PARTICULATE MATTER (PM$_{2.5}$) SPECIATION GUIDANCE
Final Draft

Edition 1

October 7, 1999

U.S. Environmental Protection Agency
Monitoring and Quality Assurance Group
Emissions, Monitoring, and Analysis Division
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

FOREWORD

This PM$_{2.5}$ Speciation Guidance summary document is intended as a "living document" that will be revised and updated as needed throughout the planning, implementation and operation phases of the chemical speciation program. Hypertext links are provided throughout in order to quickly refer to documents and guidance that provide additional detail on the subject matter. Information regarding program goals and objectives, sampling equipment and guidance for sample collection, network design, selection of target analytes, quality assurance, and network operations for the PM$_{2.5}$ speciation program are provided. The guidance provides managers, site operators, laboratory services support personnel, and regulatory compliance data analysts an overview of the information needed to implement their PM$_{2.5}$ chemical speciation program. Comments on this document are welcome. Please address comments to:

Jim Homolya
U.S. Environmental Protection Agency
Mail Drop 14
Research Triangle Park, NC 27711
homolya.james@epa.gov

or

Joann Rice
U.S. Environmental Protection Agency
Mail Drop 14
Research Triangle Park, NC 27711
rice.joann@epa.gov

Table of Contents

List of Tables

List of Figures

EXECUTIVE SUMMARY

The EPA anticipates that approximately 300[1] monitoring sites will be included in the full chemical speciation network. Fifty-four NAMS (National Ambient Monitoring Stations) will be used for determining long-term trends of selected PM$_{2.5}$ constituents and an additional 250 SLAMS (State and Local Air Monitoring Stations) will be used to enhance the trends network and provide State and local agencies information for developing effective State Implementation Plans (SIPs). Ten NAMS trends sites will be designated as daily sampling sites to support health effects and exposure needs. Approximately 50 of the 250 SLAMS will be integrated with the related Supersites monitoring program. When States and local agencies implement their individual SLAMS speciation networks, they will be given flexibility in terms of selecting sites and sampling technology, sample collection period, site mobility, and identifying additional or alternative target analytes. As States consider integrating a portion of their speciation network with the designated Supersites, they are encouraged to develop partnerships with the academic community and related agencies responsible for specific Supersites studies.

SPECIATION DATA USES

Physical and chemical speciation data are anticipated to provide valuable information for:

<   Assessing trends in mass component concentrations and related emissions, including specific source categories.
<   Characterizing annual and seasonal spatial variation of aerosols.
<   Determining the effectiveness of implementation control strategies.
<   Helping to implement the PM$_{2.5}$ standard by using speciated data as input to air quality modeling analyses.
<   Aiding the interpretation of health studies by linking effects to PM$_{2.5}$ constituents.
<   Understanding the effects of atmospheric constituents on visibility impairment and regional haze.

The approach used for chemical speciation involves both sampling and analysis components. The single channel, polytetrafluoroethylene (PTFE) filter, Federal Reference Method is not capable of completely supporting a comprehensive set of analyses required to characterize the components of a PM$_{2.5}$ sample. Since the 40 CFR Part 53, Revised Requirements for Designation of Reference and Equivalent Methods for PM $_{2.5}$, equivalency requirements provide that no designations are required for speciation samplers, their design can be flexible to include additional filter collection media best-suited for the analysis of specific components.

---

[1] 300 sites are used as an estimate of operational units for planning purposes. The actual number of sites and samplers will be influenced by network design plans submitted by State and Local agencies in relationship to the total resources budgeted for PM$_{2.5}$ chemical speciation.

The PM $_{2.5}$ target analytes are similar to those within the Interagency Monitoring of Protected Visual Environments (IMPROVE) program and consist of an array of cations, anions, carbon species, and trace elements. Each series of analytes requires sample collection on the appropriate filter medium to allow chemical analysis with methods of adequate sensitivity. The methods used for analyses of these filter media include gravimetry (electro-microbalance) fortol mass; energy dispersive X-ray fluorescence (EDXRF) for trace elements; ion chromatography (IC) for anions and cations; and controlled-combustion thermal optical transmittance (TOT) analysis for carbon.

Although the speciation sampler designs vary, all involve the collection of multiple filter sample sets. A Quality Assurance Project Plan QAPP) will be developed for the speciation trends sites to provide guidance and procedures on pre- and post-sampling filter use, handling, transport and storage. In addition to guidance on sampling and handling, the EPA has a laboratory services contract in place to provide analytical support for filter analyses. As part of this contract, a laboratory QAPP will be developed to provide documentation (including standard operating procedures) on the measurement of the target analytes which will include laboratory quality assurance guidelines specific to the methods of analysis; and guidelines on standardized data reduction, validation, and reporting formats. The EPA plans for the speciation data to be submitted to the Aerometric Information Retrieval System (AIRS)Air Quality Subsystem (AQS) data base by the laboratory contractor. The EPA is developing laboratory SOPs that are complementary to the techniques used by various agencies and research groups operating ambient air particulate matter speciation programs. The SOPs will be based on analytical methods with proven application to the analysis of ambient particulate matter filter samples.

The EPA's approach to providing the speciation laboratory support services will begin with developing the laboratory specifications, analytical standard operating procedures, and associated quality assurance requirements. These guidelines will be utilized through the national laboratory services support program. Speciation site operators will be able to access analytical support from the laboratory through EPA Regional Delivery Order Project Officers who will service site needs in those states residing in their Regions. The Office of Air Quality Planning and Standards (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 the speciation monitors is projected for the fourth quarter of calendar 1999. The laboratory services contract was awarded for the National PM $_{2.5}$ Speciation Program and the QAPP is expected to be in place September of 1999.

1.0 INTRODUCTION

PM$_{2.5}$ chemical speciation is included in the monitoring requirements and principles set forth by the **Federal Register** (62 FR 38763), promulgated as part of the PM$_{2.5}$ National Ambient Air Quality Standard (NAAQS) review completed in 1997. As a requirement of this rule, EPA will establish a PM$_{2.5}$ chemical speciation network of approximately 50 core NAMS for routine speciation monitoring to provide nationally consistent data for the assessment of trends and to provide a basic, long-term record of the characterization of the metals, ions, and carbon constituents of PM$_{2.5}$. This network will serve as a model for other chemical speciation efforts and represents a small fraction of the overall chemical speciation effort that EPA expects to support with Federal funds. About 25 of these NAMS monitors are to be collocated at the Photochemical Assessment Monitoring Stations (PAMS), with the remaining sites to be selected in coordination among EPA, Regional Office Administrators, and the States. EPA recognizes that some PAMS locations may not be prime sites for locating these monitors and will accept alternative monitoring plans with technical justification for alternate locations. Speciation samples will be collected every 3 days at the NAMS sites.

At a minimum, the NAMS chemical speciation network will quantify mass concentrations and significant PM$_{2.5}$ constituents which include trace elements, sulfate, nitrate, sodium, potassium, ammonium, and carbon. This series of analytes is very similar to those measured within the Interagency Monitoring of Protected Visual Environments (IMPROVE) program.

EPA anticipates that approximately 300 sites will comprise the full chemical speciation network. In addition to the 54 NAMS for the trends network, another 250 SLAMS will be implemented to enhance the required network and provide information for developing effective State Implementation Plans (SIPs). The SLAMS will be allowed flexibility in terms of sampling frequency, site selection, site mobility, and addition of target species to address regional and local issues as needed. For example, some areas may choose to focus on specific episodes or seasons, such as a winter time wood smoke problem.

EPA does not believe that a single nationwide approach to speciation sampling and analysis is the best approach for all locations. The EPA expects that most sites will follow a sampling and analysis program similar to the core NAMS for their SLAMS; however, alternative approaches will be considered on a case-by-case basis through negotiation by State agencies with EPA Regional Offices and Headquarters. EPA encourages State and local agencies to consider additional chemical analyses beyond the constituents specified for NAMS. For example, detailed analysis for compounds comprising the organic carbon fraction could provide valuable insight into development of more refined source-receptor relations, particularly in areas with significant carbon based aerosols. EPA also encourages the use of continuous monitoring techniques to the extent possible. Recent advances in measurement technologies have provided reliable and

practical instruments for particle quantification over averaging times of minutes to hours. Commonly used continuous particle monitors measure inertial mass, mobility, electron attenuation, light absorption, and light scattering properties. The EPA has prepared ***Guidance for Using Continuous Monitors in PM$_{2.5}$ Monitoring Networks*** (U.S. EPA, 1998b), http://www.epa.gov/ttn/amtic/files/ambient/pm25/r-98-012.pdf to provide an overview of available continuous monitoring methods for suspended particles.

1.1 Programmatic Requirements

The chemical speciation program incorporates a balance of prescribed requirements, particularly for the routine NAMS, and the allowance for alternative sampling and analysis protocols for SLAMS within the program. It is not possible to anticipate the full range of sampling and analysis approaches State and local agencies may consider, especially in light of emerging technologies and forthcoming aerosol characterizations across different locations. In addition to providing specific guidance for NAMS, this document largely provides supportive or background information that can be utilized in formulating sampling and analysis plans for SLAMS. A description of required sampling and analysis plan elements and procedures for submitting monitoring network descriptions for EPA approval is provided in the ***Guidance for Network Design and Optimum Site Exposure for PM$_{2.5}$ and PM$_{10}$*** (U.S. EPA ,1997a), http://www.epa.gov/ttn/amtic/files/ambient/pm25/network/r-99-022.pdf. The State and Local agency monitoring network descriptions should provide the speciation monitoring strategy and document any deviations from approaches used in the NAMS.

State and local agencies should submit preliminary speciation sampling and analysis plans as part of all network description submissions to the appropriate Regional Offices. The due date for final network descriptions was July 1, 1998. Recognizing that little lead time exists between availability of guidance and the implementation dates, EPA expects final submission of the speciation network design plans in year 2000. 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.

1.2 Program Goals and Objectives

The overall goal of the PM$_{2.5}$ monitoring program is to provide ambient data that support the Nation's air quality program objectives. The major objectives of the program are given in the text box on the right. The entire PM$_{2.5}$ monitoring program includes a substantial mass network in

---

NAMS OBJECTIVES

The major objectives for the routine NAMS chemical speciation program are:

<   Annual and seasonal spatial characterization of aerosols.
<   Air quality trends analysis and tracking progress of control programs.
<   Development of emission control strategies.

---

addition to the speciation program. While the elements of this large program may be administered through individual mechanisms, all elements must complement one another in meeting multiple objectives as an overall integrated program. These overarching objectives are presented as background to a more detailed discussion of specific objectives addressed through the speciation program.

1.3 Program Roles and Responsibilities

A description of the organizational structure, responsibilities of the management staff, lines of authority, and required interfaces for those planning and implementing a monitoring program are provided in the ***Office of Air Quality Planning and Standards, Quality Management Plan*** which can be found at http://www.epa.gov/oar/oaqps/qa/qmp.pdf.

1.4 Program Components

The speciation program includes multiple elements with different, yet overlapping objectives. A table that outlines the major network elements and monitoring objectives is given in Table 1-1. The major program components include:

<   *About 54 NAMS dedicated to characterizing major aerosol mass components in urban areas of the United States for discerning long-term trends and providing an accountability mechanism to assess the effectiveness of emission mitigation programs:* 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 SLAMS when adequate network descriptions and justification are provided. Ten sites will be designated daily sampling sites to support health effects needs. In addition, ten NAMS "Mini-trends" sites will be installed late in 1999 to initially be used for sampler comparison studies, cold climate operational experience, and State agency training.

<   *Approximately 250 SLAMS for evaluating source-receptor relationships in support to SIPs, including more detailed characterizations, data for source attribution tools and evaluation of air quality simulation models and emissions inventories:* This element of the speciation program is the most flexible component of the entire PM$_{2.5}$ monitoring program. In broad terms, the principal objective of SLAMS is to support the development of emission control strategies. Tasks associated with strategy development that require speciated data include airshed characterization (i.e., resolving aerosols into its spatial, temporal, chemical and size properties), operation of source attribution tools (e.g., CMB8, UNMIX), an array of observational analyses that help to understand transport

Table 1-1. Network Elements and Monitoring Objectives

Network Element	Target Species	Sampling Frequency	PM$_{2.5}$ Monitoring Objectives						
			NAAQS Comparisons	Public Information /PSI	SIP Develop.	SIPs - Trends and Assessment	Health/ Exposure	Assess Visibility	Methods Testing
FRM Mass (1100 sites)	Mass	Daily, 1/3, or 1/6 based on MSA	U			U	U		
Continuous Mass (125 sites)	Mass	Continuous		U	U		U		
Speciation NAMS (54 Trends sites)	Elements, ions, carbonaceous aerosols	1/3 days		U	U	U	U	U	
Daily Speciation (10 NAMS sites)	Elements, ions, carbonaceous aerosols	Daily			U	U	U	U	
Speciation SLAMS (250 sites)	Elements, ions, carbonaceous aerosols, others as needed	1/6 days			U	U	U	U	U
Satellite SLAMS Speciation (50 sites)	Elements, ions, carbonaceous aerosols, others as needed	As specified by Super sites plan			U	U	U	U	U
Speciation IMPROVE (100 sites)	Elements, ions, carbonaceous aerosols	1/6 days			U	U		U	
Super sites (5-8 sites)	Elements, ions, carbonaceous and semi-volatile organic aerosols, others as needed	As specified by study plan		U			U	U	U

phenomena and precursor identification (e.g., ammonia versus nitrogen oxides), and evaluation of air quality simulation models and associated emissions input fields.

<   *Between 5 to 8 "Supersites" areas identified to serve as scientific research platforms for addressing advanced monitoring technology assessments, investigating atmospheric processes and their impacts on public health and epidemiological issues:* EPA anticipates establishment and operation of the Supersites network to 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. Among other objectives, the Supersites provide a means for testing new sampling technologies that eventually may be incorporated into the speciation network. More information on this program is available in the document entitled: ***Atmospheric Observations: Helping Build the Scientific Basis for Decisions Related to Airborne Particulate Matter*** (Albritton et. al. 1998), http://www.al.noaa.gov/WWWHD/pubdocs/PMMRW.pdf.

<   *Approximately 50 of the SLAMS sites to be integrated as "satellites" to the Supersites program:* Practical considerations and area specific needs of State and local agencies logically suggest various levels of coordination, ranging from a less resource demanding information and status communications approach for the SLAMS sites to more explicit coordination for 50 satellite sites. The EPA is requesting that State and local agencies join in collaborative partnerships with the appropriate local oversight group responsible for Super Sites activities. As of November, 1998, EPA has identified Atlanta, Georgia and Fresno/Bakersfield, California as initial Super Site locations.[2]

<   *Approximately 100 IMPROVE sites dedicated to assessing regional haze progress:* Clearly, technical justification exists for merging these monitoring efforts. Similarly, there is value in combining resource planning and network deployment efforts. A combined planning effort is far less burdensome than separate efforts. The IMPROVE chemically speciated data will also be useful to 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 program. For information regarding IMPROVE and other visibility monitoring programs visit the National Park Service web site at http://www2.nature.nps.gov/ard/ or the AMTIC visibility site at http://www.epa.gov/ttn/amtic/visdata.html

---

[2] Supersite contacts for Fresno/Bakersfield include Dr. Marc Pitchford, U.S EPA (702-895-0432) and Karen Magliano (916-322-5350), California Air Resources Board; Atlanta (Dr. Ellis Cowling, North Carolina State University, 919-515-7564 and Dr. Paul Solomon, U.S. EPA, 919-541-2698).

1.5 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. 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, is used to structure 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 assures that the type, quantity, and quality of the data are appropriate for the intended application, while guarding against committing resources to data collection efforts that do not support the program objectives.

For the PM$_{2.5}$ speciation monitoring network, the DQO process will proceed down two tracks due to differing primary objectives. For the NAMS, the primary objective is to determine trends on the national level. For the remaining SLAMS, objectives may vary and depend on the regional and 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; therefore, DQOs will need to be developed with both objectives in mind.

The Monitoring and Quality Assurance Group (MQAG) within the Emissions, Monitoring, and Analysis Division (EMAD) of the OAQPS has initiated an effort to ensure that the data collected by the ambient PM$_{2.5}$ speciation network is of a sufficient quantity and

> **SPECIATION TRENDS DQO**
>
> To be able to detect a 3-5% annual trend (increasing or decreasing) with 0.8 power within 3-5 years of initiation of sampling.

quality to support the intended uses of the data. This effort includes development of DQOs for the NAMS sites dedicated to measuring national trends in the PM$_{2.5}$ species (see text box). A detailed description of the DQO process, including a definition of power and the methods and models used to develop the NAMS DQOs are provided in the ***Data Quality Objectives for Detection of National Trends in Speciated Data,*** (U.S. EPA, 1998c), document which is found at http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/dqo3.pdf. Development of a DQO technical guidance document for the SLAMS sites is expected to be available September 1999. In addition to the development of these documents for the speciation program, EPA is developing an Air Pollution Training Institute (APTI) training video about the DQO development process for SLAMS.

1.6 Related Documents and References

An expert panel met on May 12-13, 1998 to review an earlier draft of the EPA guidance document for chemical speciation. The panel represents nationally-recognized expertise in fine particle and aerosol sampling and analysis as well as linkage to the assessment of the role of aerosol chemical components to health effects research. Other participants in this meeting included the EPA Speciation Workgroup and representatives from several States. The document, ***Summary of the Recommendations of the Expert Panel on the EPA PM$_{2.5}$ Speciation Guidance Document*** (Koutrakis 1998), http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/speciate.pdf provides a summary of the panel's comments and recommendations. The expert panel met again May 18-19, 1999 to review the revised guidance and discuss progress made in the development and implementation of the speciation program. A summary of the recommendations from the panel are included in ***Recommendations of the Expert Panel on the EPA Speciation Network*** (Koutrakis 1999) which can be found at http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/lvpanel.pdf

The ***Guideline on Speciated Particulate Monitoring*** prepared by DRI under cooperative agreement with EPA (http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/drispec.pdf) includes a detailed discussion on the physics and chemistry of atmospheric particles, particulate samplers, laboratory analysis methods, and measurement artifacts and interferences. Other documents, including the active web links, are listed below and 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, 1997a), http://www.epa.gov/ttn/amtic/files/ambient/pm25/network/r-99-022.pdf.

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), http://www.epa.gov/ttn/amtic/files/ambient/pm25/qa/m212covd.pdf.

Guidance for Using Continuous Monitors in PM$_{2.5}$ Monitoring Networks (U.S. EPA, 1998b), http://www.epa.gov/ttn/amtic/files/ambient/pm25/r-98-012.pdf

Visibility Monitoring Guidance Document (U.S. EPA, 1998d), http://www.epa.gov/ttn/amtic/files/ambient/visible/r-99-003.pdf

Air Quality Criteria for Particulate Matter (U.S. EPA, 1996a), http://www.epa.gov/ORD/WebPubs/execsum.html.

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.

For information regarding IMPROVE and other visibility monitoring programs visit the National Park Service web site at http://www2.nature.nps.gov/ard/ or the AMTIC visibility site at http://www.epa.gov/ttn/amtic/visdata.html

2.0 NETWORK DESIGN

This section provides the list of those sites selected for the speciation NAMS network and the general concepts to be applied when planning a PM$_{2.5}$ network outside the scope of the core NAMS. It is important to emphasize the need for integrating field and laboratory operations at the very early stages of program design. For example, SLAMS field and analytical laboratory personnel should be involved in DQO development, target species selection, and sampler selection and procurement to ensure compatibility among sampling and analysis methods, filter media, and practical quantifiable limits.

The PM$_{2.5}$ SLAMS network 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 developing planning areas, 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, 1997a), http://www.epa.gov/ttn/amtic/files/ambient/pm25/network/r-99-022.pdf and the Chapter 8 of the ***Guideline on Speciated Particulate Monitoring*** (U.S. EPA, 1999a), http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/drispec.pdf. This reference contains information that builds upon the guidance specified for PM$_{10}$ monitoring associated with the previous NAAQS.

2.1 Establishing Monitoring Objectives

The first step in network design is to determine the overall monitoring program goals and objectives and data quality objectives. 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 SLAMS in order to meet specified data use objectives.

2.2 Site Selection

Site selection is an important task in 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 (62 FR 38763).

> **SPECIATION TRENDS SITE SELECTION**
>
> The selection of MSAs, as well as PAMS cities, was based on a balance of factors which include:
>
> <   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.

Table 2-1 lists the locations of the sites for implementation of the NAMS trends network. See text box for factors used in determining trend site selection. The current recommendation includes 20 PAMS Type 2 sites and 34 other locations either identified by AIRS location or MSA. For information regarding monitoring frequency and sampled parameters at the PAMS refer to the AMTIC file information page at http://www.epa.gov/ttn/amtic/pamsmain.html and the PAMS Homepage at http://www.epa.gov/oar/oaqps/pams/.

The locations of existing PAMS and IMPROVE sites generally leave a large portion of the Central, Midwestern, and Southeastern United States 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 2-1 illustrates the overall geographical coverage of the speciation trends network. 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. 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 MSAs, it is suggested that a community-oriented $PM_{2.5}$ core site expecting the maximum concentrations be selected as the speciation trends site. In addition, it is desirable to outfit each of the 34 MSA sites selected with a 10-meter meteorological tower for collecting data on wind direction and speed, temperature, and humidity. Local siting limitations and/or unique spatial and temporal variability of $PM_{2.5}$ may require some balance and adjustment of the criteria outlined above to determine final site selection.

Table 2-1
Sites for the PM$_{2.5}$ NAMS Trends Network

Region	State/Commonwealth	MSA or Site	PAMS City Site	AIRS #
1	Connecticut		East Hartford	09-003-1003
	Maine		Kittery	23-031-3002
	Massachusetts		Boston [1]	25-025-0042
	Massachusetts		Chicopee	25-013-0008
	Rhode Island		East Providence	44-007-1010
	Vermont	Burlington		
2	New York		Queens	36-081-0097
		Rochester		36-005-6001
	New Jersey		New Brunswick [1]	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		
	West Virginia	Huntington		
	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		Northbrook [1]	17-031-4201
	Indiana	Indianapolis		
	Michigan	Detroit		
	Minnesota	Minneapolis		
	Ohio	Cleveland		
	Wisconsin		Milwaukee	55-079-0026
6	Louisiana		Capitol	22-033-0009

Region	State/Commonwealth	MSA or Site	PAMS City Site	AIRS #
	Oklahoma	Tulsa		
	Texas		Deer Park[1]	48-201-1039
			Hinton	48-113-0069
			Chamizal	48-141-0044
7	Kansas	Kansas City		
	Missouri	St. Louis		
	Nebraska	Omaha		
8	Colorado	Denver [1]		
	Montana	Missoula		
	North Dakota	Bismark		
	Utah	Salt Lake City		
9	Arizona	Phoenix		
	California	Riverside (Rubidoux) [1]		06-065-8001
			El Cajon	06-073-0003
			Simi Valley	06-111-2002
			Sacramento	06-067-0006
		Bakersfield		06-029-0014
		Fresno		06-019-0008
		San Jose		06-085-0004
	Nevada	Reno		
10	Idaho	Boise		
	Oregon	Portland		
	Washington	Seattle [1]		
Network Totals	**43 States**	**34 MSAs/Sites**	**20 PAMS Sites**	**54 Trends Sites**

[1] **Selected as a collocated speciation sampling site.**
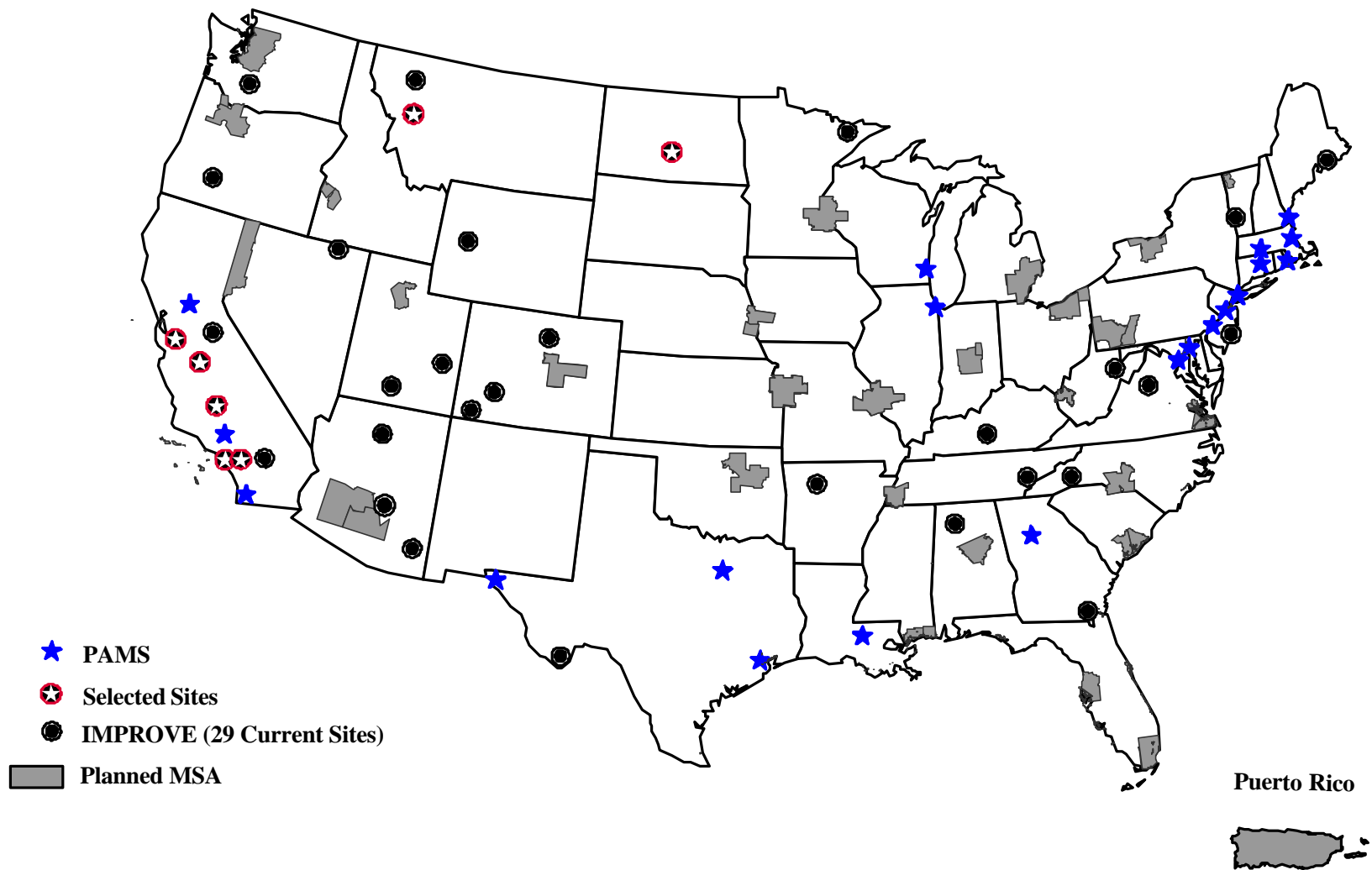
Figure 2-1. Speciation NAMS and current IMPROVE sites.

Legend:
- ★ PAMS
- ✪ Selected Sites
- ● IMPROVE (29 Current Sites)
- ▨ Planned MSA

Puerto Rico

2.3 Target Species and Sampling Frequency and Duration

For the SLAMS, the next step is to determine which chemical species beyond those specified for the routine NAMS, are to be measured and at what concentrations they are expected to be present in the ambient air. It is imperative to include those target species required to meet the data use objectives. For example, if source attribution is an objective, it may be desirable to measure species which are present in, or indicative of, the sources which are suspected of contributing to the PM$_{2.5}$ mass. Refer to Section 3.3 for a discussion of the NAMS target species.

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 versus 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. Based on the NAMS DQOs, 1 in 3 day sampling will occur for the trends sites, with a subset of 10 sites chosen for daily sampling to support the needs of health effects community.

2.4 Selection of Sampling System

Select a sampling system that provides the most cost-effective and reliable means of meeting the monitoring objectives. In complicated situations, especially those with many contributing sources, unknown sources, or secondary contributions, more complex sampling systems are needed. 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 6.0 for a discussion of the sampling methodology and candidate speciation sampler approaches for the core NAMS network.

2.5 Speciation Sampling and Analysis Plan

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 plan is given in Table 2-2.

Table 2-2

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 Elemental Analysis
2.0 AIR QUALITY IN THE STUDY AREA	6.4 Filter Extraction
2.1 Emissions	6.5 Ion Analysis
2.2 Meteorology	6.6 Carbon Analysis
2.3 Atmospheric Transformations	6.7 Specialized Analysis
2.4 Historical Air Quality Data	**7.0 QUALITY ASSURANCE**
2.5 Implications for PM$_{2.5}$ Study Design	7.1 Standard Operating Procedures
3.0 DATA ANALYSIS AND MODELING	7.2 Quality Audits
3.1 Data Evaluation	7.3 Standard Traceability
3.2 Descriptive Air Quality Analysis	7.4 Performance Tests
3.3 Descriptive Meteorological Analysis	**8.0 DATA PROCESSING, DATA BASE MANAGEMENT, AND CHAIN-OF-CUSTODY**
3.4 Source Profile Compilation	8.1 Data Base Requirements
3.5 Emissions Inventory	8.2 Data Validation
3.6 Receptor Model Source Apportionments	8.3 Data Processing
3.7 Trajectory Modeling	8.4 Substrate Data Processing
3.8 Secondary Aerosol Modeling	**9.0 MANAGEMENT, REPORTING, AND SCHEDULE**
3.9 Case Study Descriptions	9.1 Tasks and Responsibilities
4.0 PROPOSED AMBIENT MONITORING NETWORK	9.2 Resource Requirements
4.1 Sampling Sites	9.3 Reports
4.2 Sampling Frequency and Duration	9.4 Schedule and Milestones
4.3 Sampling Methods	**10.0 REFERENCES**
5.0 EMISSIONS CHARACTERIZATION	
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	

3.0 PARTICLE CHARACTERISTICS AND TARGET SPECIES

An aerosol can be defined as a suspension of solid or liquid particles in a gas, usually air and include dusts, fumes, smoke, mist and fog, haze, and smog. Aerosols are ubiquitous and not confined to only those areas where sources are located. Dusts formed by disintegration processes such as crushing, grinding, blasting and drilling can be blown up into the air; smoke can be emitted from the incomplete combustion of wood or agricultural refuse; haze or particles that incorporate some water vapor into or around them can be formed over vegetation; and smog can develop as a result of photochemical reactions is an anthropogenic emission common to large urban areas. The following section provides a general discussion of 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 for samples collected within the routine speciation monitoring network.

3.1 Particle Size Distributions

Size is one of the most important characteristics in the determination of the properties, effects and fate of atmospheric particles. Size classification of aerosol particles is greatly facilitated if the particles are assumed to be spherical. The size is then defined by radius or diameter. A size distribution can refer to number, density, volume, mass, or any other property that varies with particle size. Approaches typically used to classify particle size are given in the text box below.

Fine and coarse particles are often defined in terms of the modal structure of particle size distributions typically found in the atmosphere. An important feature of atmospheric aerosol size distributions is their multimodal nature. The PM$_{2.5}$, PM$_{10}$, and total suspended particulate (TSP) size fractions are ideally measured by air quality monitoring devices 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 ~0.1 to about 40 Fm in aerodynamic diameter, the PM$_{10}$ fraction ranges from ~2.5 to 10 Fm, and the PM$_{2.5}$ fraction ranges from ~0.1 to 2.5 Fm. No monitoring device is capable of passing 100 percent of the particles below a certain size

> **PARTICLE SIZE**
>
> Three approaches are typically used to classify particle size:
>
> <   modes, based on formation mechanisms and modal structure observed in the atmosphere (e.g., nuclei and accumulation modes which comprise the fine particle mode);
> <   cut point, based on the 50% cut-point of the specific sampling device (e.g., PM$_{2.5}$ and PM$_{10}$); and
> <   dosimetry, based on the ability of particles to enter certain regions of the respiratory tract.

and excluding 100 percent of the particles above that size. When particulate sampling occurs, each of the size ranges contain a certain number of particles above the upper size designation of each range.

For additional discussion regarding particle size distributions, refer to The ***Guideline on Speciated Particulate Monitoring*** (U.S. EPA, 1999a), http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/drispec.pdf and these references: Whitby and Sverdrup, 1980; Ondov and Wexler, 1998; Lundgren and Burton, 1995.

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. As mentioned previously, PM$_{2.5}$ is composed of a mixture of primary and secondary particles. Primary and secondary particles have long lifetimes in the atmosphere (days to weeks) and can travel long distances (hundreds to thousands of kilometers). They tend to be uniformly distributed over urban areas and larger regions, especially in the eastern United States. As a result, they are not easily traced back to their individual sources. The types of particles emitted directly (primary) include soil-related and organic carbon particles from the combustion of fossil fuels and biomass burning. The main sources of soil-related particles are road dust, construction, and agriculture. The main sources of combustion-related (secondary) 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 (NH$_3$). Gaseous organics from internal combustion engines as well as other combustion sources such as cooking are precursors to secondary organics. Sulfur dioxide, nitrogen oxides, and ammonia are important precursors to secondary aerosols (ammonium sulfate, ammonium bisulfate, ammonium nitrate) and information on their chemical abundance is useful at source and receptor locations to determine causes of high PM$_{2.5}$ levels. Table 3-1 provides a summary of the characteristics of PM$_{2.5}$.

Sulfate, acid (e.g., hydrogen ion, H$^+$), nitrate, organic and elemental carbon, trace elements, ammonium and water are often the major constituents of PM$_{2.5}$. Major sources of these substances are fossil fuel combustion by electric utilities, industry and motor vehicles; vegetative burning; and smelting or other processing of metals. Sulfur dioxide, NOx, and certain organic compounds are major precursors of secondary fine particulate matter. 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). 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.

Carbonaceous aerosols are a complex mixture of carbonate, elemental and organic carbon. Ambient studies have shown that carbonate carbon accounts for a negligible fraction of the total carbon in urban aerosol. Due to the great number of compounds with various volatility, the sampling of organic aerosols presents a difficult challenge. Carbonaceous aerosols are usually a major component of fine particulate mass. These particles consist of a multitude of organic and elemental carbon. Thousands of compounds have been identified in the ambient air, but in studies where individual organic compounds have been quantified, the sum of the measured compounds amount for only a few percent of the total organic mass (Bennett and Stockburger, 1994). Organic

aerosols in the atmosphere may result from direct source emissions (primary) or condensation of low vapor pressure products of gas phase reactions of hydrocarbons onto existing atmospheric particles (secondary) or the reaction product of primarily emitted organic compounds with atmospheric oxidants. Elemental carbon is emitted directly from fossil fuel combustion sources.

Table 3-1
Characteristics of PM$_{2.5}$

Formation Pathways	Chemical reactions Nucleation Condensation Coagulation Cloud/fog processing
Composition	Sulfate Nitrate Ammonium Hydrogen ion Elemental carbon (EC) Organic compounds Water Metals (Pb, Cd, V, Ni, Cu, Zn, Mn, Fe, etc.)
Solubility	Largely soluble, hygroscopic
Sources	Combustion (coal, oil, gasoline, diesel, wood) Gas-to-particle conversion of NO$_x$, SO3, and VOCs Smelters, mills, etc.
Atmospheric lifetime	Days to weeks
Travel distance	100s to 1000s of km

Source: Adapted from Wilson and Suh (1997)

Most of the PM$_{2.5}$ mass in urban and nonurban areas can be defined by a combination of the following components that are both primary and secondary aerosols:

<   **Sulfate:** Ambient sulfate can be either a primary or secondary constituent. 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.

<   **Nitrate:** Ammonium nitrate is the most abundant particulate 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 phase 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).

< **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. Ammonium sulfate is present primarily as neutralized ammonium sulfate while ammonium bisulfate and sulfuric acid are not present in great abundance. Atmospheric ammonia (NH_3) is a primary basic gas present in the atmosphere. Significant sources of NH_3 are animal waste, ammonification of humus followed by emission from soils, and losses of NH_3-based fertilizers from soils. Ammonia can absorb on wet surfaces or react with nitric acid to form ammonium nitrate.

< **Organic Carbon:** Particulate organic matter is an aggregate of thousands of separate compounds that usually contain more than 20 carbon atoms. Due to the number of organic compounds present, analysis of organic carbon presents a difficult challenge. No single analytical technique can characterize the organic compounds present in the atmosphere. Particulate organic carbon originates from combustion, geological processes, road dusts, and photochemistry. 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 are method dependent as well.

< **Elemental Carbon:** Particles emitted from combustion sources contain light absorbing elemental carbon, often called "black carbon". Particulate elemental carbon is a tracer for combustion-derived particles, whereas soil- and marine-derived aerosols contains negligible amounts and geological material contains variable abundances of elemental carbon. Elemental carbon is present along with organic carbon, and discrimination of particulate elemental from organic carbon depends on the analytical method used. For example, thermal optical analysis methods 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 and 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 water or fog droplets containing sodium chloride evaporate, many of the "dry" core particles are below 2.5 Fm 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.

<   **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 may not give up water, even when the particles are equilibrated at lower relative humidity.

<   **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.

3.3 Targeted Chemical Species

The target species of interest for the PM$_{2.5}$ chemical speciation program were selected based on the chemical speciation program data use objectives, primary constituents of PM$_{2.5}$, capability of current analytical methods, availability of filter types, and known analytical method performance characteristics. The target species are given in the text box at the right.

Although the target list contains chemical species that have been measured in previous studies, semi-volatile organic species are considered to be research-oriented or non-routine in nature. Promising, novel approaches for determination of semi-volatile organic aerosols and reducing artifacts due to sampling 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 for SLAMS. 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. Table 3-2 provides the filter types, target species, and analytical methods used for the routine NAMS program.

> **TARGET CHEMICAL SPECIES FOR NAMS**
>
> The target species for this program consist of:
>
> <   **anions** (particulate sulfate, nitrate) and cations (particulate ammonium, sodium, and potassium);
> <   **trace elements** (about 20 key elements from sodium through lead on the periodic table; for typical atmospheres, the analysis is useful for aluminum, silicon, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, nickel, copper, zinc, arsenic, selenium, bromine, cadmium, and lead).
> <   **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
> <   **particulate mass**.

Table 3-2
Chemical Speciation Filter Medium, Target Species and Analytical Methods

Filter Medium	Target Species	Analytical Technique
PTFE (Teflon®) filter	Elements and mass	EDXRF (IO-3.3) and Gravimetry
Nylon filter with nitric acid denuder	Nitrate, sulfate, ammonium, sodium, and potassium	IC (National Park Service Method)
Pre-fired quartz fiber filter	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. These ions will be measured at all NAMS speciation sites. The analysis of other important ions such as hydrogen and chloride are optional and may be included at SLAMS depending upon the network 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 PTFE or nylon filters and aqueous extracts of these filters analyzed using ion chromatography (IC). It is important to utilize the appropriate denuder for SO_2 gas while making particulate sulfate measurements using nylon filters and to maintain the denuder for optimal efficiency while in use. 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.

< **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 IC 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 the use of unanodized aluminum inlets.

Previous methods, which have used PTFE or glass fiber filters for nitrate collection, are negatively biased due to 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 PTFE or nylon filters will be analyzed using IC 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 as discussed above. 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 and consequently, a fraction of volatilized ammonium (in the form of ammonia) can be retained on a PTFE filter by reaction with the acid compounds. Therefore, it is reasonable to assume that ammonium loss will be less than the nitrate loss.

< **Potassium and Sodium:** 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 PTFE or nylon filters will be analyzed using IC 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 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. EDXRF is performed on PTFE (Teflon®) filters and determines the concentration of approximately forty elements (from sodium through lead on the periodic table); however, for typical atmospheres, the analysis is most useful 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 Carbonaceous Aerosols

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. For the purposes of this guidance document, we define total carbon as $C_t = C_o + C_e + C_c$. 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 using NIOSH method 5040 (NIOSH 1996, 1998).

The measurement of organic and elemental carbon is operationally-based and dependent 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 analytical method used. Because of this issue, it is extremely important that the same analytical method be used to determine carbon at the NAMS trends sites for consistency. Although no standards are currently available for the organic and elemental carbon content of particulate carbon from a sample filter, 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 using different analytical methodologies obtained variable results, but this can be expected with an operational-based method. The fact that a method is operationally-based does not mean it is not well-characterized or reasonably accurate. When the definition of an analyte is 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 used for calibration (e.g., sucrose) have no or little elemental carbon content.

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 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.

4.0 SAMPLING ARTIFACTS, INTERFERENCES, AND LIMITATIONS

This section briefly discusses some general difficulties that may be encountered while making aerosol measurements. Particle and gas removal by inlets, nitrate particle volatilization, adsorption of SO$_2$ and NO$_x$, organic carbon adsorption and volatilization, liquid water content, electrostatic charge, and passive deposition and recirculation are discussed. Some of these biases can be avoided or counteracted with alternative sampling and filter handling techniques. For additional information on humidity, electrostatic charge and contamination due to handling refer to ***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), http://www.epa.gov/ttn/amtic/files/ambient/pm25/qa/m212covd.pdf.

4.1 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. Due to availability and economy, most samplers are manufactured from aluminum, plastic, or galvanized steel. 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 allow nitric acid to pass through 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 measurement of nitric acid is an important 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 "static" charge which might attract suspended particles. However, the dimensions of most ambient sampling system inlets are sufficiently large that the attraction is negligible.

4.2 Nitrate Particle Volatilization

Nitrate losses during and after sampling have been well documented. 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. Losses of nitrate, ammonium, and chloride from glass and quartz-fiber filters that were stored in unsealed containers at ambient air temperatures for 2 to 4 weeks prior to analysis exceeded 50 percent (Witz et al. 1990). Storing filters in sealed containers and under refrigeration will minimize these losses.

4.3 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 artifacts 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 (Figure 4-1). 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 (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).

Volatilization of organic carbon is typically addressed by sampling with two quartz filters in series and correcting the carbon found on the first filter by the amount of carbonaceous material found on the second filter (Eatough et al., 1995, Appel et al., 1989, McDow et al., 1990). However, it is difficult to distinguish between the gas phase organic compounds collected on the particulate filter and the backup filter. In addition to collection of gas phase organics by the particle collecting filter, particulate semi-volatile organic compounds (SVOCs) can volatilize from the collected particles during sampling. These SVOCs can be absorbed by the filter or pass through the filter and be lost (Figure 4-1). If only a fraction of the SVOCs which can be adsorbed by the quartz filter is adsorbed by the first filter, then the second filter may contain either gas phase organic compounds, SVOC lost from particles and subsequently adsorbed, or both (Eatough et al., 1995).
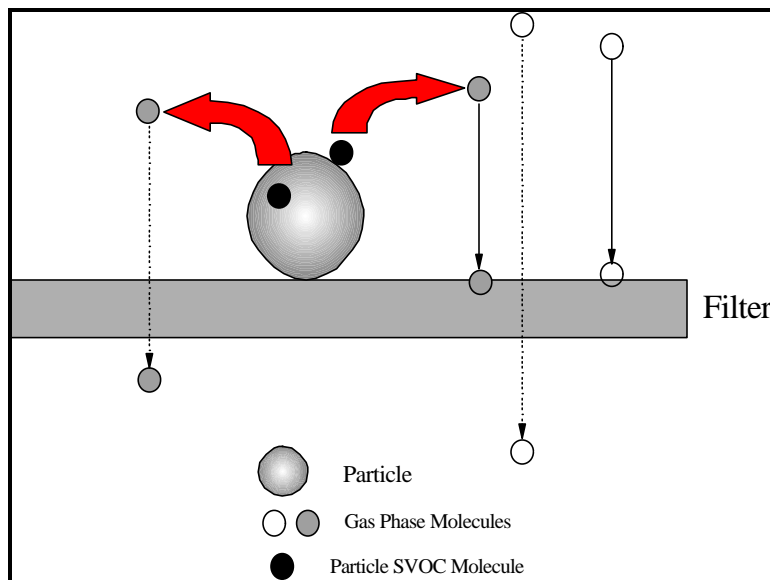
Figure 4-1. Artifacts associated with collection of particulate carbonaceous material (Adapted from Cui et al. 1997)

The capability for determination of semi-volatile organic aerosols will be added to the NAMS program as the technology further develops and is validated for routine use. The approach to be used for the NAMS speciation program to correct 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 will also be necessary to collect the gas phase semi-volatile organic

compounds volatilized from the particulate and the filter medium. The candidate speciation samplers have been designed to accommodate the necessary components as the collection methodology develops.

4.4 Sample Moisture

The importance of the liquid water content of ambient aerosol has been 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.

4.5 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, 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).

To minimize the static charge during gravimetric analysis, it is necessary to place a radioactive antistatic strip inside the microbalance chamber prior to weighing. It may also be necessary to pass each filter near, but not touching, the antistatic strip prior to weighing. The most commonly used low-level radioactive antistatic strips contain 500 picocuries of polonium-210 (Po^{210}E). 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.

4.6 Passive Deposition

Passive deposition of windblown dust on the filter prior to, and following sampling, can positively bias PM measurements. This deposition is expected to be minimal and dependent on sampler type and local conditions during the specific collection time. 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 is not expected to have an effect on PM$_{2.5}$ mass measurements; however, it can effect carbon and trace metal speciation 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.

4.7 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. When filters are handled, the analyst should wear gloves that are antistatic and powder-free to act as an effective contamination barrier. Gloves that are packaged in a box can carry an electrostatic charge and should be discharged by touching a good electrical ground after putting them on. The filters should be handled carefully by the support ring, if present, rather than the filter material using smooth, non-serrated forceps 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. Prior to use, forceps should be cleaned with alcohol and lint-free wipes before handling filters and then allowed to air dry. These precautions reduce the potential effect of body moisture or oils that may contact the filters and subsequently affect the analytical results.

4.8 Filter Media Artifacts

Sampling filters can collect gases as well as particles onto the surface, or onto the particles collected on the surface, constituting an artifact. This process may change the weight of the filter, causing artifacts that significantly alter the estimated concentration. Artifacts can be formed by oxidation of acid gases (e.g., SO_2, NO_2) or by retention of gaseous nitric acid on the surface of alkaline or other filter types. The magnitude of the effect is dependent on the concentration of the gases and also affected by the sampling period, filter composition and pH, and relative humidity. The magnitude and significance of the artifact is variable and dependent on local conditions and can be minimized or eliminated by use of an acid gas denuder. It is important to utilize the appropriate denuder for acid gases while making particulate speciation measurements and to maintain the denuder to provide optimal efficiency while in use. A regular denuder replacement schedule must be incorporated into any PM$_{2.5}$ speciation program. However, if the denuder is not properly maintained or replaced on a regular preventative schedule, acid gas breakthrough and the potential for artifact formation may occur.

Artifact formation due to the conversion of SO_2 on nylon filters has been shown to be highly variable and dependent on sampling conditions (Chan et al., 1986). The extent of the conversion of SO_2 to sulfate on Nylasorb® nylon filters was found to depend on both the concentration of SO_2 and the relative humidity. The conversion was higher at lower SO_2 concentrations. More recent work (Batterman 1997) to test the sorption of SO_2 on various filter types has shown the artifact formation for Teflon® and quartz fiber filters to be insignificant. The study did not directly address the potential for bias of sulfate measurements and examined the sorption on only clean filters without the presence of particles. Other work has shown there to be no statistical difference in measured sulfate on nylon filters with and without a denuder (Ashbaugh 1998).

Nitrate lost from inert filters (e.g., Teflon®) by volatilization and reaction with acidic materials also presents the potential for negative artifacts as discussed in Section 5.2. Nitrate losses during and after sampling have been reported. Generally, at temperatures greater than 30EC, most nitrate will be in the gas phase as nitric acid (HNO_3), while at temperatures lower than 15EC, 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 the 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 proper ventilation of the sampler housing is maintained. Volatile compounds can also leave the filter after sampling and prior to filter weighing or chemical analysis.

5.0 SAMPLING METHODOLOGY

Specific guidance for sampler selection and operation is provided for NAMS to ensure consistency across the network for comparison of spatial data and trends analyses. To allow flexibility for speciation sampling at SLAMS sites, State and local agencies can tailor sampling methodologies to their individual program needs. However, the SLAMS speciation network will be subject to a balance between the competing need for national consistency and the flexibility needed to address regional and local issues.

The "National PM$_{2.5}$ Sampler Procurement Contract" includes the provision for the purchase of over 300 speciation monitors, including accessories, for establishing the speciation monitoring network. In general, the speciation sampler design is flexible and can 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, 1997c); however, it is imperative that all methods incorporate particle inlets and size fractionators with equivalent particle size efficiency curves to the reference method for PM$_{2.5}$. See text box below for desirable features of a speciation sampler.

FEATURES OF A SPECIATION SAMPLER

Desirable features of a speciation sampler include the following:

< 	The inlet cut-point and separation profile must be comparable to the WINS, FRM.
< 	The sampler should use proven denuder technology to obtain nitrate and anion/cation measurements. The denuders should be tested for 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.

The final report from the PM$_{2.5}$ Speciation Expert panel suggests that selection of sampling devices for the speciation network be based on performance criteria and agrees that more than one type of sampler could be adopted for the trends network. The suggestion for performance based criteria was based on the need to allow flexibility to employ more than one sampling technique for the trends network and encourage further development of new sampling technologies. Refer to the Expert panel report for detailed discussion of the recommended performance based criteria for speciation monitors, ***Recommendations of the Expert Panel on the EPA Speciation Network*** (Koutrakis 1999), which can be found at http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/lvpanel.pdf.

There are several samplers which employ multiple channels and the appropriate filter media for use by State and local agencies in implementing the PM$_{2.5}$ NAMS speciation program. The samplers mainly differ by inlet design and approach to collection of particles less than 2.5µm. Designs include the capability to collect semi-volatile organic aerosol particles using diffusion

denuders followed by quartz fiber filters and solid sorbent traps. Three candidate sampler designs (RAAS™, MASS, SASS™) described below are being made available through the EPA's National PM$_{2.5}$ Sampler Procurement Contract. For information regarding acquisition of IMPROVE samplers, contact Lowell Ashbaugh at "*ashbaugh@crocker.ucdavis.edu*".

5.1 Operating Principle

The principle of operation involves several common components. Most fine particulate samplers have a size-separation device to separate particles so that only fine particles (those of approximately 2.5 microns or less) are collected onto the sample filter. Air is drawn through the sample filter at a controlled flow rate by a pump located downstream of the sample filter. The systems have two critical flow rate 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 optimized 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, temperature and barometric pressure probe and microprocessor control are also typical components of a speciation sampler. Key components of the candidate samplers for the speciation program are discussed below.

5.1.1 Particle Size Inlets

The inlet cut-point and separation profile must be comparable to the FRM 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. The IMPROVE, RAAS™, and SASS™ use a cyclone; the MASS uses a PM$_{2.5}$ FRM WINS assembly.

5.1.2 Denuder

Denuders are used immediately behind the size-selective inlet to remove gases that interfere with the aerosol measurements, 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. The annular denuder design allows for higher sampling flow rates and is well characterized for a wide range of applications involving acidic aerosols, ammonia, formaldehyde, and other chemical species. 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 may 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 are part of the sampler design primarily for the collection of nitrate on the nylon filter and organic carbon on the quartz filter. At this time, 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. The capacity and efficiency must be determined for the denuders used. 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 ***Inorganic Compendium Method Chapter IO-4*** (U.S. EPA, 1997b).

5.1.3 Filter Types

Each series of target species requires sample collection on the appropriate filter medium and chemical analysis by methods of adequate selectivity, sensitivity and reliability. The filter substrates used to collect particulate matter are chosen for compatibility with the species collected and the particular chemical analyses. Filter media include polytetrafluoroethylene (PTFE), quartz, and nylon. PTFE filters are employed to obtain atmospheric particulate matter samples for mass concentration determination and for subsequent measurement of a wide variety of trace elements. Pretreated quartz fiber filters are used to collect samples for determination of atmospheric carbonaceous aerosol concentrations. The nylon filter is used to capture nitrate species and water soluble anions and cations.

5.1.4 Flow Rate Measurement

Flow measurement and control for the speciation network are expected to be similar to the PM₂.₅ FRM requirements. The sampling system shall have a sample air flow rate control capable of providing a sample air volumetric flow rate, measured over intervals of not more than 5 minutes over a 24-hour period, that should 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 reduce data quality.

5.1.5 Filter Temperature Measurement

Filter temperature measurement and control is an important element of the PM₂.₅ chemical speciation network. This is due to the characteristics of the aerosols 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. The temperature should not differ from the transfer or independent temperature standard by more than ±2EC.

5.1.6 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. The

pressure should not differ from the transfer or independent pressure standard by more than ±10 mm Hg.

5.1.7 Relative Humidity Measurement

Particle growth due to accumulation of moisture is recognized in Section 4.4. When relative humidity is above 70%, particle growth due to accumulation may become significant. The capability for the sampler to measure ambient relative humidity is useful for input into the overall data interpretation process.

5.2 Sampler Intercomparison Study

Several different speciation sampler designs may be used in the overall sampling program. Therefore, an intercomparison study was performed to collect data which show intercomparison between the samplers relative to the performance of the FRM inlet, chemical species, and corresponding mass measurement. EPA's goal for the intercomparison study was to determine if there are differences between the three PM$_{2.5}$ speciation samplers available under the EPA National Sampler Contract, samplers historically used for PM$_{2.5}$ and the FRM. Sampler intercomparisons were also recommended as a result of the review by the Speciation Expert Panel.

Development of chemical speciation samplers for the EPA Sampler Contract was based on performance, rather than design criteria. This has allowed innovation in the development of these samplers and resulted in development of three slightly different approaches for meeting the performance criteria. The intercomparison also includes other historically accepted samplers (e.g., the IMPROVE sampler) and the FRM. The chemical species determined during the intercomparison study include only a subset of those specified for the routine NAMS speciation program.

A secondary objective of this study is to evaluate the operational performance or practicality of the samplers in the field, that is, reliability, ruggedness, ease of use, and maintenance requirements. While the FRM is considered the "gold" standard for mass, there are no such standards for the chemical components of PM$_{2.5}$. Thus, this intercomparison can only establish the relative equivalence of the samplers to each other on a species-by-species basis. For semi-volatile species (those in dynamic equilibrium between the gas and particle phases), the FRM which uses a PTFE filter provides only a lower limit of these species on the expected mass loading, since there is potential for loss of nitrate and SVOCs from the inert PTFE filters. For stable species (e.g., sulfate), the FRM should provide an accurate estimate of the mass loading for those species. Historical chemical speciation samplers like the Versatile Air Pollution Sampler (VAPS), developed under an EPA contract, are included in the study to provide a less biased value for semi-volatile species and provide an additional set of samples for comparison. To read the draft *Field Program Plan for The PM$_{2.5}$ Chemical Speciation Sampler Evaluation Study* (Solomon et al., 1998), refer to the following Internet site: http://www.epa.gov/ttn/amtic/files/ambient/pm25/casac/progra1.pdf.

5.2.1 Study Design

The design of this program is constrained by time limitations and resources available to complete the program (e.g., number of samplers, personnel, and funding). However, the statistical design was prepared with an understanding of these limitations and the design chosen provides a robust evaluation of the samplers relative to each other, to several samplers used historically to obtain similar data, and to the FRM. The major scientific hypotheses to be addressed by this intercomparison study are shown in the text box below.

MAJOR HYPOTHESES OF THE INTERCOMPARISON STUDY

<   The first is associated with reconstructing the FRM mass.
<   The second is associated with inter-comparing the concentrations from the various speciation samplers, which consist of two parts: The first part is associated with examining differences among the samplers, without regard to why there are differences, if they exist. This will be addressed through analysis of variance (ANOVA). The second part will examine why there are differences, if they exist. Some are expected due to the different methods employed. This will be primarily addressed using the Student's t-Test.
<   A third set of hypotheses is given dealing with the potential affect of different analytical methods on measured concentrations of the chemical components of PM$_{2.5}$. These include the effect of vacuum XRF or atmospheric pressure XRF on nitrate concentrations measured on PTFE filters and the effect of thermal optical reflectance (TOR) vs. thermal optical transmittance (TOT) on OC/EC concentrations.

The first two hypotheses are predicated on the assumption that the cut points for the samplers in this study are the essentially the same. This is a required assumption to address the hypotheses. Also, it is important to establish the precision of the instruments and this will be done by collocating samples at one site. While this provides only a limited assessment of the precision, it will provide a first cut estimate of the precision for the statistical analysis to be performed. If for example, the precision is estimated at 50%, then determining differences among samplers will not be as informative as if the precision were 10-15%. As a benchmark, the coefficient of variation for the differences in concentrations from collocated FRM instruments is required to be less than 10%, according to 40 CFR Part 58, Appendix A. Depending on the species, a range of precision from less than 10% to about 30% is anticipated (Solomon et al., 1998).

5.3 Available Candidate Sampling Approaches

The candidate sampling approaches to chemical speciation include the Reference Ambient Air Sampler (RAAS™), Mass Aerosol Speciation Sampler (MASS), Spiral Ambient Speciation Sampler (SASS™) and IMPROVE. At a minimum, the speciation monitors used for these approaches contain PTFE, nylon, and quartz filter media and provide for the collection of the target analytes of interest. The PTFE filter will be used for mass and elements; quartz will be used for carbonaceous 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 particle separation device. In any case, the monitor design must have the capability of collecting particles in a manner comparable to the FRM and with an aerodynamic diameter equal to or less than 2.5 Fm. The following is a brief description of candidate chemical speciation monitor configurations for both NAMS and SLAMS networks. For detail information, refer to the manufacturer's operation manual. In addition, a very short description of single channel, continuous, saturation and special purpose monitors also appropriate for use in non-routine SLAMS or special studies is provided. Table 5-2 provides a comparison of the sampler designs, filter types and target species analyzed.

5.3.1 IMPROVE

Each IMPROVE sampling module consists of an inlet stack; 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; a vacuum pump to produce the flow; and solenoids for exposing filters. IMPROVE samplers consist of up to four parallel modules (three modules for PM$_{2.5}$ and one for PM$_{10}$) and a common controller. A programmable clock, located in one of the filter modules or in a separate module, controls pump and solenoid switching for all filter modules. The pump(s) is housed separately. A schematic diagram and photographs of the IMPROVE sampler PM$_{2.5}$ modules configuration can be found at http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pm25pict.pdf. Each of three modules utilizes a cyclone operating at a flow rate of 22.7 L/min to provide for a cut point of 2.5Fm.

One PM$_{2.5}$ module uses a PTFE membrane filter to collect aerosols for mass measurement and subsequent analysis for mass and trace elements. A second module is equipped with a sodium carbonate denuder and nylon filter to measure particulate nitrate, anions and cations. The third 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 magnehelic gauges which measure pressure drop across the cyclone and filter. A secondary measurement, using a pressure gauge behind the filter, provides a quality assurance check and ensures that the cassettes are properly seated. Flow control is maintained by a critical orifice between the filter and pump.

Table 5-2
Target Analytes Associated with Filter Type and Sampler Design

Sampler Type	Channel or Module	Denuder & Filter Media	Mass	Elements	SO_4^{2-}	NO_3^-	Particulate NO_3^-	Volatilized NO_3^-	NH_4^+, Na^+, K^+	TC, OC, EC, CC
IMPROVE	1	PTFE	U	U						
	2	Na$_2$CO$_3$/Nylon			U		U		U	
	3	Quartz 1								U
MASS 400	1	Na$_2$CO$_3$ /PTFE	U	U	U	U			U	
		Backup Nylon						U		
MASS 450	1	Quartz								U
RAAS™	1	Quartz								U
	2	PTFE	U	U						
	3	Optional								
	4	MgO/Nylon			U	U	U		U	
SASS™	1	PTFE	U	U						
	2	PTFE								
	3	MgO/Nylon			U	U	U		U	
	4	Quartz								U
	5	Optional								

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. Additional information on the IMPROVE can be found at the National Park Service web site at http://www2.nature.nps.gov/ard/ or the AMTIC visibility site at http://www.epa.gov/ttn/amtic/visdata.html.

5.3.2 *Mass Aerosol Speciation Sampler (MASS 400 and MASS 450)*

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

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

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

The MASS 450 sampler configuration for the collection of organic and elemental carbon and semi-volatile organic particles may be accomplished through the use of a XAD-coated denuder; a quartz filter pack downstream of the denuder collects only the condensable organics. The semi-volatile organic species that evaporate from the filter during sampling are collected using a PUF/XAD trap downstream of the filter. The extract of the trap may be analyzed by GC/FID/MS methods to quantify the mass of 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 their adsorption (positive artifact).

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

5.3.3 Reference Ambient Air Sampler (RAAS™)

The RAAS™ consists of an inert inlet, two size selective cyclones, four sampling channels, filter media for sample collection, critical orifices to provide the proper flow, flow sensing devices and a vacuum pump. Ambient air is pulled through a wind direction and wind speed insensitive inlet and through an inert inlet line that is insulated from direct heating by the sun. The inlet has no size selective function. The air sample is directed via the sample downtube to a primary sample flow splitter into two streams. Each of the two flow streams in turn move through a AIHL-design cyclone separator which removes coarse particles with diameters larger than 2.5 Fm. The cyclone requires a precise flow of 24-liters-per-minute to produce the correct cut point for sample collection. Following one side after splitting, the remaining particulate and gases are split again through the sample manifold into one, two or three outlet channels. The flow streams are then directed through the sample filters. The flow rate through each filter holder is controlled by a critical orifice that can be changed if a different sampler configuration flow rate is desired for special studies. The other half of the primary flow stream duplicates this flow path. A total of six channels are available for various speciation sampling objectives. For the routine chemical speciation program a total of 4 channels are used as shown in the schematic and photographs found at http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/pm25pict.pdf.

All inlet, manifold, connector and cyclone parts are fabricated from polytetrafluoroethylene (PTFE)-coated aluminum. Any combination of reactive annular denuders or filter materials can be attached with consideration for the flow requirements and species to be measured. In the normal sampling mode, the combined flow rate to both filter holder assembles is 24-liters-per-minute, which is divided into one 16.7 and one 7.3 liter per minute subdivisions. Two of these sampling lines collect fine particles on standard 46.2-mm diameter PTFE filters for subsequent mass, elements and ion analyses. Two PTFE filters are used because samples intended for X-ray fluorescence analysis may be placed in a vacuum chamber during analysis leading to the expected loss of volatile aerosol components, thereby making it desirable to use a second PTFE filter for analysis of ionic species.

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

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

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

5.3.4 Spiral Ambient Speciation Sampler (SASS™)

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

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

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

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

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

5.4 Other Monitor Types

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

5.4.1 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 targeted chemical species. This approach may be used in cases where chemical speciation analyses are performed on a Teflon® filter, after gravimetric analyses has 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 other filter media 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. 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.

5.4.2 Continuous Monitors

The EPA encourages the use of continuous monitors as part of the SLAMS speciation monitoring program. Continuous monitors should only be considered for use at routine 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 analyzer, 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), http://www.epa.gov/ttn/amtic/files/ambient/pm25/r-98-012.pdf for additional information regarding the use of continuous in-situ measurements of suspended particles, their chemical components, and their gaseous precursors.

5.4.3 Saturation Monitors

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.

5.4.4 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). The SPMs will not be used as NAMS samplers; although they may be collocated with NAMS speciation and FRM samplers.

Special purpose monitors are a separate component of the PM$_{2.5}$ network and as such are not part of the core network. 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$_{2.5}$ network and how data will be evaluated.

6.0 SAMPLE ANALYSIS

With the goal of ensuring data quality for several thousand filter analyses per year, which utilize a range of analytical methods for the species required, 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 national laboratory services support program consisting of contracted services with a qualified laboratory capable of providing consistent laboratory services support for all target analytes. The extent of the services required depends on the total number of sites and the sampling frequency, as well as the level of participation by State and local agency laboratories that provide analytical services.

The contract laboratory is required to develop an EPA-approved laboratory QAPP and undergo an on-site QA audit prior to analysis of samples. The laboratory QAPP is to include laboratory quality assurance guidelines specific to the methods of analysis and guidelines on standardized data reduction, validation, sample handling, chain-of-custody, and report formats. The laboratory QAPP will include SOPs based the analytical techniques specified by EPA. These techniques are based on methods with proven application to the analysis of the species of interest and complimentary to those used by various agencies and research groups operating ambient air particulate matter speciation programs. The speciation analytical guidelines developed by EPA can also be used by State laboratories with facilities to provide local support, if appropriate, for an individual State-level monitoring network. In addition, EPA is considering a process of evaluating alternative test methodology which may be proposed as part of an alternative monitoring plan.`In such a process, an equivalency methodology guideline would have to be developed that can be used by States and EPA to determine that the proposed method is acceptable.

The operational schedule for providing the speciation laboratory support services began with development of a program team of EPA Office of Air Quality Planning and Standards (OAQPS) and Regional Office personnel. The OAQPS has provided the development of the required guidance and method selection with input from the Office of Research and Development (ORD), EPA Regional Offices, and the PM$_{2.5}$ monitoring technical community. Initial deployment of NAMS speciation monitors for the "Mini-trends" network is projected for the end of 1999. Allowing time for the contract laboratory QAPP to be developed and the on-site laboratory QA audit to occur, the laboratory services support contract will be in place by July 1999.

Analytical support from the contract laboratory will be accessed through three EPA Regional Delivery Order Project Officers (DOPOs) in Regions 2,5 and 8. The contract laboratory will designate a Services Program Manager (SPM) for work performed under the contract. The SPM is responsible for the performance of the work issued in accordance with the terms and conditions of the contract. The SPM provides information on the status and progress of the services to the EPA Project Officer and the EPA Delivery Order Project Officers (DOPOs). The SPM notifies the PO/DOPO regarding any problems encountered in the performance of work and works in conjunction with the PO/DOPO to resolve those problems.

Analytical needs are initially submitted by a State to the corresponding EPA Regional Speciation Coordinator (RSC). The RSC consolidates all analytical requests received from States within their Region and submits them to the appropriate EPA DOPO. The DOPO, in turn,

consolidates analytical requests from several Regions and communicates requests to the EPA PO. The Project Officer, as necessary will issue Delivery Orders to the Contract Laboratory. The Contract Laboratory prepares the appropriate filter media for sampling and delivers the media to the State. After sample collection, the State returns the samples along with sampler information to the Contract Laboratory. In addition, selected field quality assurance samples will be collected by the States and submitted to an appropriate EPA QA laboratory for analysis. The Contract Laboratory performs analysis, Level 0 and Level I data validation on all data sets and then enters the data into AIRS. After data validation and AIRS data entry has been completed, the contractor submits the data sets in both hard copy and electronic format to the appropriate State. The contractor submits copies of the Level I data validation checklists and hard copies of the monthly analytical data reports to the States and the appropriate EPA DOPO for review, acceptance, and recommendation for payment to the EPA Project Officer. As part of the laboratory services support contract, the speciated data are to be submitted directly to the Aerometric Information Retrieval System (AIRS), Air Quality Subsystem (AQS) data base. AIRS submittal will occur within 30 days following level I data validation by the contract laboratory.

6.1 Analysis Techniques

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.

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. The analysis techniques performed on a particular filter type may vary depending on the specific sampler type and configuration used for sample collection. The following sections outline the filter analysis methods for the target chemical species categories of elements, ions, and carbonaceous aerosols to be used for NAMS.

6.1.1 Elements

Energy dispersive X-ray fluorescence (EDXRF) by Method IO-3.3 (U.S. EPA, 1997d) is chosen to characterize the elemental composition of the aerosol deposits on PTFE filters for the NAMS. Interest in elemental composition is commonly derived from concerns about health effects and the utility of

> **ELEMENTS**
>
> EDXRF by Method IO-3.3 is the method of choice for analysis of elements for the NAMS speciation program.

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 may cause volatile compounds (nitrates and organics) to evaporate. As a result, species that can volatilize such as ammonium nitrate and certain organic compounds can be lost during the analysis. The effects of this volatilization are important if the PTFE filter is to be subjected to subsequent analyses of volatile species.

6.1.2 Ions

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

> **IONS**
>
> Ion Chromatography (IC) is the method chosen for analysis of ions for the NAMS.

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, and ammonium 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 chosen for the NAMS speciation program for the analysis of the target cations (ammonium, sodium, and potassium) and anions (nitrate and sulfate).

6.1.3 Carbonaceous Aerosols

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

CARBON
NIOSH 5040 (TOT) is the method selected for total, elemental, organic and carbonate carbon analysis for the NAMS.

(K_2CO_3), sodium carbonate (Na_2CO_3), magnesium carbonate ($MgCO_3$), calcium carbonate ($CaCO_3$)] may be specifically determined from a second 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 (TOT) or reflectance (TOR) throughout the analysis.

For the NAMS chemical speciation program, total, organic, elemental, and carbonate carbon will be determined by thermal/optical transmittance (TOT) and 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 routinely used for environmental and occupational monitoring of carbonaceous aerosols.

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) and carbonate carbon as simple carbonate (i.e., not a bicarbonate) can be estimated by integrating the carbonate peak (typically the fourth peak in 'thermogram'). 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 non-constant analytical parameters can affect the classification of carbon types.

6.1.4 Semi-volatile Organic Aerosols

Identification of the ideal denuder, filter combination, and sorbents and development of routine sampling and analytical methods for semi-volatile organic aerosols is complicated due to the number and variety of semi-volatile organic aerosol compounds in the atmosphere and their varying absorptive properties.

> **SEMI-VOLATILE ORGANIC AEROSOLS**
>
> Semi-volatile organic aerosols are not considered for NAMS due to the non-routine and research-oriented nature of measuring these species.

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 adsorption 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.

7.0 QUALITY SYSTEM REQUIREMENTS FOR PM$_{2.5}$ SPECIATION SAMPLING AND ANALYSIS

The EPA spends millions of dollars annually collecting environmental data for scientific research and regulatory decision making. In addition, the regulated community may spend as much as an order of magnitude more each year responding to Agency compliance requirements. To protect this investment, EPA requires that organizations implement a quality management system to assure that the environmental data the Agency uses for decision making is the type, quality, and quantity needed. The National Center for Environmental Research and Quality Assurance's Quality Assurance Division (QAD) serves as the central management authority for the Agency's Quality System and develops QA procedures and policies for implementation Agency-wide.

Any monitoring network has inherent measurement uncertainty, including the national chemical speciation monitoring network. EPA policy is to quantify this measurement uncertainty to provide the decision makers and stakeholders with useful information for use in providing direction and decision making regarding the monitoring network. To quantify this measurement uncertainty, EPA issued EPA Order 5360.1 (1998) which requires that all environmental programs conducted by EPA, or on EPA's behalf, be supported by a mandatory quality system. The quality system is a structured and documented management system describing how and by whom an organization assures quality in its work. The EPA is responsible for developing the PM$_{2.5}$ chemical speciation program quality system. The ***Strategic Plan for Development of the PM$_{2.5}$ Quality System for Chemical Speciation Trends Sites*** (U.S. EPA, 1999b) provides the general outline for development of a quality system (http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/strate1.pdf).

When properly designed, a quality system encompasses both quality assurance (QA) and quality control (QC) through a quality management process by which quality system specifications are planned, implemented, and assessed. To collect data of the right type, quality and quantity to support decisions regarding the chemical speciation component of the PM$_{2.5}$ Monitoring program, adequate planning and management of a quality system that integrates QA and QC requirements consistent with good field and laboratory practices is necessary.

7.1 Quality System Requirements

The EPA's QAD developed specific guidelines and requirements for the development of the quality system, entitled ***Quality System Requirements for Environmental Programs*** (EPA QA/R-1). To access several of EPA's Quality system documents refer to the web site at http://es.epa.gov/ncerqa/qa/qa_docs.html. A quality system must be developed to permit maximum flexibility yet ensure that the measurement uncertainty is known and under control. To ensure consistency in the application of the quality system, organizations must implement several components at the organization/program level:

<   Each EPA organization collecting data must prepare a Quality Management Plan (QMP) that details the organization's responsibilities;

<   Data Quality Objectives (DQOs) will be developed to determine the data collection needs and sampling plan;

<   One mandatory component at the project level is the Quality Assurance Project Plan
        (QAPP);

<   Standard Operating Procedures (SOPs) are developed and documented in the QAPP for
        use during data collection;

<   Technical System Audits and Reviews; and

<   Following the implementation and planning stages of the program, the Data Quality
        Assessment (DQA) is performed to determine if the data collected is meeting the intended
        uses.

Refer to 40 CFR Part 58 Appendix A section 2.0 (62 FR 38763) for more information concerning
the requirements of a quality system.

7.2 QAD Requirements and Guidance

Quality requirements for EPA organizations are defined in EPA Order 5360.1 CHG 1
(1998), *Policy and Program Requirements for the Mandatory EPA Quality System*, and the
EPA Order 5360 (1998), *EPA Quality Manual for Environmental Programs*. These are internal
policy documents; non-EPA organizations should consult the corresponding external policy
documents described below.

Quality requirements for organizations receiving financial assistance from EPA through
extramural agreements (e.g., contracts, grants, cooperative agreements, and interagency
agreements) are defined in Requirements (R-#) documents. Requirements documents are policy
statements that identify and discuss mandatory elements of the Agency's Quality System. Each
document will contain implementation requirements similar to EPA Order 5360, EPA Quality
Manual for Environmental Programs, an internal policy manual.

<   R-1: EPA Quality Systems Requirements for Environmental Programs - In Progress

<   R-2: EPA Requirements for Quality Management Plans -External Review

<   R-5: EPA Requirements for Quality Assurance Project Plans - External Review

The QAD also issues Guidance (G-#) documents to assist in the development and
implementation of a suitable Quality System. Guidance documents are non-mandatory aids on how
to achieve the mandatory QA requirements for both EPA and non-EPA organizations. These
documents are available in either final or draft form, or work is currently in progress. For more
information concerning these documents, refer to the QAD web page at:
http://es.epa.gov/ncerqa/qa/qa_docs.html

7.3 Quality Assurance Practices

The QA practices for the chemical
speciation program must include several
different components:

> **QUALITY ASSURANCE**
>
> Quality assurance (QA) is defined as an integrated
> system of management activities involving planning,
> implementation, assessment, reporting, and quality
> improvement to ensure that a process, item, or
> service is of the type and quality needed and
> expected by the customer.

<   Quantifying the accuracy of the monitoring system by performing an independent assessment to verify that data is within acceptable criteria of a known standard.

<   Quantifying the precision of the monitoring system by comparing the resultant data from two or more individual samplers within the monitoring network.

<   Accuracy, which is defined as the degree of agreement between an observed value and an accepted reference value, accuracy includes a combination of random error (precision) and systematic error (bias) which are due to sampling and analytical operations.

<   Checking the operational flow rate of the chemical speciation monitor with a National Institute of Science and Technology (NIST) certified transfer standard.

<   Checking the resultant data from the species collected with a known laboratory reference standard.

<   Precision, which is defined as a measurement of mutual agreement among individual measurements of the same property usually under prescribed similar conditions, expressed generally in terms of the standard deviation.

<   Checking the operational flow rate on a specific percentage of monitors with a specified frequency using a NIST certified transfer standard.

<   Comparing the resultant data from chemical speciation monitors that are collocated at one sampling location. The requirements for FRM collocation are identified in 40 CFR part 58 appendix A section 3.3 (62 FR 38763). Operators may use as this information as a guideline for the chemical speciation monitoring network.

<   Comparing the laboratory analysis results for two duplicate or split samples.

7.4 Quality Control Procedures

The new PM$_{2.5}$ chemical speciation monitor requires enhanced quality control measures due to its unique design and operational attributes. Each chemical speciation monitor must have an operation or instruction manual which details the procedures for proper sampling. Other quality control procedures include:

> **QUALITY CONTROL**
>
> Quality control (QC) is defined as the overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer and the operational techniques that are used to fulfill requirements for that quality.

<   Periodically checking the flow rates for all individual channels against a flow transfer standard.

<   Periodically checking the temperature and pressure sensors, as applicable, against an independent device.

<   Periodically checking the measurement uncertainty of the sampling system with the use of trip, lab, and field blanks.

<   Periodically checking the timing mechanism against a know standard to verify the sampling start-up and shut-off.

<   Periodically checking the laboratory analysis results against known standards.

There are many other QC checks which may be incorporated into the chemical speciation program. The quality assurance project plan (QAPP) for each individual network must identify these components.

7.5 Data Quality Objectives (DQOs)

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 DQO process is a seven-step systematic approach 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. The outputs of the DQO process are used in developing a sampling design for data collection and preparing the QAPP. In addition, DQO outputs and assumptions are examined and applied during the DQA process.

A PM$_{2.5}$ speciation Work Group of EPA and State participants was convened to complete the DQO process for the PM$_{2.5}$ speciation program. More detailed information on the DQOs and measurement quality objectives, including a definition of power and the methods and models used to develop the NAMS DQOs, are provided in the *Data Quality Objectives for Detection of National Trends in Speciated Data* (U.S. EPA, 1998c) document which is found at http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/dqo3.pdf.

7.6 Quality Assurance Project Plans (QAPPs)

The QAPP is a critical planning document for any environmental data operation. The QAPP documents how data operations are planned, implemented, and assessed with respect to the quality of the data required. The purpose of the QAPP is to define how specific QA and QC activities will be performed. The *EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations*, EPA QA/R-5 and *EPA Guidance for Quality Assurance Project Plans*, EPA QA/G-5 are documents that should be consulted in the preparation of the QAPP. Information concerning these documents can be found on the QAD web page at: http://es.epa.gov/ncerqa/qa/qa_docs.html. The QAPP is composed of 25 elements grouped into four classes: 1) project management; 2) measurement and data acquisition ; 3) assessment and oversight; and 4) data validation and usability. Not all elements are addressed for every project; however, other projects may require additional elements not contained in the original 25. The final decision on the elements to be included in the QAPP is made by the overseeing EPA organization. QAPPs are required for all environmental data operations that acquire, generate, or compile data and are performed by or on behalf of the EPA. A QAPP must be in place prior to the start of data collection**.**

Development of the QAPP provides a transition from planning to implementation. During implementation, data are collected in accordance with the QAPP. During the assessment phase, data are verified and validated according to procedures and criteria specified in the QAPP, and DQA analyzes the data to determine if the assumptions and criteria documented in the QAPP were met. A stand-alone QAPP is being developed by the EPA for the NAMS trends network. QA issues for filter preparation, sample handling and transport for mass measurements will be comparable to those stated in the of the ***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), http://www.epa.gov/ttn/amtic/files/ambient/pm25/qa/m212covd.pdf. With exception of the sampler specific SOPs, the QAPP will be equally applicable to the entire chemical speciation program. Prior to data collection, an approved QAPP is required for each organization implementing a NAMS or SLAMS network.

7.7 Standard Operating Procedures (SOPs)

Standard operating procedures document the specific procedures necessary to carry out routine or repetitive technical or administrative activities. SOPs are specific to the organization or facility where they will be used and ensure that the procedure is conducted in a standardized and reliable manner. SOPs provide standardization and consistency of methods and protocols used to ensure data comparability, credibility, defensibility and quality. 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.

SOPs are developed at the organizational level and applied at the project level. SOPs provide input to the QAPP, used for implementation of the data collection activities, and used as a specification during technical systems audits. SOPs are an important part of the personnel training program and must be kept current to be effective. For PM$_{2.5}$ chemical speciation sampling and analysis, SOPs are needed which effectively detail major field sampling and laboratory operations. Guidance for the preparation of SOPs is given in EPA QA/G-6, ***Guidance for the Preparation of Standard Operating Procedures,*** http://es.epa.gov/ncerqa/qa/qa_docs.html. SOPs should be reviewed and updated annually to ensure that procedures specified in the SOPs are actually being followed in field and laboratory operations.

7.8 Technical Systems Audits and Performance Evaluations

The quality auditing function consists of technical systems audits and performance evaluations. Technical systems audits include an on-site review and inspection of a State or local agency's monitoring program to assess compliance with established regulations that govern the collection, analysis, validation and reporting of the air quality data. Technical systems audits of the agencies operating the SLAMS chemical speciation program shall be conducted at least every 3 years by the EPA Regional QA laboratories. Detailed information regarding the performance of technical system audits is found in the ***Quality Assurance Handbook for Air Pollution Measurement Systems*** (U.S. EPA, 1998g), http://www.epa.gov/ttn/amtic/files/ambient/qaqc/redbook.pdf.

7.9 Regional Laboratory QA

Four EPA and Regional labs comprise the Laboratory QA support group. This group is responsible for providing routine QA support to the chemical speciation program, which includes conducting QA sample analyses, analyses for special studies, and technical QA support to the contract laboratories, States and EPA. The link of the Regional QA labs to the overall contact laboratories and the filter analysis and data processing will be discussed in the Regional Lab Quality Assurance Program Plan (QAPP) currently being developed and expected to be completed October 1999. Each EPA region is responsible for resolving Contractor laboratory QA issues, analysis of QA samples (field duplicates, round robin samples, audit samples), performing technical systems audits, and providing technical support for QA. QA support for field duplicates, collocated samples, and special studies will be provided for all routine speciation target analytes using the same methods as those used by the contract laboratory.

8.0 DATA VALIDATION AND DATA MANAGEMENT

This section provides a general discussion of the specifications relative to data validation, data base requirements, and AIRS. EPA plans to develop more specific data validation guidance as part of the NAMS speciation QAPP for use by States, Regions, and laboratories implementing the speciation program.

8.1 Data Validation

Data validation is the most important part of the overall data generation and processing system. The data must be reviewed and validated to assure the overall quality of the measurement prior to inclusion into the Aerometric Information Retrieval System-Air Quality Subsystem (AIRS-AQS) data base. Data validation is used in conjunction with the program objectives, DQOs, and program QA/QC to remove inconsistencies in the data set and to improve data quality. Data validation consists of systematic procedures developed to identify deviations from measurement assumptions and procedures. Timely data validation is required to more easily resolve data issues and unusual events and take the necessary corrective actions to minimize the generation of additional data that may be invalid or suspect. Four levels or categories generally apply to the validation of monitoring data:

Level 0)   Routine checks made during the initial data processing and generation of data, including proper data file identification, review of unusual events, review of field data sheets and result reports, instrument performance checks and deterministic relationships.

Level I)   Tests for internal consistency to identify values in the data which appear atypical when compared to values of the entire or whole data set.

Level II)   Comparison of the current data set with historical data to verify consistency over time. This level can be considered a part of the data interpretation or analysis process.

Level III)   Tests for parallel consistency with data sets from the same population (region, period of time, air mass, etc.) to identify systematic bias. This level can also be considered a part of the data interpretation or analysis process.

Level 0 validation establishes the traceability of the integrated data set and takes place mainly in the field and in the laboratory. Level 0 validation consists of flagging samples when significant deviations from measurement assumptions have occurred. Computer file entries are verified against data sheets; values are eliminated for measurements which are known to be invalid because of instrument malfunctions; and measurement values are adjusted due to quantifiable calibration or interference biases.

LEVEL 0 DATA VALIDATION

As a part of the Level 0 data validation process, the field personnel and speciation Contract Laboratory requirements include:
<   compilation of all raw field and laboratory data and calculation of analyte ambient air concentrations for each sample;
<   verification of the field chain-of-custody (C-O-C) form information and number of sample filters and laboratory analyses requested;
<   enters all C-O-C field data into the Laboratory Information Management System (LIMS); and
<   prepares and submits Level 0 data validation checklists with the monthly hard copy analytical data reports to the DOPO.

Level I validation takes place after data from various measurement methods have been assembled in the master data base or LIMS (Laboratory Information Management System). Level I applies internal consistency tests based on known physical relationships between variables of the assembled data. Several internal consistency checks can be applied to evaluate validity when different particle size fractions are measured and submitted to chemical analyses. These include comparisons between collocated measurements; comparisons between mass concentrations and the weighted sum of chemical species; checks for physical and chemical consistency; and charge balances between anions and cations. As discovered, data adjustments for quantifiable biases can be made in Level I validation.

LEVEL I DATA VALIDATION

As part of the Level I data validation process, the field personnel and contract laboratory requirements include:

C   flags samples when deviations from measurements procedures occur;
C   eliminates invalid values due to instrument malfunction;
C   establish traceability of the integrated data set;
C   applies simple statistical tests on a single-site, single-sampler basis to make sure that the maximum and minimum values, rates of change, and temporal variations are reasonable;
C   revises the raw data or flags the data as suspect or invalid;
C   performs cation and anion balance and ammonium balance calculations; and
C   prepares and submits the Level I data validation checklist with the Level 0 and monthly hard copy analytical data reports to the DOPO.

Level II validation is part of the descriptive data analysis or data interpretation process performed by the Region or State agency. Level II validation can include time series analysis, correlation matrices, material balance, quantitative statistical analyses, and modeling. 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 or outliers.

Level III validation is typically performed by the Region or State agency as part of data interpretation and consists of tests for consistency with data sets from the same population. Level III validation in done after the data is placed in the AIRS-AQS data base and can include the same interpretive analyses discussed in Level II validation. Data sets from the same Region, air mass, or period of time are analyzed for consistency.

LEVEL II DATA VALIDATION

Examples of Level II data validation include:

C   collocated comparisons;
C   sum of chemical species versus mass
         concentrations;
C   physical and chemical consistency (e.g.,
         sulfate versus total sulfur, soluble
         potassium versus total potassium, soluble
         chloride versus chlorine); and
C   nitrate volatilization determinations.

LEVEL III DATA VALIDATION

Examples of Level III data validation include:

C   descriptive data analyses (e.g., time series,
         correlation matrix, material balance);
C   quantitative statistical analyses; and
C   air quality modeling.

Given that there are separate field sampling, laboratory analysis, QA and data analysis components of the speciation program, various pieces of each level of validation will logically fall under each of these areas. No one area will contain the responsibility for an entire level of data validation. For example, components of Level I data validation will be done independent of the contract laboratory and not be duplicated by both the field and lab personnel. The State data analyst or contract laboratory personnel may perform certain components of Level II and Level III validation.

8.2 Data Base Requirements and AIRS

Substrate data processing is a very important part of the overall data management process. Data base requirements exist for the managing and processing data at the field and laboratory level, prior to submitting the data to the AIRS-AQS data base. Aerosol data processing consists of six general tasks:

1.   **Record Keeping** - All relevant information obtained at the time an operation is performed
       is registered on field data sheets, the data logger, or other transfer medium.

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

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
       concentration result. These include the pollutant concentration, which must be reported in
       μg/m^3, accuracy, and precision.

5.   **Data Validation** - Data are validated according to the Level I through IV data validation
       steps as described above.

6.   Output - Data are arranged into the desired format for input to the AIRS-AQS and subsequently formatted for data interpretation and modeling software.

Aerosol data processing requires the assignment of identification (ID) codes to filter substrates. Field data records should include a recording of the IDs and their corresponding sampling sites, sampling dates, sampling times, sampling duration, sample flow rates, and deviations from normal sampling procedures. Laboratory records should contain instrument recordings of analytical outputs. Data validation is performed and should provide for formatting and reporting of concentrations in µg/m^3 and all data validation activities.

Field data can be entered into computerized data forms. Substrate IDs 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 against the original data sheet by the data processing supervisor. A data base structure, which contains fields for chemical concentrations and a level of uncertainty is formed. Each record should contain sample IDs, sample volumes, sample times, sampling sites, and sampling dates, which are integrated into this structure from the field records. All other fields contain the missing data default value. These defaults are replaced by the result data as they become available. In this way, it is possible to determine which analyses have been completed and which have not.

The laboratory chain-of-custody is used to track the disposition of each sample and can be consulted to determine the fate of missing values in the master data base. This independent tracking is needed to prevent sample IDs from being mixed up or samples being lost.

Laboratories having the capacity to analyze a high volume of samples, usually employ a 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 read-out of the weight is not a LIMS, if the true reading cannot be adjusted if needed prior to recording. If data entered into 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), ***Good Automated Laboratory Practices*** (U.S. EPA, 1995b), http://www.epa.gov/irmpoli8/irm_galp/ which addresses principles for ensuring data integrity in automated laboratory operations.

GOOD AUTOMATED LABORATORY PRACTICES

Laboratory Management - Laboratory management ensures that personnel understand their roles; resources are adequate and available; corrective action is promptly taken; and SOPs are approved.
Personnel - Personnel must have adequate education, training, and experience to perform assigned LIMS functions; and have a current summary of their training, experience, and job description, maintained at the facility.
Quality Assurance Unit - The QA 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 maintained for the software used to collect, analyze, process or maintain the LIMS raw data.
Security - Laboratory management shall ensure 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.
Comprehensive Testing - 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.
Record 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.

After data for a record have been assembled, data validation comparisons should be conducted as discussed in Section 8.1. A data validation summary is maintained and associated with each record to provide traceability for data adjustments, replacements, or deletions. Field and laboratory data validation flags are assigned as part of the data validation process. Data validation summaries accompany the final data base. This data base must be converted to AIRS-AQS format for subsequent submission to the AIRS-AQS. All PM₂.₅ chemical speciation data must be entered into AIRS. The EPA, OAQPS, Information Transfer and Program Integration Division (ITPID) administers the AIRS-AQS. The AQS contains data submitted by States, local and reporting organizations. The AIRS-AQS includes descriptions of air monitoring sites, monitoring equipment, measured concentrations of pollutants and related parameters.

9.0 DATA ANALYSIS

The PM$_{2.5}$ program objectives described in Section 1 will be addressed through various data analysis and interpretation activities. In recent years, an increasingly greater reliance is being placed on observational data for air quality planning needs beyond NAAQS comparisons; this is especially true of the type of data that will be produced in the PM$_{2.5}$ speciation networks. Many of the recommendations from the NAS Report on Tropospheric Ozone (NRC, 1991) reflect the need to better integrate observations into air quality planning rather than rely completely on emissions-based air quality modeling approaches. The current report on the ozone science assessment conducted through NARSTO will reinforce this message. 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 in U.S. EPA, 1995a. Observations are our best attempt at representation of reality and must be a critical component of planning. Planning must be an iterative process given the current and even more substantial future system uncertainties.

A wealth of new data on PM$_{2.5}$ constituents will be made available on a routine basis with the implementation of the speciation networks. Previously, detailed aerometric data of this type have only been collected on a national scale in rural environments (i.e., CASTNet and IMPROVE) or as part of special studies of limited duration. The availability of routinely collected speciation data will enable a range of analyses which have not been possible until now.

In order to properly analyze speciated PM data, a clear understanding of the goals of the analysis (i.e., a precise statement of the questions to be answered by the investigation), familiarity with the range of possible analytical techniques along with their individual advantages and limitations, and proper interpretation of the results are necessary.

The key points of data analysis are provided below:

<   The PM$_{2.5}$ speciation networks will generate data useful for expanded understanding of fine particulate formation and removal processes, general characterization and comparison purposes, trends analysis, source attribution, control strategy development, checks of control strategy effectiveness, emission inventory and model evaluation, and other related uses.

<   The EPA will issue guidance detailing potential uses for the PM$_{2.5}$ mass and speciation data. These guidance documents will be based on (1) techniques described in the published literature and (2) concepts offered by the State and local agencies, the Regional Offices, and EPA. After a panel of experts peer reviews each document, the documents will be made publicly available through the Internet.

<   The EPA will sponsor development of tools to assist with some of the analyses described in the guidance documents. Many software packages have already been developed for other criteria pollutants and some may be modified to accommodate PM$_{2.5}$ mass and speciation data. Examples include VOCDat and PAMSDAS. Also, an EPA web site called PM Fine Data Analysis will be available, consisting of topics such as General Information; Publications, Papers and Reports; and Data Analysis Support. The site will provide direct

links to PAMS data analysis, Toxics data analysis, and the Data Analysis Workbook web site http://capita.wustl.edu/databases/userdomains/pmfine/.

< The EPA will issue periodic reports describing the national trends and the quality of the data collected by the PM$_{2.5}$ network. Trends for mass and key constituents, for example, will be highlighted in the annual National Ambient Air Quality and Emissions Trends Reports.

< States need to consider the goals of the data collection in their network design, especially in the non-Trends portion. These considerations include siting, monitoring schedule (more frequent than every 3rd day and/or intervals less than 24-hours), and availability (collocated or nearby monitoring) of other related pollutant and meteorological parameter data.

< The creation and evolution of guidance documents, tools, workshops, and reports will be aided by the PM$_{2.5}$ Data Analysis interactive web site that will solicit ideas and comments from the ambient air monitoring and analysis community at large, particularly from groups such as NESCAUM, MARAMA, WESTAR, LADCO, TNRCC, CARB, A&WMA, and STAPPA/ALAPCO. In addition, more focused groups and subgroups comprised of individuals from EPA, Regions, and States who have expertise in areas such as ambient air data analysis, chemistry, and meteorology will help address specific and pressing issues.

< Training and workshops will be conducted to demonstrate proven data analyses, present potential limitations of the conclusions from the data analyses, and demonstrate the software tools that have been developed/modified specifically for PM$_{2.5}$ data analysis.

In addition to data analysis guidance provided at the web site given above, EPA is currently developing a data analysis chapter. This chapter will provide more detail on each of the bullets presented in this summary and shortly be posted on our web site. When the guidance is completed, this document will be revised and a link provided to the data analysis chapter.

10.0 REFERENCES

Appel, B.R.; Cheng, W.; Salaymeh, F. (1989). Sampling of Carbonaceous Particles in the Atmosphere-II, *Atmos. Environ*. 1989, 23, 2167-2175.

Albritton, Daniel L. and D. S. Greenbaum (1998). *Atmospheric Observations: Helping Build the Scientific Basis for Decisions Related to Airborne Particulate Matter. Report of the PM Measurements Research Workshop*, Chapel Hill, NC, Health Effects Institute and the Aeronomy Laboratory of the National Oceanic and Atmospheric Administration, October 1998. http://www.al.noaa.gov/WWWHD/pubdocs/PMMRW.pdf

Ashbaugh, L. (1998). Personal communication, July 16, 1998.

Batterman et al. (1997). SO_2 Sorption Characteristics of Air Sampling Filter Media Using a New Laboratory Test, *Atmos. Environ.*, Vol. 31, No. 7, pp. 1041-1047, 1997.

Bennett, Roy L. and L. Stockburger (1994). *Sampling Carbonaceous Aerosols: Review of Methods and Previous Measurements*. U.S. Environmental Protection Agency. Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, November 1994; EPA/600/SR-94/192.

Birch, Eileen M. (1998). Analysis of Carbonaceous Aerosols: Interlaboratory Comparison. *Analyst*, May 1998, Vol. 123 (851-857).

Birch, Eileen M. and R.A. Cary (1996). Elemental-Carbon Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust, *Analyst* 1996, *25*, 221-241.

Cahill, T.A., M. Surovik, I. Wittmeyer (1990). Visibility and Aerosols During the 1986 Carbonaceous Species Methods Comparison Study, *Aerosol Sci. Technology*. 12(1): 149-160, 1990.

Chan et al. (1986). An Evaluation of Artifact SO_4^{2-} Formation on Nylon Filters Under Field Conditions, *Atmospheric Environment*. 20(12): 2397-2401, 1986.

Cui, W., J. Machir, L. Lewis, D.J. Eatough, and N.L. Eatough (1997). Fine Particulate Organic Material at Meadview During the Project MOHAVE Summer Intensive Study, *J. Air and Waste Mgmt. Assoc.*, Volume 47, March 1997.

Dzubay, T.G. and R.K. Stevens (1975). Ambient Air Analysis with a Dichotomous Sampler and X-ray Fluorescence Spectrometer, *Envir. Sci. Technology*. 9(7): 663-667 (1975).

Eatough, D.J., Tang, H.; Cui, W.; Machir, J. (1995). Determination of the Size Distribution and Chemical Composition of Fine Particulate Semi-volatile Organic Material in Urban Environments Using Diffusion Denuder Technology, *Inhalation Toxicology*, 1995, 7, 691-710.

Eatough, D.J., Wadsworth, A.; Eatough, D.A.; Crawford, J.W.; Hansen, L.D.; Lewis, E.A. (1993). A Multiple-system, Multi-channel Diffusion Denuder Sampler for the Determination of Fine Particulate Organic Material in the Atmosphere, *Atmos. Environ.* 1993, 27, 1213-1219.

EPA Order 5360, *EPA Quality Manual for Environmental Programs*, July 1998.

62 FR 38421. *Implementation of Revised Air Quality Standards for Ozone and Particulate Matter*, U.S. Environmental Protection Agency, <u>Federal Register</u>, July 18, 1997, page 38421-38432).

62 FR 38761. *National Ambient Air Quality Standards For Particulate Matter; Availability of Supplemental Information and Request For Comments, Final Rule*, U.S. Environmental Protection Agency, 40 Code of Federal Regulations Parts 50, <u>Federal Register</u>, July 18, 1997.

62 FR 38763. *Revised Requirements For Designation of Reference and Equivalent Methods For PM$_{2.5}$ and Ambient Air Quality Surveillance for Particulate Matter, Final Rule,* U.S. Environmental Protection Agency, 40 Code of Federal Regulations Parts 53 and 58, <u>Federal Register</u>, July 18, 1997.

62 FR 41137. *Regional Haze Regulations, Proposed Rule,* U.S. Environmental Protection Agency, U.S. Environmental Protection Agency, 40 Code of Federal Regulations Parts 51, <u>Federal Register</u>, July 31, 1997.

Jaklevic, J.M., B.W. Loo, F.S. Goulding (1977). Photon-Induced X-Ray Fluorescence Analysis Using Energy-Dispersive Detection and Dichotomous Sampler, *X-Ray Fluorescence Analysis of Environmental Samples, 2nd Edition*. Ann Arbor Science Publishers, Inc., Ann Arbor, MI, pp. 3-18.

Koutrakis, P., Wolfson, J.M., Thompson, K.M., Spengler, J.D., Keeler, J.G., and Slater, J.L. (1992). Determination of Aerosol Strong Acidity Losses Due to Interaction of Collected Particles: Results from Laboratory and Field Studies, *Atmospheric Environment*. 26A, 987-995.

Koutrakis, P. (1998). Recommendations of the Expert Panel on the EPA Speciation Network. July 22, 1998. http://www.epa.gov/ttn/amtic/pmspec.html

Koutrakis, P. (1999). Recommendations of the Expert Panel on the EPA Speciation Network. May 18-19, 1999. http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/lvpanel.pdf

Lundgren, D.A. and R.M. Burton (1995). Effect of Particle Size Distribution on the Cut Point Between Fine and Coarse Ambient Mass Fractions, *Inhalation Toxicology*, 7(1):131-148.

Malm, W.C. et al. (1994), Spatial and Seasonal Trends in Particle Concentration and Optical Extinction in the United States, *J. Geophysical Res.*, Vol. 99, No. D1, pp. 1347-1370, January 20, 1994.

McDow, S.R.; Huntzicker, J.J. (1990). Vapor adsorption artifact in the sampling or organic aerosol, *Atmos. Environ.* 1990, 24, 2563-2571.

NIOSH (1996). Elemental Carbon (Diesel Particulate): Method 5040, in: *NIOSH Manual of Analytical Methods, 4th ed. (2nd Supplement)*, ed. Eller, P. M., and Cassinelli, M. E., National Institute for Occupational Safety and Health, DHHS (NIOSH), Cincinnati, OH; Publication No. 96-135, 1996.

NIOSH (1998). NIOSH Method 5040, Elemental Carbon (Diesel Particulate), *NIOSH Manual of Analytical Methods (NMAM)*, Fourth Edition, Issue 2, Draft dated January 15, 1997.

NRC (1991). Rethinking the Ozone Problem in Urban and Regional Air Pollution, National Research Council, National Academy Press, Washington D.C. 1991

Ondov, J.M. and A.S. Wexler (1998). Where Do Particulate Toxins Reside? An Improved Paradigm for the Structure and Dynamics of the Urban Mid-Atlantic Aerosol. *Environ. Sci. Technol.*, 32, 2547-2555, 1998.

Solomon, P.A. et al. (1998). *Field Program Plan for the PM$_{2.5}$ Chemical Speciation Sampler Evaluation Study, Draft*. November 13, 1998.
http://www.epa.gov/ttn/amtic/files/ambient/pm25/casac/progra1.pdf

U.S. EPA (1994). *Recommendations for Analysis of PAMS Data*. U.S. Environmental Protection Agency, Prepared under Contract No. 68-D3-0019, February 28, 1994.
http://www.epa.gov/oar/oaqps/pams/analysis.html.

U.S. EPA (1995a). *A New Approach for Demonstrating Attainment of the Ambient Ozone Standard: Modeling, Analysis, and Monitoring Considerations*, U.S. Environmental Protection Agency. Office of Research and Development. Washington, D.C. July 1995; EPA/600/R-96/134.

U.S. EPA (1995b). *Good Automated Laboratory Practices*, EPA-2185, U.S. EPA Office of Information Resources Management, Research Triangle Park, NC, 1995. The documentation is also available on the Internet at: http://www.epa.gov/irmpoli8/irm_galp/

U.S. EPA (1996a). *Air Quality Criteria for Particulate Matter*. U.S. Environmental Protection Agency. Office of Research and Development. Washington, D.C., April 1996; EPA/600/P-95/001aF. http://www.epa.gov/ORD/WebPubs/execsum.html

U.S. EPA (1996b). *Guidance for Data Quality Assessment: Practical Methods for Data Analysis*, U.S. Environmental Protection Agency. Office of Research and Development. Washington, D.C. July 1996; EPA/600/R-96/084.

U.S. EPA (1996c). *Photochemical Assessment Monitoring Stations 1996 Data Analysis Results Report*. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, NC, October 1996; EPA-454/R-96-006.

U.S. EPA (1996d). *Quality Management Plan*. U.S Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, NC, June 21, 1996.

U.S. EPA (1997a). *Guidance for Network Design and Optimum Site Exposure for PM$_{2.5}$ and PM$_{10}$*, U.S Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, NC, December 15, 1997.
http://www.epa.gov/ttn/amtic/files/ambient/pm25/network/r-99-022.pdf

U.S. EPA (1997b). *Chapter IO-4: Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles in Ambient Air Using the Annular Denuder Technology*, Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air: Atmospheric Acidic Constituents, U.S. Environmental Protection Agency. Office of Research and Development. Washington, D.C. September 1997; EPA/625/R-96/010a.

U.S. EPA (1997c). *Monitoring PM$_{2.5}$ in Ambient Air Using Designated Reference or Class I Equivalent Methods*; U.S. Environmental Protection Agency, Office of Research and Development. Draft, November 1997.

U.S. EPA (1997d). *Method IO-3.3. Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy*, Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air: Atmospheric Acidic Constituents, U.S. Environmental Protection Agency. Office of Research and Development. Washington, D.C. September 1997; EPA/625/R-96/010a.

U.S. EPA (1998a). *Quality Assurance Guidance Document 2.12: Monitoring PM₂.₅ in Ambient Air Using Designated Reference or Class I Equivalent Methods*, U.S. Environmental Protection Agency, April 1998. http://www.epa.gov/ttn/amtic/files/ambient/pm25/qa/m212covd.pdf.

U.S. EPA (1998b). *Guidance for Using Continuous Monitors in PM₂.₅ Monitoring Networks*, U.S. Environmental Protection Agency, May 29, 1998.
http://www.epa.gov/ttn/amtic/files/ambient/pm25/r-98-012.pdf

U.S. EPA (1998c). *Data Quality Objectives for Detection of National Trends in Speciated Data*, U.S. Environmental Protection Agency, December 16, 1998.
http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/dqo3.pdf

U.S. EPA (1998d). *Visibility Monitoring Guidance Document*. U.S. Environmental Protection Agency, June 1999. http://www.epa.gov/ttn/amtic/files/ambient/visible/r-99-003.pdf

U.S. EPA (1998e). *National Air Quality and Emissions Trends Report, 1996*. U.S Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, NC, January 1998; EPA-454/R-97-013.

U.S. EPA (1998f). *CMB8 Application and Validation Protocol for PM2.5 and VOC, Draft*. U.S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Research Triangle Park, NC, October 1998. http://capita.wustl.edu/PMFine/

U.S. EPA (1998g). *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Part 1, Ambient Air Quality Monitoring Program Quality System Development*, August 1998; EPA-454/R-98-004. http://www.epa.gov/ttn/amtic/files/ambient/qaqc/redbook.pdf

U.S. EPA (1999a). *Guideline on Speciated Particulate Monitoring*, Revision 3, January 4, 1999.

U.S. EPA (1999b). *Strategic Plan for Development of the PM₂.₅ Quality System for Chemical Speciation Trends Sites*, April, 16, 1999.
http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/strate1.pdf

Whitby, K.T. and G.M. Sverdrup (1980), California Aerosols: Their Physical and Chemical Characteristics, *Adv. Environ. Sci. Technol.*, 10, 477, 1980.

Wilson, W.E. and H.H. Suh (1997). Fine Particles and Coarse Particles: Concentration Relationships Relevant to Epidemiologic Studies, *J. Air Waste Management Assoc*. 47:1238-1249.

Witz, S., R.W. Eden, M.W. Wadley, C. Dunwoody, R.P. Papa, K.J. Torre (1990), Rapid Loss of Particulate Nitrate, Chloride and Ammonium on Quartz Fiber Filters During Storage, *J. Air Waste Management Assoc*. 40:53-61.