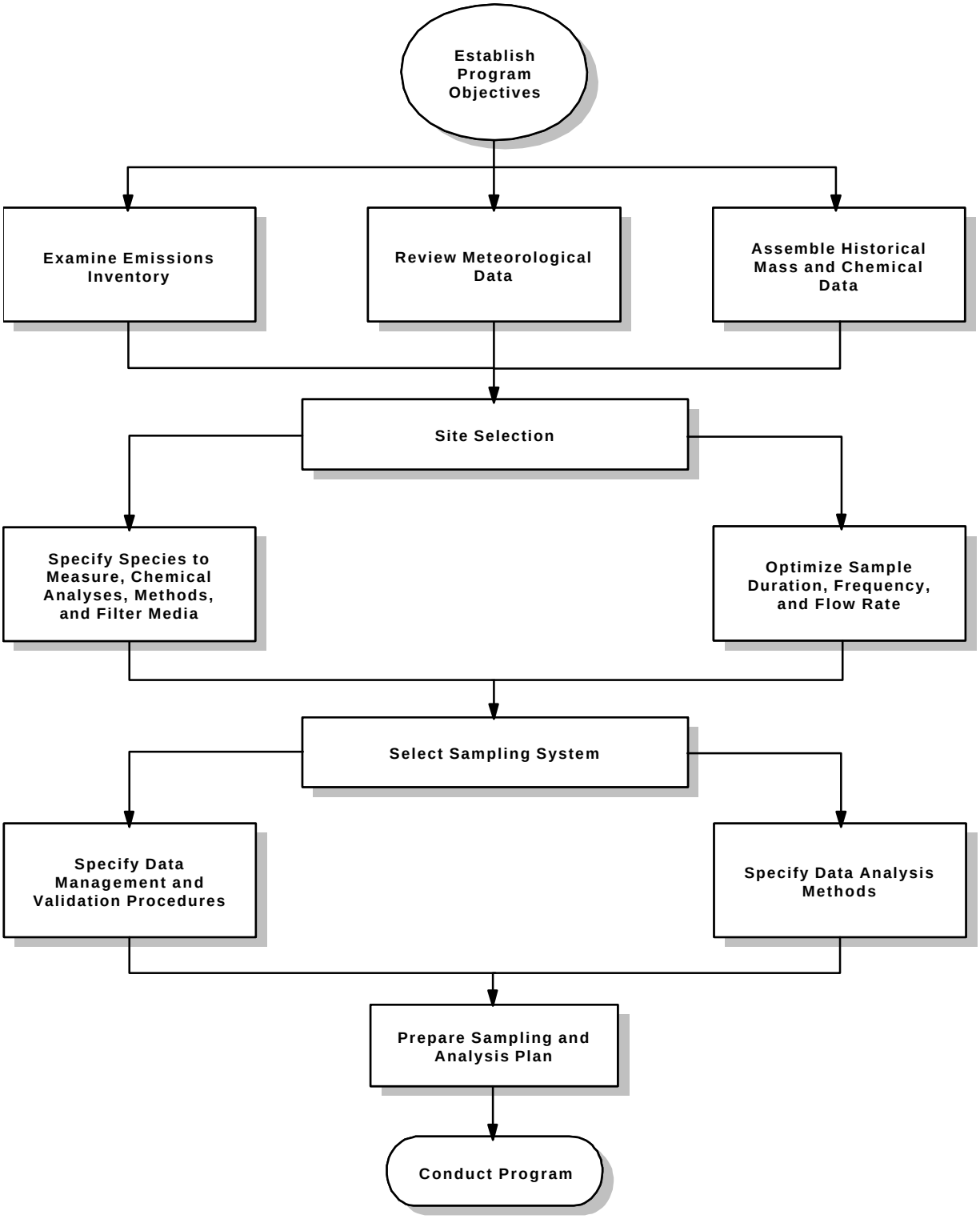

Figure 4-1. Network design flow diagram

4.2 Site Selection

Site selection is an important task in the design of a monitoring network and must result in the most representative sampling locations with characteristics that match the monitoring objectives. Proper siting requires precise specification of the monitoring objectives which usually includes a desired spatial scale of representativeness. Information from emissions inventories, meteorology data, and available historical mass and chemical data are used to determine candidate locations for sampling. This information is used in conjunction with the program objectives to determine the appropriate site selection. Specific criteria to be used in siting the NAMS monitoring stations, including spacing from roadways and vertical and horizontal probe placement can be found in Appendix E of CFR Part 58 (Federal Register, 1997).

Appendix D of the Part 58 $PM_{2.5}$ Regulations (Federal Register, 1997) address the selection of sampling sites for implementing a $PM_{2.5}$ Speciation Trends Network. The general requirements include a national network of approximately 50 sites to include approximately 25 $PM_{2.5}$ core sites collocated at PAMS sites (1 type 2 site per PAMS area). Selection of the remaining sites will be based on recommendations from EPA with review and comment from state and local agencies.

PAMS type 2 sites were established as maximum ozone precursor emission impact sites. These sites were established to monitor the magnitude and type of precursor emissions in the area where maximum precursor emissions representative of a MSA/CMSA are expected to impact and are suited for monitoring urban air toxic pollutants. Generally, the type 2 sites are located immediately downwind of the area of maximum precursor emissions and are typically placed near the downwind boundary of the central business district or primary area of precursor emissions mix to obtain neighborhood scale measurements.

Monitoring and sampling parameters are generally consistent among PAMS type 2 sites. For most sites, an intensive sampling period takes place during the summer (approximately June-August) while a reduced set of measurements are made less-frequently during the remainder of the year. During the intensive summer period, the following sampling and monitoring parameters and minimum monitoring frequencies are measured:

- Volatile organic compounds (VOCs) - Eight 3-hr samples daily, hourly automated measurements are typically taken at the Type 2 sites;
- Carbonyls - Eight 3-hr samples daily;
- Ozone - Continuous sampling; and
- $NO/NO_2/NOx$ or NO/NO_y - Continuous sampling.

During the remainder of the year, sampling for VOCs and carbonyls occur as one 24-hr sample every sixth day. In addition to pollutant parameters, each type 2 site is equipped with a ten meter meteorological tower to provide surface meteorology for wind speed and direction, temperature and humidity. Each site also has access to area upper air data and surface measurement of barometric pressure, precipitation, and solar/UV radiation. Therefore collocating selected $PM_{2.5}$ Speciation Trends Sites with PAMS type 2 sites offers some benefits with respect to having the ability to accumulate long-term data on organic compounds, particulate nitrate precursors, and local meteorology in conjunction with $PM_{2.5}$ mass and composition data. In most cases, the existing site platforms are rugged and are capable of incorporating a modest amount of additional sampling equipment. It is desirable to locate a $PM_{2.5}$ Federal Reference Method sampler at the PAMS site in addition to the speciation sampler to provide a basis for long-term comparison of particulate mass and chemical constituents.

Table 4-1 lists recommended locations for 53 sites used to implement the speciation trends network. With one exception, each of the 24 PAMS city sites is an existing type 2 site. The PAMS New Jersey site recommended is a type 1 site which is heavily-instrumented as a research platform and is approximately half-way between Trenton and Newark, New Jersey. The remaining 29 sites are identified as MSAs. The selection of MSAs, as well as PAMS cities, was based on a balance of several factors, including:

- Location of existing PAMS and IMPROVE sites;
- Geographic location of MSAs using 1996 population statistics;
- Ozone non-attainment areas; and
- PM_{10} non-attainment areas.

The locations of existing PAMS and IMPROVE sites generally leave a large portion of the Central, Midwestern, and Southeastern US void of monitoring data that could be used for trends purposes. Therefore, we have balanced our recommendations for trends sites to specifically include major population areas in these regions which, in many cases, also include areas of higher $PM_{2.5}$ primary and precursor emissions within the region. The map given in Figure 4-2 illustrates the overall geographical coverage of the recommended speciation trends network (24 PAMS cities sites + 29 MSA sites). The IMPROVE program will also expand its total number of sites and preliminary information indicates that additional sites will be located in the Great Plains area and in New Mexico. This will further complement the integration of the IMPROVE and $PM_{2.5}$ chemical speciation network. In locating the speciation site within each of the suggested MSAs, it is suggested that a community-oriented $PM_{2.5}$ core site expecting the maximum concentrations be selected as the speciation trends site. Also, it is desirable to outfit each of the 29 MSA sites

selected with a ten meter meteorological tower for collecting data on wind direction and speed, temperature, and humidity. Local siting limitations and/or unique spatial and temporal variabilities of $PM_{2.5}$ may require some balance and adjustment of the criteria outlined above to determine final site selection.

Table 4-1
Recommended Sites for the $PM_{2.5}$ NAMS Trends Network

Region	State / Common.	MSA	PAMS City Site	AIRS #
1	Connecticut		East Hartford	09-003-1003
	Maine		Kittery	23-031-3002
	Massachusetts		Lynn	25-009-2006
	Massachusetts		Chicopee	25-013-0008
	Rhode Island		East Providence	44-007-1010
	Vermont	Burlington		
2	New York		Bronx Gardens	36-005-0083
		Rochester		
	New Jersey		New Brunswick	34-023-0011
	Puerto Rico	San Juan		
3	Washington DC		McMillan Reservoir	11-001-0043
	Maryland		Essex	24-005-3001
	Pennsylvania		E. Lycoming	42-101-0004
		Pittsburgh		
	Virginia	Norfolk		
4	Alabama	Birmingham		
	Florida	Miami		
		Tampa		
	Georgia		S. Dekalb	13-089-0002
	Mississippi	Biloxi		
	North Carolina	Charlotte		
	South Carolina	Charleston		
	Tennessee	Memphis		
5	Illinois		Chicago-Jardine	17-031-0072
	Indiana	Indianapolis		
	Michigan	Detroit		
	Minnesota	Minneapolis		
	Ohio	Cleveland		
	Wisconsin		Milwaukee	55-079-0041

Region	State / Common.	MSA	PAMS City Site	AIRS #
6	Louisiana		Capitol	22-033-0009
	Oklahoma	Tulsa		
	Texas		Clinton Dr.	48-201-1035
			Hinton	48-113-0069
			Chamizal	48-141-0044
7	Kansas	Kansas City		
	Missouri	St. Louis		
	Nebraska	Omaha		
8	Colorado	Denver		
	Montana	Great Falls		
	North Dakota	Grand Forks		
	Utah	Salt Lake City		
9	Arizona	Phoenix		
	California		Pico Rivera	06-037-1601
			Banning	06-037-0002
			El Cajon	06-073-0003
			El Rio	06-111-3001
			Natomas Airport	Not Available
			Golden St. Ave.	06-029-0010
			Clovis-Villa	06-019-5001
	Nevada	Reno		
10	Idaho	Boise		
	Oregon	Portland		
	Washington	Seattle		
Network Totals	**39 States**	**29 MSAs**	**24 PAMS Sites**	**53 Trends Sites**

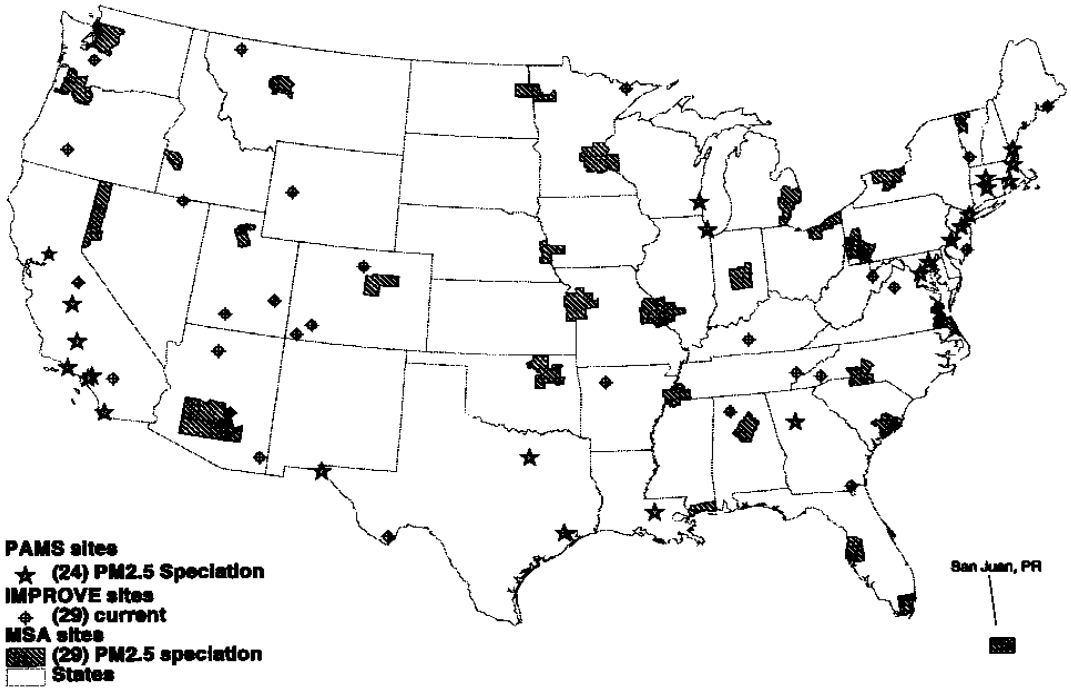

Figure 4-1. 53 Proposed $PM_{2.5}$ Speciation National Trends and Current IMPROVE Sites

locations of vacant lots, storage piles, major highways, construction sites, and industrial operations. These are plotted on a map with notes regarding the visual appearance of each potential emitter. For example, if chimneys are present in a residential neighborhood, this observation is recorded and photographs are taken. Roads in the vicinity of sampling sites are classified with respect to the type of traffic on them and whether or not they have sidewalks and paved shoulders.

Expected emissions cycles should be examined to determine sampling periods and durations. For example, residential wood burning will usually show up on samples taken during the night, whereas agricultural burning will usually show up during the daytime. While these two source types may be indistinguishable based on their chemical profiles, their diurnal cycles will provide convincing evidence that one or the other is a major contributor when both activities occur simultaneously. If local, cyclical emissions are occurring, variable sampling times (e.g., 24-hr vs. day/night 12-hr cycles) may be important in understanding the contribution of local emissions to measured $PM_{2.5}$ concentrations. The timing of other events, such as major prescribed burning or accidental wildfires, may be more difficult to predict.

Particle size is of value in separating one source from another. Particle size fractions, chemical analyses, sampling frequencies, and sample durations need to be considered because more frequent samples, or samples taken at remote locations, may require a sequential sampling feature to minimize operator costs. Shorter sample durations may require a larger flow rate to obtain an adequate sample deposit for analysis. The types of analyses and size fractions desired affect the number of sampling ports and different types of filter media needed.

Calculate the expected amount of deposit on each filter for each chemical species and compare it to typical detection limits for the analyses being considered. Urban samples acquire adequate deposits for analysis with flow rates as low as ~20 L/min for as short as 4-hour sample durations. Samples at nonurban sites may require >100 L/min flow rates for 24-hour durations to obtain an adequate deposit for chemical speciation. However, sampler flow rates as well as filter surface areas also have effects on the collection efficiency of certain target analytes.

4.3 Sampling System Selection

Apply, create, adapt, or purchase a sampling system which provides the most cost-effective and reliable means of meeting the monitoring needs. In complicated situations, especially those with many contributing sources, unknown sources, or secondary contributions, more complex sampling systems are needed which do not have reference status. Both reference and research sampling systems have been operated side-by-side in many PM_{10} studies when this is the case, and the same practice can be applied to $PM_{2.5}$ monitoring. Refer to Section 5.0 for a discussion of the sampling methodology and candidate speciation sampler approaches for the NAMS.

4.4 Speciation Sampling and Analysis Plan Preparation

The final step is to create a written sampling and analysis plan. The plan specifies the study objectives, sampling locations, analysis methods, filter media, sampling systems, sampling frequencies and durations. Details should be included which prescribe nominal flow rates, methods and schedules for inlet cleaning, calibration and performance tests, filter transport and handling procedures, database management system, data analysis methods, and record keeping protocols. An example of an outline of the contents for a program plan is given in Table 4-2.

Table 4-2
Example of Program Plan Outline for $PM_{2.5}$ Measurements

1.0	**INTRODUCTION**		**6.0**	**LABORATORY OPERATIONS**	
	1.1	Background		6.1	Substrate Preparation
	1.2	Objectives		6.2	Gravimetric Analysis
	1.3	Overview		6.3	Light Absorption
2.0	**AIR QUALITY IN THE STUDY AREA**			6.4	Elemental Analysis
	2.1	Emissions		6.5	Filter Extraction
	2.2	Meteorology		6.6	Ion Analysis
	2.3	Atmospheric Transformations		6.7	Carbon Analysis
	2.4	Historical Air Quality Data		6.8	Specialized Analysis
	2.5	Implications for $PM_{2.5}$ Study Design	**7.0**	**QUALITY ASSURANCE**	
3.0	**DATA ANALYSIS AND MODELING**			7.1	Standard Operating Procedures
	3.1	Data Evaluation		7.2	Quality Audits
	3.2	Descriptive Air Quality Analysis		7.3	Standard Traceability
	3.3	Descriptive Meteorological Analysis		7.4	Performance Tests
	3.4	Source Profile Compilation	**8.0**	**DATA PROCESSING, DATA BASE MANAGEMENT, AND CHAIN-OF-CUSTODY**	
	3.5	Emissions Inventory		8.1	Data Base Requirements
	3.6	Receptor Model Source Apportionments		8.2	Levels of Data Validation
	3.7	Trajectory Modeling		8.3	Continuous Data Processing
	3.8	Secondary Aerosol Modeling		8.4	Substrate Data Processing
	3.9	Case Study Descriptions	**9.0**	**MANAGEMENT, REPORTING, AND SCHEDULE**	
4.0	**PROPOSED AMBIENT MONITORING NETWORK**			9.1	Tasks and Responsibilities
	4.1	Sampling Sites		9.2	Resource Requirements
	4.2	Sampling Frequency and Duration		9.3	Reports
	4.3	Sampling Methods		9.4	Schedule and Milestones
5.0	**EMISSIONS CHARACTERIZATION**		**10.0**	**REFERENCES**	
	5.1	Emissions Activities and Micro inventories			
	5.2	Geological Source Profiles			
	5.3	Motor Vehicle Exhaust Characterization			
	5.4	Residential Wood Combustion Characterization			
	5.5	Industrial Source Emission Characterization			
	5.6	Other Source Characterization			

5.0 SAMPLING ARTIFACTS, INTERFERENCES, AND LIMITATIONS

This section discusses some of the general difficulties in making aerosol measurements with respect to particle and gas removal by inlets, nitrate particle volatilization, adsorption of sulfur dioxide and oxides of nitrogen, organic carbon adsorption and volatilization, liquid water content, electrostatic charge, and passive deposition and recirculation. Some of these biases can be avoided or counteracted with alternative sampling and filter handling techniques.

5.1 Inlet Surface Deposition

The materials from which inlets are manufactured can affect the collected aerosol, especially when gas and particle phases are being quantified for volatile species such as ammonium nitrate. Most samplers are manufactured from aluminum, plastic, or galvanized steel, due to availability and economy. These materials can absorb some gases, especially nitric acid, and can change the equilibrium between volatile particles on a filter and the surrounding air.

Nitric acid has a tendency to adhere to surfaces. Surfaces coated with perfluoroalkoxy (PFA) Teflon® can pass nitric acid with 80 percent to 100 percent efficiency. Aluminum surfaces common to many samplers and inlets have a large capacity (60-70 percent) for absorbing nitric acid vapor while transmitting particles with high efficiency. If measurements of nitric acid are important to the non-NAMS component of the speciation program, then coating of the inlet is necessary.

Denuders are often used as part of, or located immediately behind, size-selective inlets to remove gases that might interfere with the aerosol measurement. See Section 5.2.2 for a more detailed discussion of denuders.

Plastic surfaces can acquire an electrical charge which might attract suspended particles, though the dimensions of most ambient sampling systems are sufficiently large that the attraction is negligible.

5.2 Nitrate Particle Volatilization

Nitrate losses during and after sampling have been reported in numerous measurement programs. At temperatures greater than 30 C, most nitrate will be in the gas phase as nitric acid (HNO_3), while at temperatures lower than 15 C, most nitrate will be in the particle phase as ammonium nitrate (NH_4NO_3). There will be varying amounts of nitric acid and ammonium nitrate at the intermediate temperatures. Relative humidity and concentrations of ammonia and nitric acid gases also affect this equilibrium, but temperature is by far the most important variable. When air temperature changes during sampling, some of the ammonium nitrate already collected

on the filter can volatilize. Nitrate volatilization is minimized when ambient temperatures are low and with proper ventilation of the sampler housing.

Volatile compounds can also leave the filter after sampling and prior to filter weighing or chemical analysis. Greater than 50 percent losses of nitrate, ammonium, and chloride from glass and quartz-fiber filters that were stored in unsealed containers occurred at ambient air temperatures for 2 to 4 weeks prior to analysis. Storing filters in sealed containers and under refrigeration will minimize these losses.

5.3 Organic Carbon Volatilization

The collection and determination of particulate organic material is complicated by changes in equilibrium between organic material in the gas and particulate phases during sample collection. Volatilization of individual semi-volatile organic species depends on both temperature and filter face velocity due to flow rate. Gas phase organic molecules in the sample stream or on the particulate matter may either be adsorbed by the quartz filter or pass through the filter during sampling. If corrections are not made for collection of gas phase components by the quartz filter, the amount of carbonaceous material determined from the analysis of the filter for carbon may result in a positive bias (positive artifact) in the determination (Cui et al., 1997). Also, a larger negative error results from the loss of 20-80 percent of the particulate phase organic material during sampling (Eatough et al., 1993).

This sampling artifact is typically addressed by sampling with two quartz filters and correcting the data found on the first filter with the amount of carbonaceous material found on the second filter (Eatough et al., 1995, Appel et al., 1989, McDow et al., 1990). It is difficult to distinguish between the collection of gas phase organic compounds on the particulate quartz filter and the backup quartz filter. If a fraction of the SVOCs which can be adsorbed by a quartz filter is adsorbed by the first quartz filter, then the second quartz filter may contain either gas phase organic compounds adsorbed by the quartz, SVOC lost from particles and subsequently adsorbed by quartz, or both (Eatough et al., 1995).

The approach used for the NAMS component of the speciation program to correction for these artifacts during the collection of particulate organic carbon is to incorporate the use of a diffusion denuder to remove the gas phase organic compounds (including volatile organic and semi-volatile organic compounds) prior to the collection of particles on a single quartz filter. A post-filter sorbent material like XAD-4 is also necessary to collect the gas phase semi-volatile organic compounds volatilized from the particulate and the filter medium. The capability for determination of semi-volatile organic aerosols will be added in as the technology further develops

and is validated for routine use. The candidate speciation samplers have been designed to accommodate the necessary components.

If the determination of semi-volatile organics is required, the analysis of the gas-phase semi-volatile organics collected by the denuder, in addition to the quartz filter and post-filter sorbent will be necessary. However, determination of semi-volatile organic aerosols is considered nonroutine and research oriented in nature as discussed in Section 2.1.

5.4 Sample Moisture

The importance of liquid water content in ambient aerosol is recognized. As ambient relative humidity exceeds 70 percent, particle growth due to accumulation of moisture becomes significant. Theoretical calculation or experimental measurement of aerosol liquid content is complicated because growth rates vary with aerosol composition, ambient relative humidity and surface tension.

The current $PM_{2.5}$ NAAQS requires filter equilibrium for relative humidity between 30 percent and 40 percent. If samples are acquired in a very humid environment where soluble particles tend to aggregate in liquid water molecules, and then equilibrated in a laboratory environment where relative humidity is controlled at 35 percent, a difference in mass concentrations may occur depending on particle and filter composition. When samples are acquired in an environment rich in sulfuric acid or ammonium sulfate, this bias could be as high as 15 percent to 20 percent. Therefore, to minimize the effect of liquid water on measured particles, it is recommended that relative humidity equilibration ranges be kept at the low end of the 30 to 40 percent range for filter weighing.

5.5 Electrostatic Charge

One problem that occurs when using a microbalance for filter weighing is electrostatic charge. Electrostatic charge is also referred to as static, static electricity, electrostatic, static charge, and triboelectric charge. Electrostatic charge is the accumulation of electrical charges on a nonconductive, dielectric surface such as the surface of a Teflon®-membrane or polycarbonate-membrane filter. Residual charge on a filter can produce an electrostatic interaction that induces non-gravimetric forces between the filter on the microbalance weighing pan, and the metal casing of the electrobalance, thereby, biasing mass measurements. As electrostatic charges build up during the weighing session, the readout of the microbalance becomes increasingly unstable (e.g., noisy, sudden drifts or shifts).

To minimize the static charge during gravimetric analysis, it is necessary to place a radioactive antistatic strip inside the microbalance chamber prior to weighing. Filters also need to be placed on an antistatic strip for at least 60 seconds to remove electrostatic charges. The most commonly used low-level radioactive antistatic strips contain 500 picocuries of polonium-210 (Po^{210}). Polonium strips are commercially available and have a half-life of 138 days. Polonium strips neutralize electrostatic charges on items within an inch of the strip surface. Antistatic solutions can also be used to coat the interior and exterior nonmetallic surfaces of the weighing chamber. This coating increases surface conductivity and facilitates the draining of electrostatic charges from non-metallic surfaces to metallic surfaces.

Earth-grounded conductive mats should also be placed on the laminar flow hood, where the balance is located or near the weighing table and equilibration chamber, to reduce electrostatic charge buildup.

5.6 Passive Deposition

Passive deposition of windblown dust on the filter prior to and following sampling can positively bias PM measurements. This deposition is minimal and dependent on local conditions during specific collection times. Bias due to deposition can be minimized by more frequent sample filter changing (i.e., reduce the passive deposition period), pre-loading filters in the laboratory, and transporting unexposed and exposed filter cassettes in covered cassette holders.

Recirculation of the sampling pump exhaust does not have a large effect on $PM_{2.5}$. However, it can effect carbon and trace metal measurements when pump and armature wear are entrained in the exhaust. This contamination can be minimized by filtering pump exhausts or ducting them away from nearby sampling inlets. Even though $PM_{2.5}$ pumps may be adequately filtered, nearby high volume samplers for PM_{10} or TSP can still affect the $PM_{2.5}$ measurements and require filtration or ducting.

For $PM_{2.5}$ sampling, static field blanks should be periodically placed in the sampling system, without air being drawn through them, to estimate the magnitude of passive deposition during the period of time that filters are exposed in the sampler (24 hours). A static field blank should be collected for each filter medium used. These blanks may also be used as trip blanks to evaluate the level of contamination during transport. Since static field blanks values are dependent on local conditions during specific collection times, it is not appropriate to perform blank correction. The results are used to demonstrate that the contribution of passive deposition was negligible under the normal conditions of sampling.

5.7 Contamination Due to Handling

In order to avoid measurement errors due to damaged filters or a gain or loss of collected particles on the filters, careful handling of the filter during sampling, transport, equilibration, and weighing is necessary. The filters should be handled carefully using smooth, nonserrated forceps used only for this purpose. It is a good idea to mark the forceps to distinguish them from forceps used for other purposes, such as handling mass reference standards. These precautions reduce the potential effect of body moisture or oils contacting the filters and subsequently affecting the analytical results.

6.0 SAMPLING METHODOLOGY

This section describes the sampling methodology for use in the NAMS chemical speciation $PM_{2.5}$ program. For this component of the program, specific guidance for sampler selection and operation is provided to ensure consistency across the network for comparison of spatial data and trends analyses. To allow flexibility for speciation sampling at non-NAMS sites, State and local agencies can tailor sampling methodologies to their individual program needs. However, these non-NAMS speciation sites will be subject to a balance between the competing need for national consistency and the flexibility needed to address local issues.

The approach to be used for chemical speciation involves both sampling and analysis components. The "National $PM_{2.5}$ Sampler Procurement Contract" includes the provision for the purchase of over 300 speciation monitors, including accessories, and replacements for establishing the speciation monitoring network. The design of speciation samplers can be flexible to include additional filter collection media best-suited for the analysis of specific components. The 40 CFR Part 53 requirements for designation of reference and equivalent methods for $PM_{2.5}$ do not require designations for speciation monitors (U.S. EPA, 1997f). However, it is imperative all non-reference or equivalent methods incorporate particle inlets with equivalent particle size efficiency curves to the reference method for $PM_{2.5}$.

Desirable features of a speciation sampler include the following:

- The inlet cut-point and separation profile must be comparable to the WINS, FRM inlet. A number of laboratory and field tests should be conducted to demonstrate that the fine particle mass collected by the speciation monitor and the FRM are in good agreement (for example, have a slope of 1 ± 0.1 and r^2 better than 0.90).

- The sampler should use approved denuder technology to obtain nitrate and anion/cation measurements. The nitric acid denuder should be tested for its capacity and efficiency as a function of exposure time and relative humidity. If it is proposed that a denuder will be used for more than one sampling day, it will be important to demonstrate the collection efficiency over time.

- The sampler should collect samples at a face velocity and sample volume similar to that of the FRM with 46.2-mm diameter filters.

- The sampler must be reliable, rugged, and employ field-proven monitoring approaches.

There are several samplers employing multiple channels with appropriate sample

pretreatment and filter media for use by State and local agencies for implementing the $PM_{2.5}$ routine speciation program. The samplers mainly differ by inlet design and approach to collection of particles < 2.5µm. These more recent designs include the capability to collect semi-volatile organic aerosol particles using channels consisting of diffusion denuders followed by quartz fiber filters and solid sorbent traps. Three candidate sampler designs described below are being made available through the EPA National $PM_{2.5}$ Sampler Procurement Contracts. As several different speciation sampler designs could be used in the overall routine sampling program, studies are needed to collect data which show intercomparisons between the samplers relative to the performance of the FRM inlet and corresponding mass measurement.

6.1 Available Candidate Sampling Approaches

The candidate sampling methods and approaches to chemical speciation include IMPROVE, the Reference Ambient Air Sampler (RAAS™), Mass Aerosol Speciation Sampler (MASS), and Spiral Ambient Speciation Sampler (SASS™). At a minimum, these speciation monitors contain PTFE (Teflon®), nylon, and quartz filter media and provide for the collection of the specific target analytes of interest. The PTFE will be used for mass and elements from aluminum through lead; quartz will be used for total, organic, elemental, carbonate carbon, and semi-volatile organic aerosols; and nylon will be used for the collection of nitrate and other cations, and anions. The sampling system must also be capable of collecting a 24-hour $PM_{2.5}$ sample. The candidate speciation monitor designs differ in their approach and are configured either as a multi-channel device operating from a single inlet, or a series of separate inlets or instruments, each with its own particulate separator mechanism. In any case, the monitor design must have the capability of collecting only particles with an aerodynamic diameter equal to or less than 2.5 μm.

6.2 Operating Principle

The principle of operation involves several common components. Most fine particulate samplers have a size-selective inlet to separate particles so that only fine particles (those less than 2.5 microns) are collected onto the sample filter. Air is drawn through a sample filter at a controlled flow rate by a pump located downstream of the sample filter. The flow rate system has two critical components for the capture of fine particulate: 1) the flow of air through the sampler must be at a flow rate to ensure that the size cut at 2.5 microns occurs, and 2) the flow rate must be designed to capture the desired amount of particulate loading with respect to the analytical method detection limits. Other components such as a flow rate measurement device, denuder, recorder, temperature probe, isolation valve, and microprocessor control are also included in a

speciation sampler. Key components of candidate samplers for the speciation program are discussed below.

6.2.1 Particle Size Inlets

The inlet cut-point and separation profile must be comparable to the WINS, FRM inlet and be capable of removing particles which exceed the aerodynamic particle diameter of fine particulate matter. Size selective inlets typically use a variety of means to remove particles larger than the specified aerodynamic size and the size cutoff is based on sample flow rate. In the IMPROVE and RAAS, a cyclone is used to separate coarse and fine particles. The SASS™ uses a spiral inlet and the MASS uses the $PM_{2.5}$ FRM WINS assembly.

6.2.2 Denuder

Denuders are used immediately behind size-selective inlets to remove gases that interfere with the aerosol measurement, or to quantify the concentrations of gases that are precursors to secondary aerosols. Denuders take advantage of the fact that gas molecules diffuse through air much more rapidly than small particles. Denuder surfaces are made of, or coated with, substances that absorb the gases of interest while letting the particles pass through. Denuder geometries can be rectangular, cylindrical, honeycomb, or annular; the annular designs provide higher gas collection efficiencies than coated cylinders. Honeycomb designs are composed of an array of narrow cylinders that combine high surface area with compact size. When the walls of the denuder are coated with substances that absorb the gases, the denuders can be washed and the extract submitted for special chemical analyses. This method is often used to measure nitric acid, sulfur dioxide, and ammonia gases along with suspended particles. These gases are common precursors to secondary sulfate and nitrate compounds.

For the chemical speciation program, denuders will be part of the sampler design for the collection of nitrate on the nylon filter and organic carbon on the quartz filter. For removal of nitric acid, denuders coated with sodium carbonate or magnesium oxide will be used. For semi-volatile organics, technology for the routine removal of gas-phase semi-volatile organics has not been fully developed. The EPA and research community expect this capability to become available in the near future (using coated XAD-4 denuders). Denuders will not be extracted and analyzed for vapor phase components as part of the NAMS.

Denuders have specific efficiencies and capacities depending on the design and coating materials used. It is recommended that acid gas denuders be recoated or replaced every 3 months, depending on the anticipated acid gas concentrations for each site or recommendations

from the denuder manufacturer. For a detailed discussion regarding the use of annular denuder technology in the determination of acidic and basic gases (including sulfate, nitrate, and ammonium) of atmospheric fine particles refer to ***Compendium Chapter IO-4*** (U.S. EPA, 1997e).

6.2.3 Filter Types

Filter media include polytetrafluoroethylene (PTFE), quartz, and nylon. Other filter media types may be used in the non-NAMS component of the speciation network. Refer to Table 3-1 of this document for a matrix of filter types, target analytes and analytical methods used. Some physical and chemical characteristics of the filter media are given in Table 5-1. Section 7 includes a brief discussion of the filter medium sample preparation procedures for lab analyses. Filter holders are expected to be made of inert material. Since many of these materials are expected to be polymers, consideration should also be given to static electricity problems.

6.2.4 Flow Rate Measurement

Flow measurement and control for the speciation network are expected to be similar to the FRM requirements (not vary more than ± 5 percent from the manufacturer's specified flow rate over the entire sampling period). Having tight control of sampler flow rate is a critical component of the speciation program since calculations of ambient air concentrations require knowing the volumetric flow rate through the sampler. Deviations from the expected flow rate that cannot be quantified would reduce data quality.

Table 6-1
Physical and Chemical Characteristics of Speciation Filter Media

Filter Type	Physical Characteristics	Chemical Characteristics
PTFE	Thin film of PTFE attached to ring without adhesive	Usually low blank levels
	White surface, nearly transparent	Made of carbon-based material, so inappropriate for carbon analysis
	Minimal diffusion or transmitted light	Inert to adsorption of gases
	High particle collection efficiency	Low hygroscopicity
	Cannot be accurately sectioned	Low blank weight
	Melts at approx. 60 C	
	High flow resistance	
Nylon	Thin membrane of pure nylon	High HNO_3 collection efficiency
	White opaque surface, diffuses transmitted light	Passively adsorbs low levels of NO, NO_2, PAN, and SO_2
	Melts at approximately 60 C	Low hygroscopicity
	High flow resistance	Low blank weight
Pure quartz-fiber	Mat of pure quartz fibers	Pre-washed during manufacturing
	White opaque surface, diffuses transmitted light	Low blank levels for ions
	High particle collection efficiency	Contains large and variable quantities of Al and Si; May contain other metals
	Soft, friable edges that have tendency to flake	Passively adsorbs organic vapors; Adsorbs little HNO_3, NO_2, and SO_2
	Melts at >900 C	Low hygroscopicity
	Moderate flow resistance	

6.2.5 Filter Temperature Measurement

Filter temperature measurement and control is an important element of the $PM_{2.5}$ chemical speciation network. This is due to the characteristics of the particulate that are being captured. If sampler performance resulted in significantly higher temperature at the sample media compared to the ambient temperature, then volatile chemical species may be underestimated. If filter media were colder than ambient temperature, as may be the case during a rapid temperature rise in the morning under conditions of a very low dew point, then more volatile chemical species may be trapped in the sample media than otherwise would occur under normal conditions. This would not necessarily invalidate data, however, it should be appropriately qualified. For these reasons, it is necessary for the sampler to provide a means to limit the temperature fluctuations and to monitor both ambient and filter media temperatures.

6.2.6 Barometric Pressure Measurement

The sampler must have the capability to measure barometric pressure and record the maximum, minimum, and mean measurements over the sampling period. The barometric pressure measurement is used for the purpose of computing the actual sample collection volume.

6.3 Candidate Monitor Configurations for NAMS

The following is a description of candidate chemical speciation monitor configurations that may be used for both NAMS and non-NAMS sites. In addition, a very brief description of single channel, continuous, saturation and special purpose monitors also appropriate for use in non-NAMS or special studies is provided.

6.3.1 IMPROVE

The standard IMPROVE sampling module consists of a size selective inlet; a cyclone to provide particle size cut based on flow rate; filter media for sample collection; a critical orifice that provides the proper flow rate for the desired size cutoff; and a vacuum pump to produce the flow. IMPROVE samplers consist of up to four parallel modules and a common controller. An example diagram of a single IMPROVE sampler module is shown in Figure 6-1.

Each of three modules utilizes a cyclone to allow for the collection of $PM_{2.5}$. The fourth module is used for sampling PM_{10} aerosols. The fine particulate modules incorporate a cyclone with a flow rate of 22.7 L/min to allow for collection of particles less than 2.5μm.

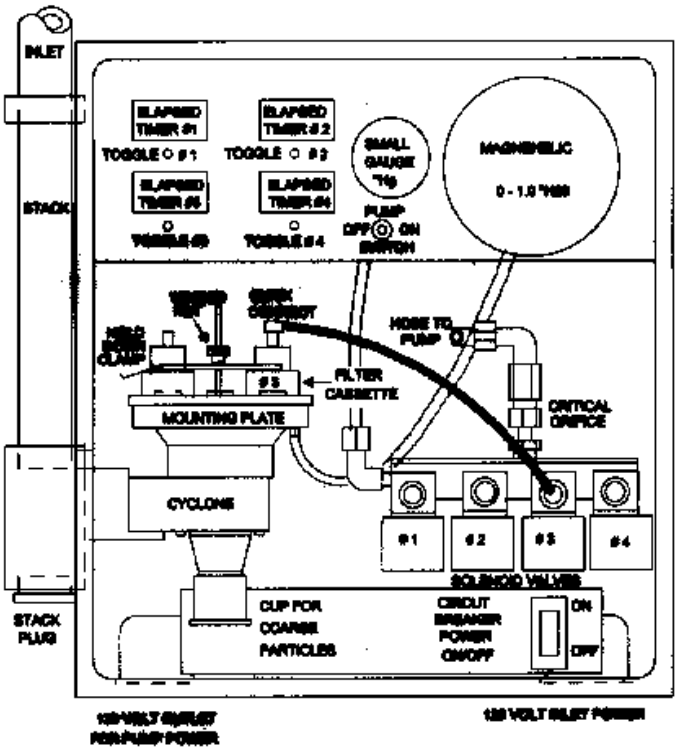

Figure 6-1. IMPROVE module with four solenoids

A single $PM_{2.5}$ module uses a PTFE membrane filter to collect aerosols for mass measurement and subsequent analysis for trace elements. A second $PM_{2.5}$ module is equipped with a potassium carbonate denuder and nylon filter to measure total particulate nitrate. The third $PM_{2.5}$ module contains two pre-fired quartz-fiber filters in series to measure organic and elemental carbon on the first filter and to assess the extent of organic artifacts on the backup filter. The flow rate is monitored by two independent gauges which measure pressure drop across the cyclone and filter.

IMPROVE samplers have historically been used at regional background and transport sites to fulfill SLAMS requirements. They were developed to quantify PM chemical components that affect visibility at Federal Class I areas that include national parks, national monuments, and wilderness areas.

6.3.2 Mass Aerosol Speciation Sampler (MASS)

The MASS consists of two stand-alone samplers. These samplers are identical except that the MASS400 has a sodium carbonate coated denuder followed by a two stage Teflon® and nylon filter pack, while the MASS450 has an XAD-4 denuder, single stage quartz filter pack, and a PUF/XAD-4 sorbent trap to collect semi-volatile organic aerosols.

To obtain the fine particulate matter, the sample air inlet particle size separator is as specified in 40 CFR Part 50 Appendix L and identical to the FRM WINS. This provides an identical cut point and efficiency curve. 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 to place a high capacity annular denuder between the PM head and WINS inlet. This denuder is changed once every three measurements.

Perfluoroalkoxy (PFA) Teflon® coating of the inlet is an option. This would allow 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.

The sampler configuration for the collection of cations, anions, and elements is shown in Figure 6-2. While an aluminum inlet will remove some of the nitric acid, it is not 100 percent efficient. Nitric acid is removed by using an annular denuder coated with Na_2CO_3 that quantitatively removes the acidic gases, including HNO_3, from the air stream. If aerosol acidity (H+) are to be measured, a citric denuder needs to be used to remove the ammonia in the air stream. The NH_3 will react with the acid sulfate aerosol during sampling and, thus, neutralize the aerosol. If NH_3 measurements are needed in conjunction with the aerosol measurement the denuder may be extracted and analyzed for NH_4+ ion content. In addition, if ammonia reacts with acid sulfates on the filter, a positive mass artifact would result. The use of the citric acid denuder minimizes this effect.

The sampler configuration for the collection of organic and elemental carbon and semi-volatile organic particles is accomplished through the use of an XAD coated annular denuder, a quartz filter pack downstream of the denuder collects only the condensable organics. The Semi-volatile organic species that evaporate from the filter during sampling are collected with a PUF/XAD trap downstream of the filter. The extract of the trap is analyzed by GC/FID/MS methods to quantify the mass of organics 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 the adsorbing (positive artifact).

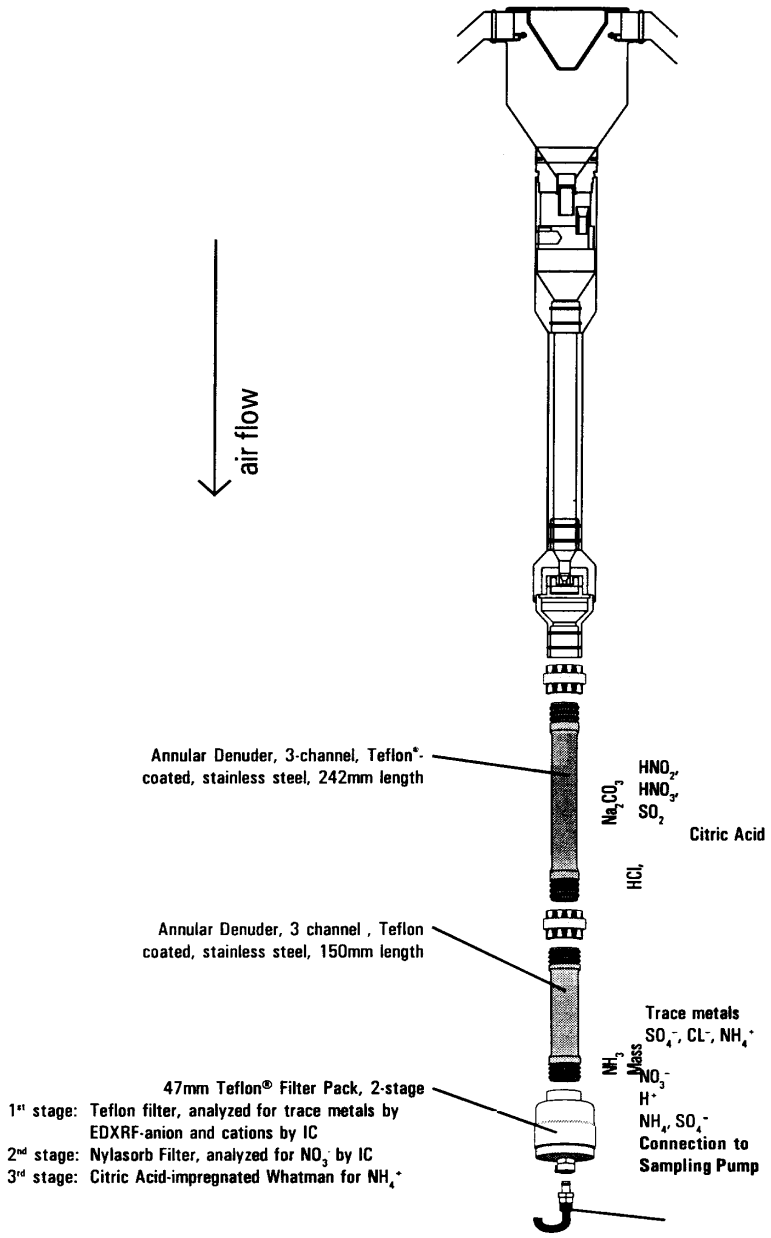

Figure 6-2. MASS speciation monitor for ions, metals and nitrates

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.

6.3.3 Reference Ambient Air Sampler (RAAS™)

Ambient air is pulled through a wind direction and 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 then passes through an AIHL-design cyclone separator operating at a flow rate of 24 L/minute, which removes coarse particles with diameters larger than 2.5 μm. The cyclone functions reliably without the use of oil or other bounce prevention agents. The elimination of oil makes maintenance easier and reduces sampling artifacts as compared to the WINS impactor used in all Federal Reference Method samplers. All inlet, connector and cyclone parts are fabricated from polytetrafluoroethylene (PTFE)-coated aluminum.

The air stream, containing only fine particles and gases, then enters an inert PTFE-coated sampling manifold where it is split between four separate low-volume filter holder assemblies. The flow rate through each filter holder is controlled by a critical orifice that can be changed if a different sampler configuration is desired for special studies. In normal sampling, the total flow rate is 24 liters per minute divided into four 6 liter per minute subdivisions.

Two of these sampling lines collect fine particles on standard 46.2-mm diameter PTFE filters for subsequent chemical analysis. Two PTFE filters are used because samples intended for X-ray fluorescence analysis are 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 quartz fiber filters from which carbonaceous species can be measured by thermal evolution and combustion analysis. It is protected by a diffusion denuder coated with XAD to remove gaseous semi-volatile organics from the incoming air stream. A backup trap using polyurethane foam (PUF) or XAD resin is used to capture any semi-volatile organic components evaporating from the particulate captured on the filter.

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. This system eliminates the well known negative sampling artifact for nitrates that can occur in locations such as Los Angeles and many cities in the West, that experience significant fine particle ammonium nitrate concentrations. A single denuded nylon filter is used rather than a nylon filter downstream from one of the PTFE filters to guard against the evaporative loss of ammonium nitrate (NH_4NO_3) from the PTFE filter after sampling has ceased but before samples are retrieved from the field. An optional PTFE-coated filter holder equipped with a nylon filter can be located in parallel with those filters that are directly downstream of the cyclone separator which will permit nitric acid concentrations to be measured by the denuder difference technique.

The filter substrates used to collect particulate matter are chosen to be compatible with particular chemical analyses. Pretreated quartz fiber filters are used to collect samples destined for determination of atmospheric carbonaceous aerosol concentrations. PTFE filters are employed to obtain atmospheric particulate matter samples for mass concentration determination and for subsequent measurement of a wide variety of major and trace elements and water soluble anions and cations. The nylon filter is used below the diffusion denuder. .

Filters are installed prior to sampling, and the sampler is started and stopped at operator set times, and the samples are removed the day after sample collection. System operation and data logging are handled by the same controller used in Andersen Reference Method samplers. As a precaution to help ensure the integrity of the samples after collection, the sampling protocol requires the filters to be stored either in sealed filter holder assemblies or in self-sealing plastic petri dishes sealed with Teflon tape. The samples are cooled until returned to the laboratory, and then frozen until sample analysis.

6.3.4 Spiral Ambient Speciation Sampler (SASS™)

This sampler provides five parallel sample cassettes as shown in Figure 6-3. Each cassette has its own $PM_{2.5}$ inlet, denuder, and tandem filter holder. The five cassettes are mounted in an aspirated radiation shield that maintains the sampler temperature close to ambient. Cassette inlets point downward. The sampling head has five independent sampling channels, each operated at a sample flow rate of about 6.0 L/min. Ambient air enters each independent sampling inlet and the particle size separated by the Spiral Inlet (John 1997). The separator does not require the use of grease or oil anti-bounce agents. The $PM_{2.5}$ inlet is built into the cassette which allows the inlet

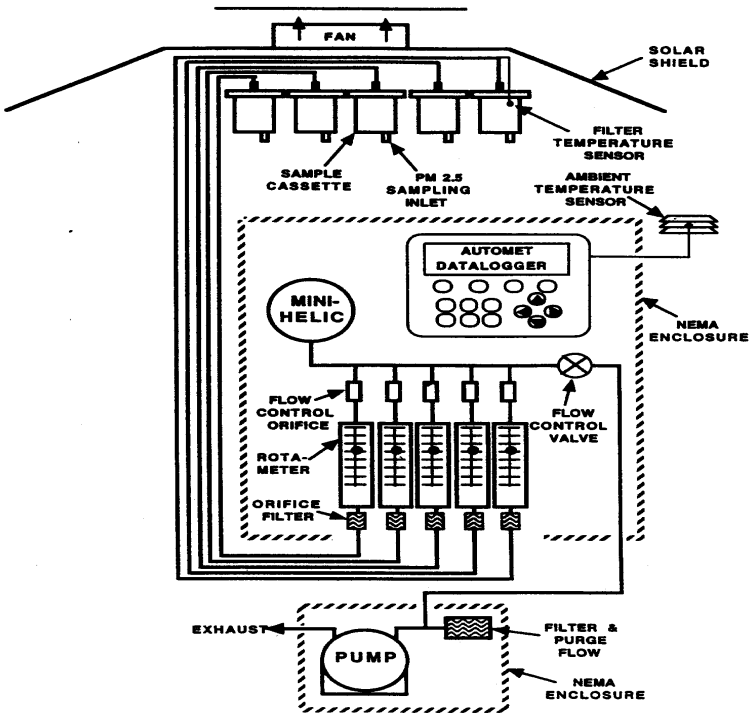

Figure 6-3. Spiral Ambient Speciation Sampler (SASS™)

to be cleaned in the laboratory before or after each sample event to ensure accurate performance. The sampler does not use a plenum or sample tube which requires field maintenance.

Two types of denuders which are of multi-cell configuration are provided. The nitric acid denuder is made of aluminum and is coated with magnesium oxide. The carbon denuder is made using activated carbon. These denuders remove interfering gases but are not designed to be extracted for direct analysis.

The five cassettes provided with the sampler can be used in multiple configurations. A suggested configuration for the five cassettes incorporates:

- a Teflon® filter for mass and trace elements in cassette #1;
- MgO-denuder followed by a nylon filter for inorganic ions and nitrates in cassette #2;
- a carbon-denuder followed by a quartz filter for organic carbon in cassette #3; and
- two QA filters of choice for replicate sampling or field blank collection in cassettes #4 and #5.

Any cassette can be configured with one or two filters or a denuder followed by one or two filters. The filter cassette temperature is monitored and the data logged. The DC fan aspirated solar radiation shield houses the five individual cassettes and maintains the cassette filter temperature during a sample event to less than 5 C above ambient temperature. A shielded ambient temperature sensor mounted to the control module data logs the ambient temperature.

The flow from each cassette passes through a rotameter, a valve and a critical orifice to a common pumping manifold. The critical orifice controls the sample flow rate. The valve located

on the downstream side of the filter can be used to close sample lines not in use. The rotameters are not used for flow measurement, but rather to provide a quick indication of flow. Sample flow rates are measured and recorded manually at the cassette inlet before and after each sample is collected. A sample line exits each rotameter into a flow control precision orifice and then to a common manifold. The manifold pressure is read by a mechanical differential pressure gauge leading to a control valve prior to the vacuum pump. The pump uses a rotary carbon vane rated for 20,000 to 30,000 hours of use between vane replacement. The pump is mounted in its own separate enclosure to minimize heat, vibration, isolate AC power and protect the sampling system from re-entrained dust.

6.4 Other Monitor Types

The monitor types briefly discussed below can also be considered in configuring a non-NAMS speciation network. Selection of these monitor types are dependent on the monitoring network and data use objectives.

6.4.1 Single Channel Monitors

Single channel (single inlet assembly and filter medium), FRM samplers are not expected to be routinely used in speciation sampling. A designated FRM or FEM sampler, operated with the appropriate filter media, can be used to collected a sample that may be subsequently analyzed for the targeted chemical species on that filter media. This approach may be used in cases where chemical speciation analyses are performed on a Teflon® filter, after gravimetric analyses determined a high fine particulate loading. In the case of a Teflon® filter media, the sample can be analyzed for trace elements. The single channel sampler could also be used with a nylon or quartz filter to collect fine particulate for other targeted chemical species. Multiple FRM/FEMs with multiple filter media would be needed to cover the entire group of target chemical species. For example, three collocated FRM samplers could be used, one sampler each with a Teflon®, nylon, and quartz filter. Alternatively, a uniquely designed sampler could be used to capture fine particulate on nylon and quartz filters, and a FRM sampler used to capture fine particulate on a Teflon® filter.

6.4.2 Continuous Monitors

The EPA encourages the use of continuous monitors as part of the speciation monitoring program. Continuous monitors should only be considered for use at the core NAMS as the technology develops and is demonstrated as adequate for use to meet the program and data quality objectives. Continuous monitoring data can be used to provide more timely data reports

to the public and collection of data on a more real time basis. Continuous monitors can be used to characterize diurnal patterns of exposure and emissions and are extremely useful in collecting samples during extremely high or low particulate periods.

Currently available continuous monitors for mass include the Tapered Element Oscillating Microbalance (TEOM®), Piezoelectric Microbalance, Beta Attenuation Monitor (BAM), and the Pressure Drop Tape Sampler (CAMMS). Chemical-specific particle monitors include single particle mass spectrometers, a particulate carbon monitor, sulfur analyzer with Flame Photometric Detection (FPD), nitrate analyzers, and elemental analyzers. Precursor gas continuous monitors include a chemiluminescence ammonia analyzer, fluorescence ammonia gas analyzer, and nitric acid analyzers. Refer to the ***Guidance for Using Continuous Monitors in $PM_{2.5}$ Monitoring Networks*** (U.S. EPA, 1998b), for additional guidance regarding the use of continuous in-situ measurements of suspended particles, their chemical components, and their gaseous precursors.

6.4.3 Saturation Monitors

The EPA encourages State and local air pollution control agencies to conduct short-term, multi-site pollutant monitoring studies using a technique known as saturation monitoring. Saturation monitors are non-reference method, small portable samplers which are readily set-up, operated, and easy to site. Also, because they are relatively inexpensive, it is possible to "saturate" an area with these monitors to assess air quality in areas where high concentrations of pollutants are possible. Saturation monitors are expected to be used to determine “hot spots” of fine particulate. This information can be used to help air pollution control agencies gather preliminary information for speciation sampler siting and evaluate and develop their monitoring networks. Saturation monitoring may also be conducted to characterize the spatial distribution of pollutant concentrations or to evaluate the contributions of sources in support of receptor modeling.

6.4.4 Special Purpose Monitors

A strength in the design of the speciation program is sufficient flexibility to accommodate coordination between the user’s needs and advances in sampling technology as they become available. Hence, there is a provision for special purpose monitors (SPMs) as part of the $PM_{2.5}$ program. These monitors can serve a variety of uses including research, regulatory support (i.e., SIPs) and others. The SPMs will not be used as NAMS samplers; they may be collocated with NAMS speciation and FRM samplers. The SPMs may be utilized as part of the speciation program in the sense that subsequent laboratory analysis of the captured particulate may be performed as part of the speciation program, if resources are available.

Special purpose monitors are a separate component of the $PM_{2.5}$ network and as such are not part of the 1,500 network sites. The use of special purpose monitors is expected to complement or be complemented by the use of speciation monitors. Specific requirements of special purpose monitors are not prescribed, so that study designers may tailor monitoring components to the end user needs. Any use of a special purpose monitor should take into consideration the design of the speciation components of the PM fine network and how data can be evaluated.

6.5 Sampling Procedures

Published sampling procedures from several sources are expected to be utilized for compiling the sampling procedures used in the speciation component of the $PM_{2.5}$ program. Sources may include, but are not limited to: sampler manuals, section 2.12 of the QA handbook (U.S. EPA, 1998a), and other sampling methods published from the peer-reviewed literature.

7.0 SAMPLE ANALYSIS METHODS

With the goal of ensuring data quality for several thousand filter analyses per year which may utilize a range of analytical methods, it is critical to establish an analytical laboratory framework which is consistent to support these needs. One key aspect of the framework is the establishment of a standardized of SOPs for speciation analyses. The SOPs must be based on analytical methods with proven application to the analysis of ambient particulate matter filter samples. In addition to guidance on sampling and handling, the EPA will also develop guidance and documentation for SOPs on the laboratory analysis of the target analytes given in Table 3-1 of this document. The guidance will include laboratory quality assurance guidelines specific to the methods of analysis and guidelines on standardized data reduction, validation, sample handling, chain-of-custody, and reporting formats. The EPA plans for the speciation data to be submitted to the Aerometric Information Retrieval System (AIRS) data base. The U.S. EPA is developing laboratory SOPs for the NAMS that are complementary to the techniques used by various agencies and research groups operating ambient air particulate matter speciation programs.

The operational schedule for providing the speciation laboratory support services begins with development of a program team of EPA Office of Air Quality Planning and Standards (OAQPS) and Regional Office personnel. The OAQPS will lead the development of the required guidance information and the SOPs with input from the Office of Research and Development (ORD), EPA Regional Offices, and the $PM_{2.5}$ monitoring technical community. Initial deployment of approximately 50 of the speciation monitors is projected for the second quarter of calendar year 1999. Allowing for time by site operators to be trained in the use of the monitors, we project that the laboratory services support portion of the National $PM_{2.5}$ Speciation Program will be in place by May of 1999. The speciation analytical guidelines developed by EPA can also be used by State laboratories with appropriate facilities to provide local support, if appropriate, for an individual State-level monitoring network. In addition EPA is studying the process of evaluating alternative test methodology which may be proposed by States. In such a process, an equivalency methodology guideline would have to be developed that can be used by States to prove that their proposed method performs well as defined by the guidelines.

The methods used for analyses of the filter media include gravimetry (electro-microbalance) for mass and various instrumental methods for determining the chemical composition of the particles. In addition to chemical analyses, special measurement needs may include determining particle size and morphology through optical and/or electron microscopy.

A national laboratory services support program consisting of contracted services with up

to three qualified laboratories capable of providing consistent laboratory service support for all of the target analytes will be developed. The extent of the services will depend upon capacity needed, as well as the level of participation by State and local government laboratories for providing analytical services. Analytical support from the contract laboratories will be accessed through three EPA Regional Project Officers or Delivery Order Project Officers (DOPOs) who will be located at Regional Offices in the eastern (Region 1), Midwestern (Region 5), and western (Region 8) parts of the country. The Project Officers will coordinate site needs for those States located in the three geographic areas. Selected EPA Regional laboratories will operate in a quality assurance role for the contractor laboratories involved in the speciation program. A flow diagram of the sample analysis delivery order process is given in Figure 7-1.

The most commonly applied aerosol analyses methods can be divided into the following categories: mass, elements, ions, and carbon. It is possible to obtain several different analyses from the same substrate, but not possible to obtain all desired chemical species from a single substrate; therefore, the appropriate filter media, sampling hardware, and analysis methods must be combined. Depending on the study objectives and sources in an area, different chemical species may need to be added or omitted. A flow diagram of filter processing and analysis activities for the NAMS is shown in Figure 7-2.

The following sections outline the filter analysis methods for the target chemical species categories of elements, ions, and organic carbon.

7.1 Elemental Analysis

Energy dispersive X-ray fluorescence (EDXRF) is the analytical method of choice to characterize the elemental composition of the aerosol deposits on PTFE filters for the $PM_{2.5}$ NAMS chemical speciation program. Interest in elemental composition is commonly derived from concerns about health effects and the utility of these elements to trace the sources of suspended particles or source characterization. Since sample filters often contain very small amounts of particle deposits, preference is given to methods that can accommodate small sample sizes and require little or no sample preparation or operator time after the samples are placed into the analyzer. X-ray fluorescence (XRF) meets these needs and leaves the sample intact after analysis so it can be submitted for additional examinations by other methods as needed. To obtain the greatest efficiency and sensitivity, XRF typically places the filters in a vacuum which causes volatile compounds (nitrates and organics) to evaporate. Volatilization will not be an issue for the NAMS since PTFE filters will not be subsequently analyzed for volatile species.

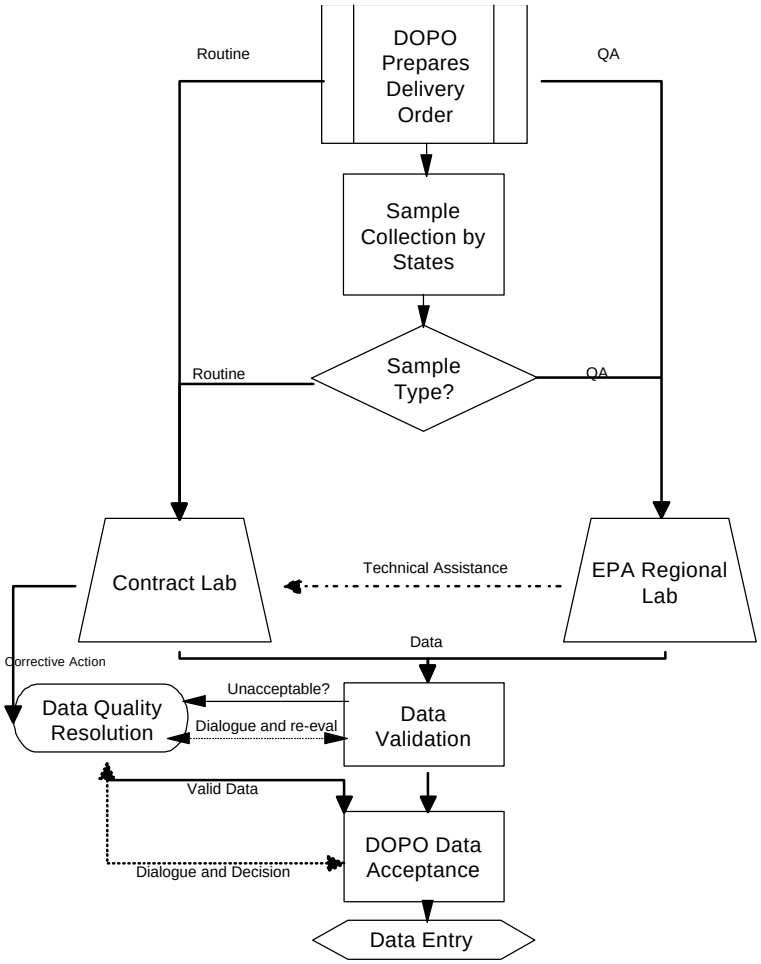

Figure 7-1. Sample analysis Delivery Order process flow diagram

In XRF the filter deposit is irradiated by high energy X-rays which causes the ejection of inner shell electrons from the atoms of each element in the sample. When a higher energy electron drops into the vacant lower energy orbital, a fluorescent X-ray photon is released. The energy of this photon is unique to each element, and the number of photons is proportional to the concentration of the element. Concentrations are determined by comparing photon counts for a sample with those obtained from thin-film standards of known concentration. XRF methods can be broadly divided into two categories: wavelength dispersive XRF (WDXRF), which utilizes crystal diffraction for observation of fluorescent x-rays, and energy dispersive x-ray fluorescence (EDXRF), which uses a silicon semiconductor detector. The WDXRF method is characterized by high spectral resolution which minimizes peak overlaps. WDXRF requires high power

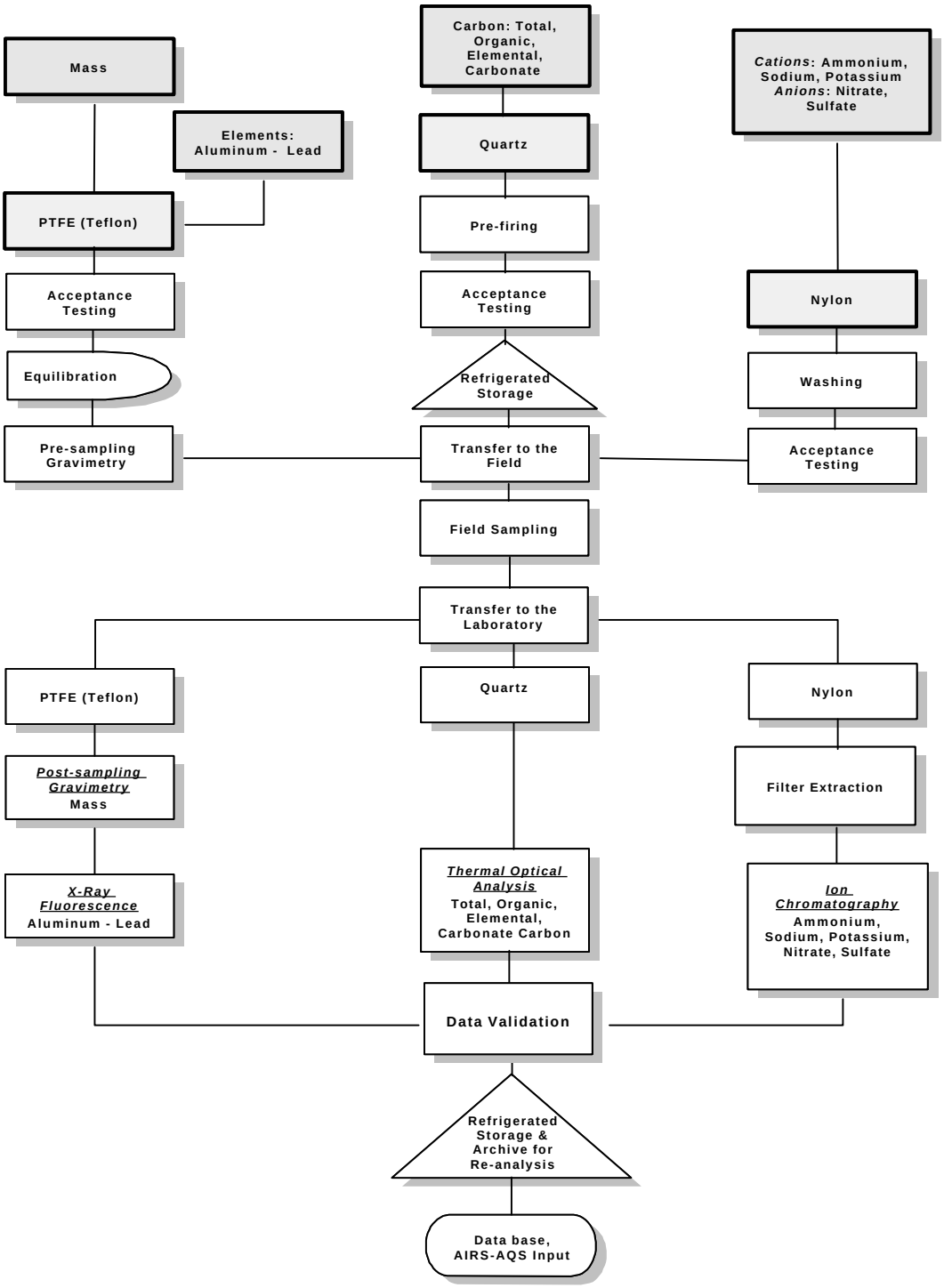

Figure 7-2. Flow diagram of filter processing and analysis activities

excitation to overcome low sensitivity which results in excessive sample heating and potential degradation. Conversely, EDXRF features high sensitivity but less spectral resolution, requiring complex spectral deconvolution procedures.

The type of filter is important and thin membrane filters (PTFE) are required so that the background is low and penetration of particles into the matrix of the filter is small. The XRF provides rapid, simultaneous, and nondestructive detection of the target elements from Na to Pb. Advantages of using XRF are the quantitative analysis of bulk elemental composition, the ability to perform trace level particulate analysis with sensitivity to ppm levels, and the availability of instrumentation. The XRF method of analysis employs an energy dispersive spectrometer. Analysis atmospheres are selectable with choices of helium or air; helium is used for all target elements except Gd where air is employed because it gives a lower background. Vacuum is not used, therefore, avoiding the loss of volatile compounds.

Calibration is by far the most complicated task in the operation of the XRF. Recalibration is only performed when a change in fluorescers or x-ray tubes is made or a serious instrument malfunction occurs. Three types of XRF standards are available for calibration: vacuum deposited thin film elements; polymer films; and NIST thin-glass films. The vacuum deposited thin film standards are available for almost all elements analyzed and are used to establish calibration curves. Some standards have high inherent volatility and do not serve well as calibration standards. These are selenium (Se), bromine (Br), mercury (Hg), and elemental arsenic (As). The same set of standards is used every time the spectrometer is calibrated. These standards are sufficiently durable to last many years. Polymer films contain two elements in the form of organo-metallic compounds dissolved in the polymer as described in Dzubay et al., 1988. These standards are available for elements with atomic numbers above 21 (titanium or heavier). The polymer films and NIST standards are typically used for quality control measures. NIST produces reference materials for iron, lead, potassium, silicon, titanium, and zinc (SRM 1833).

The sensitivity of this method is on the order of few ng/m_3 for 24-hour samples (flow rates of 10-20 liters per minute). Nonetheless, quite often environmental samples have elemental measurements below the detection limit of this method. Thus, analytical uncertainties can have a significant impact on the quality of the data analysis such as for source apportionment studies. It should be mentioned that, during the analysis using XRF, the sample is introduced into a chamber that is evacuated and the sample is slightly heated due to the absorption of X-rays or protons. As a result, species that can volatilize such as ammonium nitrate and certain organic compounds can be lost during the analysis. This volatilization is important if the Teflon® filter is to be subjected to subsequent analyses.

7.2 Ion Analysis

Aerosol ions refer to chemical compounds which are soluble in water. The water-soluble portion of suspended particles associates itself with liquid water in the atmosphere when relative humidity increases, thereby changing the light scattering properties of these particles. Different emissions sources may also be distinguished by their soluble and nonsoluble fractions as in the case of soluble potassium. Gaseous precursors can also be converted to their ionic counterparts when they interact with chemicals impregnated on the filter material.

Polyatomic ions such as sulfate, nitrate, ammonium, and phosphate are quantified by methods such as ion chromatography (IC). Simple ions, such as chloride, and fluoride may also be measured by IC along with the polyatomic ions. When the aerosol deposit is suspected of being acidic, its hydrogen ion content can be determined by a pH electrode or by micro titration. It is important to keep the filter away from ammonia sources, such as human breath, to minimize neutralization of the acidic compounds.

Applied to aerosol samples, the anions and cations are most commonly analyzed by IC. IC can be used for anions (fluoride, phosphate, chloride, nitrate, sulfate) and cations (potassium, ammonium, sodium) by employing separate columns. All ion analysis methods require a fraction of the filter to be extracted in deionized distilled water and then filtered to remove insoluble residues prior to analysis. The extraction volume should be as small as possible to avoid over-diluting the solution and inhibiting the detection of the desired constituents at levels typical of those found in ambient $PM_{2.5}$ samples. IC is the method of choice for the $PM_{2.5}$ NAMS speciation program for the analysis of the target cations (ammonium, sodium, and potassium) and anions (nitrate and sulfate).

A major sampling requirement for analysis of water-soluble species is that the filter material be hydrophilic, allowing the water to penetrate the filter and fully extract the desired chemical components. A nylon filter is used for volatilized and particulate nitrate and sulfate anions and a pre-fired quartz fiber filter is used for the ammonium, sodium, and potassium cations. The anions are extracted with a sodium carbonate/sodium bicarbonate solution, and the cations are extracted with a dilute hydrochloric acid/distilled water solution.

In IC, the sample extract passes through an ion-exchange column which separates the ions for individual quantification, usually by a electroconductivity detector. The anions are separated when passed through a resin consisting of polymer beads coated with quaternary ammonium active sites. The separation is a result of the different affinities of the anions for these sites. After separation and prior to detection, the column effluent and anions enter a suppressor column where

the cations are exchanged for H^+ ions. Species are then detected as their acids by a conductivity meter. The ions are identified by their elution/retention times and are quantified by the conductivity peak area or peak height. The IC is especially desirable for particulate samples because it provides results for several ions with a single analysis, low detection limits, and uses a small portion of the filter extract with low detection limits.

The cations are analyzed in the same manner except the sample extract passes through a surface-sulfonated ion exchange resin where separation occurs. After separation and prior to detection, the cations enter a suppressor column where all the anions are exchanged for OH^- ions. The species are then detected as their bases (hydroxides) by a conductivity meter. Concentrations of ions and cations are proportional to the conductivity changes.

7.3 Particulate Organic Speciation

Organic compounds are important components of particulate matter, whether in urban, rural, or remote areas. Most of the particulate organic carbon is believed to reside in the fine particle fraction. $PM_{2.5}$ samples were collected at four urban locations in southern California in 1982 to quantify several individual organic compounds. This study identified and quantified over 80 individual organic compounds in the $PM_{2.5}$ fraction, including n-alkanes, n-alkanoic acid, one n-alkenoic acid, one n-alkanal, aliphatic dicarboxylic acids, aromatic polycarboxylic acids, polycyclic aromatic hydrocarbons, polycyclic aromatic ketones, polycyclic aromatic quinones, diterpenoid acids, and some nitrogen-containing compounds. In general, the same type of organic compounds, although in different proportions, are found in direct emissions from various sources such as diesel and gasoline powered vehicle exhaust, charbroilers and meat cooking operations, cigarette smoke, biogenic sources, etc. Thus, organic compounds are potentially valuable tracers for characterizing different emission sources as well as for atmospheric transformation processes.

7.3.1 Carbon Analysis

Three classes of carbon are typically measured in ambient aerosol samples collected on pre-fired quartz-fiber filters: 1) organic, volatilized, or non-light absorbing carbon; 2) elemental or light-absorbing carbon; and 3) carbonate carbon. Carbonate-source carbon [i.e., potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), magnesium carbonate ($MgCO_3$), calcium carbonate ($CaCO_3$)] is determined from a separate filter section after acidification. Without acidification, the determination of carbonate carbon is not specific and is detected as either organic or elemental carbon.

Two thermal-optical methods currently are in use for the analysis of carbonaceous

aerosols. The measurement principle is fundamentally the same, but the methods differ with respect to calibration, analysis time, temperature ramping and settings, types of carbon speciated, and pyrolysis correction technique. The method's pyrolysis correction feature allows correction for the char that forms on the filter during analysis of some materials (e.g., cigarette smoke). Correction for pyrolysis is made by continuously monitoring the filter transmittance (NIOSH Method 5040) or reflectance (TOR) throughout the analysis.

For the NAMS chemical speciation program, total, organic, elemental, and carbonate carbon will be determined by thermal/optical instrumentation specified in NIOSH Method 5040 (NIOSH, 1996, 1998) and described in the literature (Birch and Cary, 1996). Method 5040 was developed for occupational monitoring of diesel particulate, but its evaluation also included a round-robin study involving a variety of carbonaceous aerosols (Birch, 1998). The thermal-optical method is applicable to nonvolatile, carbon-containing species only. Thermal-optical analyzers are practical, economical, and are routinely used for environmental and occupational monitoring of carbonaceous aerosols. Although the number of commercial laboratories currently is limited, an adequate number (3 in the U.S.) are available to cover the analytical demands of this program.

Thermal-optical analyzers operate by liberating carbon compounds under different temperature and oxidation environments. A small portion (or punch) is taken from a quartz-fiber filter sample and placed in the sample oven. The oven is purged with helium and the temperature is then stepped to a preset value. Volatilized compounds are converted to carbon dioxide (CO_2) in an oxidizer oven (MnO_2 at 870 C or higher), the CO_2 is subsequently reduced to methane (CH_4) in a methanator (nickel-impregnated firebrick heated to ~550 C in a stream of hydrogen), and CH_4 is quantified by a flame ionization detector (FID). In the second part of the analysis, an oxygen-helium mix is introduced and the remaining carbon is removed through combustion and quantified in the same manner. A schematic of the thermal-optical analyzer evaluated by NIOSH researchers is shown in Figure 7-3; an example of the instrument's output, called a 'thermogram,' is given in Figure 7-4.

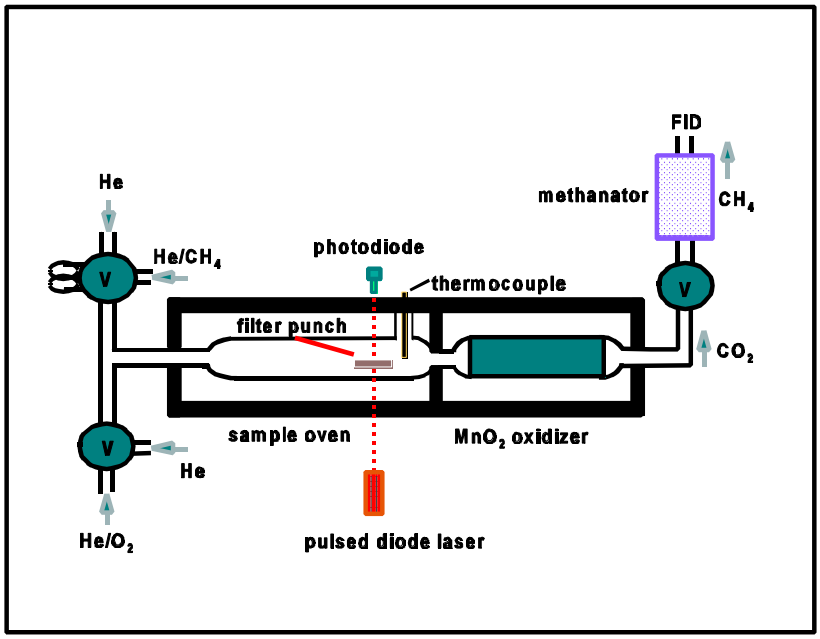

Figure 7-3. Schematic of a Thermal-Optical Analyzer

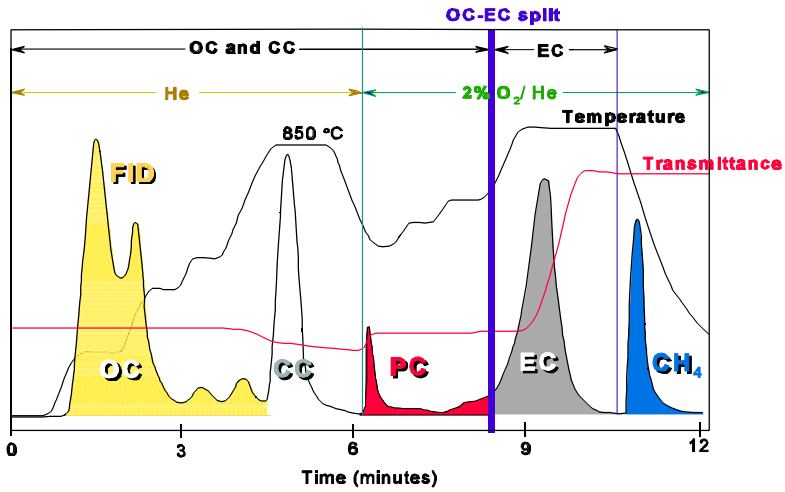

Figure 7-4. Thermogram for a sample containing organic, carbonate, and elemental carbon (OC, CC, and EC)

In NIOSH Method 5040, the sample oven is purged with helium and the temperature is stepped (to 250, 500, 650 and 850 C) to volatilize the organic and carbonate-source carbon. It is critical to ensure that trace oxygen is not present during the first part of the analysis. Potential sources of oxygen include leaks and inadequate helium gas purification. If present, trace oxygen will cause organic carbon to be overestimated and elemental carbon correspondingly underestimated. In the second part of the analysis, the temperature is lowered, a 2% oxygen/98% helium mix is introduced, and the temperature is then stepped to a maximum of 940 C. At the end of the analysis, a calibration gas standard (CH_4) is injected. Correction for pyrolysis is made by continuously monitoring the filter transmittance throughout the analysis. The point at which the filter transmittance returns to its original value is defined as the split between organic and elemental carbon. Designation of the split in this manner allows assignment of pyrolyzed organic carbon to the organic fraction.

In general, thermal-optical methods classify carbon as ‘organic’ or ‘elemental.’ Organic carbon is non-light absorbing carbon that is volatilized in helium as the temperature is stepped to a preset maximum (850 C). Elemental carbon is light-absorbing carbon (elemental or organic) and any non-light absorbing carbon evolved after pyrolysis correction. Depending on the sampling environment, carbonates [e.g., potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), magnesium carbonate ($MgCO_3$), calcium carbonate ($CaCO_3$)] also may be present in the sample. Carbonate-source carbon is quantified as organic by NIOSH Method 5040, wherein the sample is exposed to 850 C during the first part of the analysis (i.e., in helium only). Under these conditions, thermal decomposition of carbonate occurs. To quantify carbonate carbon, a second portion of the filter sample is analyzed after its acidification. Carbonate is taken as the difference between the pre- and post-acidification results (Note: the approach assumes a homogeneous filter deposit). Alternatively, carbonate carbon in a simple carbonate (i.e., not a bicarbonate) can be estimated by integrating the carbonate peak (typically the fourth peak in ‘thermogram’). The carbonate peak can be integrated separately within the instrument’s calculation software. This approach normally is taken when higher loadings of carbonate are present. In the case of the TOR method, carbonate in a filter portion is determined through on-line measurement of the carbon dioxide (CO_2) evolved upon acidification. Acid (0.04 M HCl) is injected directly onto the filter portion through an injection port. The sample oven is kept at ambient temperature while CO_2 is evolved, reduced to methane and quantified. (Note: This approach is subject to potential interference of adsorbed CO_2). Typically, carbonate carbon is not speciated in environmental samples because it has been found to constitute less than 5 percent of the total carbon in most samples (Chow et al., 1993).

It is important to remember that elemental and organic carbon have meaning only in the operational sense. That is, results reflect the method used and the appropriateness of a method

depends on its purpose. Operational methods differ from those used for specific, identifiable analytes (e.g., sulfate or sulfur), where a well-defined entity is quantified and laboratory standards are available for its determination. Because elemental and organic carbon are defined operationally, the details of the measurement method must be rigorously prescribed.

Only one organic and one elemental carbon fraction are reported in NIOSH 5040 (total carbon is the sum of these two). In contrast, four types of organic carbon and three types of elemental are defined by the TOR technique. In both instances, different classes of carbon are evolved from the sample during the analysis. In the case of Method 5040, the division into two fractions reflects the purpose of the method (i.e., occupational monitoring of diesel particulate). For other applications (e.g., source apportionment), additional fractions may be appropriate provided that the applied temperature program is repeatable over time. Otherwise, relative information will not be meaningful because nonconstant analytical parameters can affect the classification of carbon types.

7.3.2 Semi-volatile Organic Aerosols

Semi-volatile organic aerosols should not be considered on a routine basis due to the nonroutine and research-oriented nature of measuring these species. Identification of the ideal denuder, filter combination, and sorbents and development of routine sampling and analytical methods is complicated due to the variety of semi-volatile organic aerosol compounds in the atmosphere and their varying absorptive properties.

The collection of particulate organic matter can be accomplished using particulate sampling instruments equipped with quartz fiber or Teflon®-impregnated glass fiber filters. However, since many organic compounds are distributed between the gas and particle phases, additional sampling techniques are required to measure the particle phase semi-volatile organics. This methodology is susceptible to negative (desorption of semi-volatile compounds from the particles on the filters) and positive (adsorption of gases by the filter material) artifacts. Considerable experimental and theoretical effort has been expended to understand and correct for these vaporization and condensation effects. Denuder technology has been employed to provide a less artifact-encumbered approach for accurate determination of semi-volatile species because the gas phase is removed prior to the particulate phase. A sorbent or denuder after the filter may also be employed to collect any semi-volatile material desorbed from the filter.

For quantitation of individual organic compounds the denuder, filter, and sorbent is extracted individually with a suitable organic solvent (or a combination of solvents). The extract is then analyzed by gas chromatography (GC) combined with mass spectrometry (MS) or with

other specific detectors. Combined GC/Fourier transform infrared (FTIR)/MS techniques or high performance liquid chromatography (HPLC)/MS techniques are also used.

8.0 QUALITY SYSTEM REQUIREMENTS FOR $PM_{2.5}$ SPECIATION SAMPLING AND ANALYSIS

The quality system is a structured and documented management system describing how and by whom an organization assures quality in its work. When properly designed, a quality system encompasses both quality assurance and quality control through a quality management process by which quality system specifications are planned, implemented, and assessed. The implementation of a chemical speciation sampling and analysis component for the National $PM_{2.5}$ Monitoring Network requires adequate planning and management of a quality system to integrate the QA and QC requirements consistent with good field and laboratory practices. Quality assurance is an integrated system of management activities to ensure that a process or service is of the type and quality needed and expected by the end user (e.g., State or local regulatory agencies, EPA, general public, etc.). Quality control is defined as the overall system of technical activities that compares performance against defined standards to verify that stated requirements are met.

Every measurement consists of a value, a precision, an accuracy, and a validity. Quality control and quality auditing establish the precision, accuracy, and validity of measured values. Quality assurance integrates quality control, quality auditing, measurement method validation, and sample validation into the measurement process. The results of quality assurance are data values with specified precision, accuracy, and validity. Quality auditing is performed by personnel who are independent of those performing the procedures. A separate quality assurance officer performs these audits.

Quality control is the responsibility of each operator and is intended to prevent, identify, correct, and define the consequences of difficulties which might affect the precision and accuracy, and or validity of the measurements. The QC activities include: modifying standard operating procedures (SOPs) to be followed during sampling, chemical analysis, and data processing; equipment overhaul, repair, acceptance testing, and spare parts; operator training, supervision, and support; periodic calibrations and performance tests, which include blank and replicate analyses; and quality auditing.

There are several formal tools which can be employed through the quality management process to establish the quality system for a field monitoring and laboratory analysis program. They include:

- Quality Management Plans (QMP's)
- Data Quality Objectives (DQOs)

- Quality Assurance Project Plans (QAPPs)
- Standard Operating Procedures (SOPs)
- Audits and Reviews
- Data Quality Assessments (DQAs)

The development of data quality objectives and quality assurance project plans support the planning needs of monitoring studies. The implementation phase of a study is carried out using the quality assurance project plan and standard operating procedures. Assessment and redirection, if necessary, of activities within a study are performed by conducting management system reviews, technical assessments and audits, data quality assessment, and data validation. A properly developed quality management plan QMP encompasses the use of all the activities above. The QMP becomes the responsibility of the senior management within the organization administering the monitoring activities and discusses how and by when the following activities will be carried out:

- Management and organization;
- Quality system description;
- Personnel qualifications and training;
- Procurement of items and services;
- Documentation and records;
- Computer hardware and software;
- Planning;
- Implementation of work processes;
- Assessment and responses; and
- Quality improvement.

The reference listing at the end of this document, gives valuable guidance for the development of a monitoring and laboratory study quality system managed through the quality management process.

8.1 Standard Operating Procedures (SOPs)

The following section describes the requirements for SOPs and gives examples on quality auditing. The SOPs codify the actions which are taken to implement a measurement process over a specified time period. State-of-the-art scientific information is incorporated into the SOP with each revision. For $PM_{2.5}$ chemical speciation sampling and analysis, SOPs are needed which effectively detail major field sampling and laboratory operations. Each SOP should include the following basic elements:

- A brief summary of the measurement method, its principles of operation, its expected accuracy and precision, and the assumptions which must be met for it to be valid.
- A list of materials, equipment, reagents, and suppliers. Specifications are given for each expendable item.
- Designation of the individual to be responsible for each part of the procedure.
- A general traceability path, the designation of primary standards or reference materials, tolerances for transfer standards, and a schedule for transfer standard verification.
- Start-up, routine, and shut-down operating procedures and an abbreviated checklist.
- Copies of data forms with examples of filled-out forms.
- Routine maintenance schedules, maintenance procedures, and troubleshooting tips.
- Internal calibration and performance testing procedures and schedules.
- External performance auditing schedules.
- References to relevant literature and related standard operating procedures.

A QA handbook will be issued by U.S. EPA to address $PM_{2.5}$ monitoring with designated FRM or Class I FEM's. In addition to the field operations handbook, additional handbooks containing relevant procedures for laboratory operations and data processing/data validation operations should also be assembled for the $PM_{2.5}$ monitoring network. Table 8-1 gives an example of the SOPs required for $PM_{2.5}$ chemical speciation. These SOPs should be reviewed annually to ensure that procedures specified in the SOPs are actually being followed in field and laboratory operations.

8.2 Quality Audit Objectives

The quality auditing function consists of systems and performance audits. Systems audits start with a review of the operational and QC procedures to assess whether they are adequate to assure valid data that meet the specified levels of accuracy and precision. After reviewing the procedures, the auditor examines all phases of the measurement or data processing activity to determine that the procedures are being followed and the operational staff are properly trained. The systems audit is intended to be a cooperative assessment resulting in improved data rather than a judgmental activity.

Performance audits establish whether the predetermined specifications are being achieved in practice. The performance audit challenges the measurement/analysis system with known standards traceable to a primary standard. For data processing, the performance audit consists of

Table 8-1
Examples of Standard Operating Procedures

Subject	Observation/Method	Standard Operating Procedure
Chain-of-Custody	Filter Pack/Cassette Handling	Assembling, Disassembling, and Cleaning Procedures
	Shipping and Receiving	Sample Shipping, Receiving, and Chain-of-Custody
	Nylon Filter Cleaning	Preparation of Nylon Filters for Nitric Acid or Total Nitrate Sampling
	Quartz Filter Pre-Firing	Pre-firing of Quartz Fiber Filters for Carbonaceous Material Sampling
Chemical Analysis	Sample Sectioning	Sectioning of Teflon® and Quartz Filter Samples
	Filter Extraction	Extraction of Ionic Species from Filter Samples
	Mass	Gravimetric Analysis Procedures
	Elements (Na to Pb)	X-Ray Fluorescence (XRF) Analysis of Aerosol Filter Samples
	Nitrate NO_3) Sulfate (SO_4^{2-})	Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography
	Ammonium (NH_4^+)	Analysis of Filter Extracts for Ammonium by ion chromatography
	Soluble Sodium (Na^+) Soluble Potassium (K^+)	Analysis of Filter Extracts by ion chromatography
	High Temperature Organic Carbon (OH) Total Organic Carbon (OC) High Temperature Elemental Carbon (EH) Total Elemental Carbon (EC) Total Carbon (TC)	Thermal Optical Carbon Analysis of Aerosol Filter Samples
Aerosol Data	Data Validation	Field, Mass, and Chemical Data Processing and Data Validation

independently processing sections of the data and comparing the results. Performance objectives should be specified for the field or laboratory instruments on which performance audits are conducted. Audit findings are compared against these values to decide whether or not remedial action is needed.

8.3 Laboratory Performance Audit

The laboratory performance audit consists of the submission of known standards to routine laboratory procedures and of an interlaboratory comparison of those standards. Gravimetric analysis can be audited by weighing independent Class M or NIST-traceable standard weights and Teflon®-membrane filters, which will be pre-weighed and post-weighed at the primary laboratory and the audit laboratory for comparison. To audit the analysis of soluble species on quartz-fiber filters, a solution containing sulfate, sodium, nitrate, ammonium, and potassium is prepared and deposited in known amounts on quartz-fiber filters. Samples at a minimum of three concentrations are submitted to the routine chemical analyses for nitrate, ammonium, potassium, and sulfate by ion chromatography. To audit the analysis of the elements by x-ray fluorescence (XRF) on Teflon®-membrane filters, several thin film micromatter pure-element deposits are submitted for routine XRF analysis.

At the present time there are no widely accepted standards for elemental and organic carbon. Potassium acid phthalate solutions can be deposited on quartz-fiber filters to create organic carbon standards. A minimum of three sets of analyses at each concentration level and three blank filters should be analyzed for each audited chemical species.

An example of field and laboratory performance audit observations is shown in Table 8-2. Since performance audits for field operations will be addressed in U.S. EPA's quality assurance handbook, only laboratory performance audits are discussed here. The quality audit function needs to be incorporated into the $PM_{2.5}$ chemical speciation monitoring network to ensure the accuracy, precision, and validity of mass and chemical measurements.

Table 8-2
Examples of Laboratory Performance Audit Procedures

Parameter	Measurement Device	Performance Test Frequency	Performance Standard	Calibration Frequency	Calibration Standard	Audit Frequency	Audit Standard	Primary Standard
Aerosol Sample Flow	Candidate Chemical Speciation Sampler	Once per day	Calibrated Rotameter	At the Beginning and End of one-month Sampling Period or When Performance Tests are Out of Specification	Calibrated Rotameter	Once every 2 months	Mass Flow Meter	Certified Roots Meter
$PM_{2.5}$	Cahn 31 Electromicro-balance	1/10 Samples 3/10 Samples	NBS Class M Standard Weights Replicate	At Beginning of Weighing Session	NBS Class M Standard Weights	Once every 2 months	NBS Class M Standard Weights	NBS Class M Standard Weights
$PM_{2.5}$	Kevex 700/8000 XRF Analyzer	1/15 Samples 1/15 Samples	NBS Thin Film Standards Replicate	Quarterly	Micromatter Thin Film Standards	Once every 2 months	Prepared Standard Deposit	Thin Film Standard
$PM_{2.5}$ anions and cations	Dionex 2020i Ion Chromatographic Analyzer	1/10 Samples 1/10 Samples	Solution Standards Replicate	At Beginning of Each Run	ACS Certified Standard Solutions	Once every 2 months	N/A	ACS Certified Chemicals
$PM_{2.5}$ Carbon	DRI/OGC Thermal/Optical Carbon Analyzer	1/10 Samples 1/10 Samples	Methane Gas Replicate	Once/2-months or When Performance Test Tolerances Not Met	Methane, CO2, Gas and ACS Certified KHP	Once every 2 months	Standard KHP Solutions	ACS Certified Chemicals

9.0 DATA VALIDATION AND RECORDS MANAGEMENT

This section includes a discussion on the specifications relative to data base requirements and substrate data processing. Also, an outline is presented which defines a data multi-level validation scheme which includes assessment and integration of both laboratory analytical and field sampling data sets.

9.1 Data Base Requirements

Aerosol data processing consists of six general tasks:

1. **Recording** - The relevant information obtained at the time an operation is performed is registered on a data sheet, data logger, or other transfer medium.

2. **Input -** The data are transferred from the recording medium into computer-accessible files.

3. **Merging** - Data from various files pertaining to an individual sample or sampling day are retrieved and related to each other.

4. **Calculations** - Data items are combined in mathematical expressions to yield a desired result. These include pollutant concentration, accuracy, and precision.

5. **Data Validation** - Data are verified against earlier or redundant recordings, with calibration and operating records, and with each other.

6. **Output -** Data are arranged into desired formats for input to data interpretation and modeling software.

The data base management system must be cost-effective but flexible to accommodate both quantitative and qualitative information.

9.2 Data Validation

Data validation is the most important function of data processing. Sample validation consists of procedures which identify deviations from measurement assumptions and procedures. In this example, three levels of validation are applied, which will result in the assignment of a rating to each measurement: 1) valid; 2) valid but suspect; or 3) invalid.

Level I sample validation takes place in the field or in the laboratory and consists of flagging samples when significant deviations from measurement assumptions have occurred; verifying computer file entries against data sheets; eliminating values for measurements which are known to be invalid because of instrument malfunctions; replacement of data from a backup data acquisition system in the event of failure of the primary system; and adjustment of measurement values of quantifiable calibration or interference biases.

Level II sample validation takes place after data from various measurement methods have been assembled in the master data base. Level II applies consistency tests based on known physical relationships between variables to the assembled data. Several internal consistency checks that can be applied to evaluate validity when different particle size fractions are measured and submitted to chemical analyses. These include comparisons between mass and chemical concentrations in different size fractions (e.g., $PM_{2.5}$ concentrations must always be less than or equal to PM_{10} concentrations); comparisons between mass concentrations and the weighted sum of chemical species; charge balances between anions and cations; and comparisons between concentrations of the same species measured by different analysis methods (e.g., sulfate by IC and total sulfur and chlorine by XRF, soluble sodium and potassium by IC and total sodium and potassium by XRF). Data adjustments for quantifiable biases (e.g., large particle absorption corrections for aluminum) can be made in Level II validation if they are discovered after assembly of the master data base.

Level III sample validation is part of the data interpretation process. The first assumption upon finding a measurement inconsistent with physical expectations is that the unusual value is due to a measurement error. After tracing the path of the measurement, if nothing unusual is found, the value can be assumed to be a valid result of an environmental cause. Unusual values are identified during the data interpretation process as extreme values; values which would normally track the values of other variables in a time series; and values for which would normally follow a qualitatively predictable spatial or temporal pattern.

Data validation actions at each level are recorded in a data validation summary which accompanies the data base. Data base records contain flags to identify the level of validation which they have received at any point in their existence.

9.3 Substrate Data Processing

Aerosol data processing and validation requires the assignment of ID codes to substrates.

Field data records should include a recording of the ID's and their corresponding sampling sites, sampling dates, sampling times, sampling durations, sample flow rates, and deviations from normal sampling procedures. Laboratory records should contain instrument recordings of analytical outputs. Level I data validation involves flagging and editing of these individual data files with merging field laboratory data for sample sets. Level II data validation involves editing, flagging, re-analysis, calculation of ambient concentrations and precision. Also, this validation should provide for formatting and reporting of concentrations, precision, and data validation activities.

Field data can be entered into computerized data forms. Substrate ID's can be bar coded and then entered with a scanner rather than being typed. The screen forms have limits that do not allow entry of values lying outside a certain range. Every data item entered is verified by the data processing supervisor against the original data sheet.

A data base structure which contains fields for chemical concentrations and their uncertainties is formed. Each record contains sample ID's, sample volumes, sample times, sampling sites, and sampling dates which are integrated into this structure from the field file. All other fields contain the missing data default value. These defaults are replaced by laboratory analysis data as they become available. In this way, it is always possible to determine which analyses have been completed and which have not.

The laboratory chain-of-custody data base records the disposition of each sample and this data base can be consulted to determine the fate of missing values in the master data base. This independent tracking is needed to prevent sample ID's from being mixed up.

Every laboratory analysis instrument should be linked to IBM-PC compatible computers, and data should be recorded in Xbase (*.DBF) or ASCII text files. Barcode readers can be used to enter each analysis ID for an analysis run. Samples are keyed to sample ID codes, and data base programs associate records in the laboratory files with data in the master file. These programs also replace the defaults in the master data file with the laboratory values. Separate flags are entered at the time of analysis to indicate if a sample is an ambient sample, a source sample, a field blank, a laboratory blank, a replicate, a re-run, a performance test standard, or an audit standard. These flags are used to separate these quality control values from the individual data bases to generate quality control charts and precision estimates. Examples of field and laboratory validation flags are shown in Tables 9-1 and 9-2.

When data for a record have been assembled, Level II data validation comparisons should be conducted as discussed in Section 9.2. These additional validity checks should be applied to

chemically-speciated particle samples whenever possible. Statistical summaries, scatter plots, and time series plots of selected species concentrations are produced to identify outliers for investigation and potential re-run. A data validation summary is maintained in the character field associated with each record to provide a traceability trail for data adjustments, replacements, or deletions.

When sample concentration data have been assembled, the data base program creates another data base of ambient concentrations. Propagated precision and blank subtraction calculations are made at this stage. The field and laboratory data validation flags are assigned as part of the data validation process. Data validation summaries accompany this final data base.

Laboratories which have the capacity to analyze a high volume of samples usually employ laboratory information management systems (LIMS) to acquire, record, manipulate, store, and archive their data. Not all automated laboratory systems are LIMS. Automated laboratory systems that record data but do not allow changes to the data are not LIMS. For example, an instrument that measures weights and produces or maintains a readout of the weight is not a LIMS, if the true reading cannot be altered by a person prior to recording. If data entering automated laboratory systems can be manipulated or changed in any way by the action of a person prior to being recorded, then that automated laboratory system is a LIMS. The EPA has developed guidance on Good Automated Laboratory Practices (GALP) which addresses principles for ensuring data integrity in automated laboratory operations. In summary, the following areas are addressed:

- **Laboratory Management** - Following the collection, analysis, and processing of LIMS data, laboratory management shall ensure the overall quality of the data provided. Laboratory management ensures that personnel understand their roles; the QA unit monitors LIMS activities; resources are adequate and available; corrective actions are promptly taken; and approves SOPs.

- **Personnel** - have adequate education, training, and experience to perform assigned LIMS functions; have a current summary of their training, experience, and job description, including their knowledge relevant to LIMS design and operation, maintained at the facility.

Table 9-1
Examples of Ambient Field Sampling Data Validation Flags[a]

Validation Flag	Sub Flag	Description
A		Sampler adjustment or maintenance
	A1	Sampler audit during sample period
	A2	Sampler cleaned prior to sample period
	A3	Particle size cut device regreased or replaced prior to sample period
B		Field blank
D		Sample dropped
	D1	Sample dropped after sampling
	D2	Filter dropped during unloading
F		Filter damaged or ripped
	F1	Filter damaged in the field
	F2	Filter damaged when removed from holder
	F3	Filter wrinkled
	F4	Filter torn due to over-tightened filter holder
	F5	Teflon membrane separated from support ring
	F6	Pinholes in filter
G		Filter deposit damaged
	G1	Deposit scratched or scraped, causing a thin line in the deposit
	G2	Deposit smudged, causing a large area of deposit to be displaced
	G3	Filter returned to lab with deposit side down in a petri slide
	G4	Part of a deposit appears to have fallen off; particles on inside of a petri slide
		Finger touched filter in the field (without gloves)
	G5	Finger touched filter in the lab (with gloves)
	G6	
H		Filter holder assembly problem
	H1	Filter misaligned in holder - possible air leak
	H2	Filter holder loose in sampler - possible air leak
	H3	Filter holder not tightened sufficiently - possible air leak
	H4	Filter support grid upside down
	H5	Two substrates loaded in place of one
I		Inhomogeneous sample deposit
	I1	Evidence of impacting - deposit heavier in center of filter
	I2	Random areas of darker or lighter deposit on filter
	I3	Light colored deposit with dark specks
	I4	Nonuniform deposit near edge - possible air leak
L		Sample loading error
	L1	Teflon and quartz filters were loaded reversely in SFS
	L2	$PM_{2.5}$ and PM_{10} filter pack switched
	L3	Fine and coarse filters were loaded reversely in dichotomous sampler
	L4	Filter loaded in wrong port
M		Sampler malfunction
N		Foreign substance on sample
	N1	Insects on deposit, removed before analysis
	N2	Insects on deposit, not all removed
	N3	Metallic particles observed on deposit
	N4	Many particles on deposit much larger than cut point of inlet
	N5	Fibers or fuzz on filter
	N6	Oily-looking droplets on filter
	N7	Shiny substance on filter
O		Sampler operation error
	O1	Pump was not switched on after changing samples
	O2	Timer set incorrectly
	O3	Dichotomous sampler assembled with virtual impactor 180 out of phase; only PM_{10} data reported

Validation Flag	Sub Flag	Description
P		**Power failure during sampling**
Q		**Flow rate error**
	Q1	**Initial or final flow rate differed from nominal by >± 10%**
	Q2	**Initial or final flow rate differed from nominal by >± 15%**
	Q3	**Final flow rate differed from initial by >± 15%**
	Q4	**Initial or final flow rate not recorded, used estimated flow rate**
	Q5	**Nominal flow rate assumed**
R		**Replacement filter used**
	R1	**Filter that failed flow rate or QC checks replaced with spare**
	R2	**Filter sampling sequence changed from order designated on field data sheet**
S		**Sample validity is suspect**
T		**Sampling time error**
	T1	**Sampling during error of >± 10%**
	T2	**Sample start time error of >± 10% of sample duration**
	T3	**Elapsed time meter reading not recorded or recorded incorrectly. Sample during estimated based on readings from previous or subsequent sample.**
		Nominal sample during assumed
	T4	**Sample ran during prescribed period, plus part of next period**
	T5	
U		**Unusual local particulate sources during sample period**
	U1	**Local construction activity**
	U2	**Forest fire or slash or field burning**
V		**Invalid sample (Void)**
W		**Wet Sample**
	W1	**Deposit spotted from water drops**
	W2	**Filter damp when unloaded**
	W3	**Filter holder contained water when unloaded**
X		**No sample was taken this period, sample run was skipped. Analysis result reprocessed or recalculated.**

[A] **Samples are categorized as valid, suspect, or invalid. Unflagged samples, or samples with any flag except 'S' or 'V' indicate valid results. The 'S' flag indicates samples of suspect validity. The 'V' flag indicates invalid samples. Field data validation flags are all upper case.**

Table 9-2
Examples of Chemical Analysis Data Validation Flags[a]

Validation Flag	Sub Flag	Description
b		Blank
	b1	Field-dynamic blank
	b2	Laboratory blank
	b3	Distilled-deionized water blank
	b4	Method blank
	b5	Extract solution blank
	b6	Transport blank
c		Analysis result reprocessed or recalculated
	c1	XRF spectrum reprocessed using manually adjusted background
d		Sample dropped
f		Filter damaged or ripped
	f1	Filter damaged outside of analysis area
	f2	Filter damaged within analysis area
	f3	Filter wrinkled
	f4	Filter stuck to petri slide
	f5	Teflon membrane separated from support ring
	f6	Pinholes in filter
g		Filter deposit damaged
	g1	Deposit scratched or scraped, causing a think line in the deposit
	g2	Deposit smudged, causing a large area of deposit to be displaced
	g3	Filter deposit side down in petri slide
	g4	Part of deposit appears to have fallen off; particles on inside of petri slide
	g5	Unloved finger touched filter
	g6	Gloved finger touched filter
h		Filter holder assembly problem
	he	Deposit not centered
	he	Sampled on wrong side of filter
	he	Filter support grid upside down--deposit has widely spaced stripes or grid pattern
	he	Two filters in petri slide--analyzed separately
I		Inhomogeneous sample deposit
	I	Evidence of impaction - deposit heavier in center of filter
	I	Random areas of darker or lighter deposit on filter
	I	Light colored deposit with dark specks
	I	Nonuniform deposit near edge - possible air leak

Validation Flag	Sub Flag	Description
m		Analysis results affected by matrix effect
	m1	Organic/elemental carbon split undetermined due to an apparent color change of noncarbon particles during analysis; all measured carbon reported as organic
	m2	Non-white carbon punch after carbon analysis, indicative of mineral particles in deposit
	m3	A nontypical, but valid, laster response was observed during thermal optical analysis. This phenomena may result in increased uncertainty of the organic/elemental carbon split. Total carbon measurements are likely to be unaffected.
n		Foreign substance on sample
	n1	Insects on deposit, removed before analysis
	n2	Insects on deposit, not all removed
	n3	Metallic particles observed on deposit
	n4	Many particles on deposit much larger than cut point of inlet
	n5	Fibers or fuzz on filter
	n6	Oily-looking droplets on filter
	n7	Shiny substance on filter
	n8	Particles on back of filter
	n9	Discoloration on deposit
q		Standard
	q1	Quality control standard
	q2	Externally prepared quality control standard
	q3	Second type of externally prepared quality control standard
	q4	Calibration standard
r		Replicate analysis
	r1	First replicate analysis on the same analyzer
	r2	Second replicate analysis on the same analyzer
	43	Third replicate analysis on the same analyzer
	r4	Sample re-analysis
	r5	Replicate on different analyzer
	r6	Sample re-extraction and re-analysis
	r7	Sample re-analyzed with same result, original value used
s		Suspect analysis result
v		Invalid (void) analysis result
	v1	Quality control standard check exceeded ± 10% of specified concentration range
	v2	Replicate analysis failed acceptable limit specified in SOP
	v3	Potential contamination
w		Wet sample. Deposit spotted from water drops

[a] Analysis results are categorized as valid, suspect, or invalid. Unflagged samples, or samples with any flag except 's' or 'v' indicate valid results. The 's' flag indicates results of suspect validity. The 'v' flag indicates invalid analysis results. Chemical analysis data validation flags are all lower case.

- **Quality Assurance Unit** - inspect the LIMS at intervals adequate to ensure the integrity of the LIMS Raw Data.

- **LIMS Raw Data** - procedures and practices to verify the accuracy of LIMS raw data are documented and included in the laboratory SOPs, and managed.

- **Software** - SOPs are established, approved, and managed for the software used to collect, analyze, process or maintain the LIMS raw data.

- **Security** - Laboratory management shall ensure that security practices to assure the integrity of LIMS data are adequate. EPA laboratories and those of its agents (contractors) shall comply with EPA's information security policy.

- **Hardware** - LIMS hardware shall be of adequate design and capacity, and a description of the hardware documented and maintained. The hardware shall be installed and operated in accordance with the manufacturer's recommendations and be adequately tested, inspected, and maintained.

- **Comprehensive Testing** - When LIMS raw data are collected, analyzed, processed, or maintained, laboratory management shall ensure that comprehensive testing of LIMS performance is conducted, at least once every 24 months or more frequently as a result of software or hardware changes/modifications. These tests shall be documented and the documentation shall be retained and available for inspection or auditing.

- **Records Retention** - The retention of LIMS raw data, documentation, and records pertaining to the LIMS will comply with EPA contract, statute, or regulation; and SOPs for retention are documented, maintained, and managed.

- **Facilities** - The environmental conditions of the facility housing the data are regulated to protect against data loss, and the facility has adequate environmental storage capability for retention of raw data, storage media, documentation, and records.

- **Standard Operating Procedures** - Each SOP should be readily available and current. SOPs are periodically reviewed at a frequency adequate to ensure that they describe the current procedures. A historical file of SOPs shall be maintained.

Detailed information on GALP for LIMS and implementation guidance can be found in ***Good Automated Laboratory Practices*** (U.S. EPA, 1995b).

10.0 DATA QUALITY ASSESSMENT

A data quality assessment (DQA) of the speciation data is a scientific and statistical evaluation of the data to determine if they are of the right type, quality, and quantity to support their intended use. Data quality derives its meaning from the intended use of the data, that is, one must know in what context a data set is to be used in order to judge whether or not the data set is adequate. The DQA process is an iterative process comprised of five steps which are briefly described below.

1. **Review of the Data Quality Objectives (DQOs) and Sampling Design:** The DQOs are reviewed to assure that they are still applicable. If DQOs have not been developed, as may be the case for SPMs or non-NAMS monitors, specify DQOs before evaluating the data. Review the sampling design and data collection documentation for consistency with the DQOs.

2. **Preliminary Data Review:** Review QA reports, calculate basic statistics, and generate graphs of the data. Use this information to learn about the structure of the data and identify patterns or potential anomalies. In addition to the review of the QA reports by the State and regional data analysts, OAQPS/EMAD will prepare a report showing the quality of the data as the data begin to be reported. The purpose of the report is to summarize the quality of the data and to identify potential QA concerns. For example, certain speciation monitors may show more variability than others or certain seasons may show more variability. Such information is necessary for evaluating the data and providing direction for improvements in the $PM_{2.5}$ speciation network.

3. **Determination of Appropriate Statistical Test:** Select the most appropriate statistics for summarizing and analyzing the data based on review of the DQOs, the sampling design, and the preliminary data review. Identify key underlying assumptions about the data that must hold true for the statistical procedures to be valid.

4. **Verification of the Assumptions of the Statistical Test:** Evaluate whether the underlying data assumptions hold, or whether departures are acceptable, given the actual data and other information about the study.

5. **Conclusions Drawn from the Data:** Perform statistical tests and document the inferences drawn from those tests and evaluate performance of the sampling design.

The DQA process will reveal whether the decisions for which the data were collected can be made with the desired confidence, given the quality and quantity of the monitored data. If the data provide evidence strongly in favor of one conclusion, then the decision maker can proceed

knowing that the decision will be supported by unambiguous data. However, if the data do not provide strong evidence, then the decision maker has the information needed to determine whether to proceed with the decision, despite the reduced level of confidence, or whether to collect more or different data with the goal of increasing the confidence level. The strength of the DQA process is in the design which promotes an understanding of how well the data satisfy their intended use by progressing in a logical and efficient manner.

The DQA process needs to be conducted at the spatial resolution of a state or smaller geographical area. The reason for this is that the overriding objective of the speciation network will vary spatially, as may the quality of the monitored data. An exception to this is the network of 50 NAMS sites deployed with the primary objective of monitoring national trends in the constituents of $PM_{2.5}$. For these 50 sites, the objective is the same and SOPs need development to minimize the variability in the quality of the collected data. Specific details on how to conduct a DQA are described in ***Guidance for Data Quality Assessment*** (U.S. EPA, 1996).

11.0 REFERENCES

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