

**Field Program Plan
For
The PM_{2.5} Chemical Speciation Sampler Evaluation Study**

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Introduction

On July 18, 1997, the USEPA promulgated new National Ambient Air Quality Standards for particulate matter (PM). In addition to slightly revising the previous PM₁₀ standard, EPA added a new standard for fine particles less than 2.5 μm in aerodynamic diameter, known as PM_{2.5}. To develop meaningful relationships between PM_{2.5} levels at receptors and source emissions and for better understanding the causes of high PM_{2.5} concentrations, in particular secondary components formed in the atmosphere through chemical reactions and condensation, it is necessary to not only sample for PM_{2.5} mass, the NAAQS indicator, but also for the chemical components of PM_{2.5}. A sampling program of this type has been initiated by EPA that will consist of over 300 sites at which the major chemical components of PM_{2.5} will be measured in the collected aerosol. Since information from this network will be used for the identification of sources contributing to high PM_{2.5} mass concentrations, development and evaluation of control strategies, measurement of trends, and support of health studies, it is important that there be national consistency in the species concentrations measured by the PM_{2.5} speciation network. In particular, fifty of these PM_{2.5} chemical speciation sites will become part of the National Air Sampling Stations (NAMS) network and will provide nationally consistent data for assessment of trends.

Development of chemical speciation samplers for the National PM Sampler Contract, the need for which was described under 40 CFR, Part 58, Appendix D, was based on performance, rather than design criteria. This has allowed innovation in the development of these samplers and has resulted in the development of three slightly different samplers for meeting the performance criteria. Also as a result of this approach, a guidance document on chemical speciation of particulate matter has been prepared by EPA (US EPA, 1998) and reviewed by an external peer-review panel (Speciation Expert Panel; Koutrakis, 1998). In their review, the expert panel recommended an intercomparison among the chemical speciation samplers. The intercomparison will also include other historically accepted samplers (e.g., the improved IMPROVE sampler) and the Federal Reference Method (FRM). The chemical species to be determined include only those recommended by the expert panel (Koutrakis, 1998) and as specified in the guidance document for chemical speciation (EPA, 1998). This program plan outlines the approach and details the implementation of a study to intercompare the chemical speciation samplers developed under the National Procurement and several other samplers developed earlier and independently of the EPA national program.

Study Objectives

The objective of this methods evaluation and intercomparison study is to determine if there are differences among the three PM_{2.5} the three chemical speciation samplers available on the National Contract and how these samplers compare relative to other historical samplers if available, and to the FRM. While the FRM is 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; e.g., for ammonium nitrate, the FRM using Teflon filters provides only a lower limit on the expected mass loading, since there is potential for loss of nitrate and semi-volatile organic species (SVOCs) from the inert Teflon filters. For stable species, the

FRM should provide an accurate estimate of the mass loading for that species. Historical chemical speciation samplers [e.g., the Versatile Air Pollution Sampler (VAPS) developed under an EPA contract, the Caltech gray box sampler (Solomon et al., 1989), or the South Coast Air Quality Management District's PTEMP sampler (SCAQMD, 1996) should provide a less biased value for semi-volatile species and provide an additional set of samples for comparison; however, they still can only be compared on equivalent bases.

Overview of the Intercomparison

Collecting atmospheric particulate matter using the FRM with Teflon filters can result in negative sampling artifacts associated with the collected sample. Potential artifacts include the loss of volatile species, such as ammonium nitrate and semi-volatile organic compounds. Use of other filter media may result in negative or positive sampling artifacts. The magnitude of these potential artifacts depends upon the atmospheric concentration of the species being affected, the temperature, relative humidity, and, other variables. The chemical speciation samplers have been designed to overcome these potential biases or artifacts by the use of denuders to remove gas phase species and reactive substrates to collect species volatilized from the inert filters collecting the aerosol. Therefore, to evaluate the performance of these chemical speciation samplers they must be able to properly determine the chemical components of PM_{2.5} under a variety of atmospheric conditions, each of which will place different stresses on the performance of the sampler designs. This can be accomplished by sampling at different locations throughout the country, since the composition of the atmospheric aerosol is not uniform across the country. For example, some areas have high nitrate and low sulfate level, while others have relatively high sulfate and low nitrate. Still, other areas are dominated by aerosol rich in organic compounds derived from automobile exhaust, by organic aerosol derived from wood smoke combustion, or from by organic aerosol derived from natural biogenic emissions. Some areas of the country are highly influenced by crustal material. In actuality, several of these conditions exist simultaneously, with one or two components being higher than the others.

A variety of atmospheric chemical conditions also may be observed at one location during different seasons. For example, sulfate is likely highest in the east during the summer when photochemistry is high, while nitrate is highest in the west in the winter when cool temperatures drive the ammonium nitrate equilibrium with nitric acid and ammonia to the aerosol phase. Due to time constraints, the study will be conducted over about an eight week period at four different locations to obtain as wide a difference in chemical atmospheres as possible. These constraints, however, result in limitations and follow-on studies will have to occur to fully test the equivalency of these samplers. For example, by sampling in the winter in the east, we are missing the highest sulfate concentrations, we are not sampling at a site with high wood smoke emissions, and we are sampling in Phoenix for crustal material in the winter when highest concentrations are likely to be observed in the summer.

Due to time and resource limitations, the study design will be conducted in two phases, the latter phase dependent on additional available resources. Phase I will centered on sampling in areas with the following atmospheric conditions: high sulfate and low nitrate, high nitrate and low sulfate, and high crustal material. A fourth site was chosen locally near ORD headquarters in Research Triangle Park to allow for a more thorough evaluation of the samplers and their in-field operational

performance. Phase II will consist of going to several other locations. For example, immediately following Phase I, samplers may be sent to Bakersfield where a methods evaluation study is taking place for one month, to Utah or Washington state to sample under conditions with high wood smoke emissions, and/or to Atlanta to sample under conditions with high biogenic carbon emissions, or back to Phoenix and the northeast US under summertime conditions to maximize the crustal component and sulfate concentrations, respectively.

If resources are obtained to conduct parts of Phase II than this program plan will be expanded to include the additional geographical areas. At this time, Bakersfield is fairly likely and will be likely operated by CARB, including chemical analysis and just the 3 newly designed, commercially available chemical speciation samplers. Seattle or Spokane are also likely, but details are still being worked out for resource allocations. If operated high wood smoke conditions collocated speciation samplers will be operated with and without organic denuders to evaluate the effect of the denuder. If possible, we hope to operate each sampler in duplicate, two with denuder and two without. These samplers will undergo the same chemical analysis as in Phase I. Once again, this assumes resources are available for the follow on studies.

The time schedule for Phase I of the study also dictates that we sample more frequently than every 6th day, as the results are needed at OAQPS by early March for input into the decision process for choosing chemical speciation monitors for the NAMS network. Therefore, samples will be collected every-other-day. Phase II will likely operate on the same schedule in the hopes that the second data set will have some input into the decision process. The statistical design requires a minimum of 10-15 samples. To ensure that a sufficient number of samples are collected to meet that objective, 16 sampling periods will be attempted with a contingency of four additional sampling periods for a total maximum of 20. Samples will be analyzed for the major chemical components using standard analytical techniques as described below and by the expert panel that reviewed the guidance document (Koutrakis, 1998). Data analysis will provide a robust test of the similarity of the samplers studied and, within the limitations of the study, reasons for differences among the methods tested.

Study Design

The design of this program is constrained by limitations in the time frame allowed for the experiment and in resources available to complete the program (e.g., number of samplers, personnel, and funding). However, the statistical design was prepared understanding these limitations and the design chosen will provide a robust evaluation of the samplers relative to each other, to several samplers used historically to obtain similar data, and to the FRM. The overall design is detailed below.

Statistical Design

The primary objective of this study is to determine if there are differences in the measured concentrations of the chemical components of PM_{2.5} mass as determined by the three PM_{2.5} chemical speciation samplers available on the National Contract. Comparisons also will be made to two historical samplers and to the FRM using these samplers as a relative reference. 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.

There are two major scientific hypotheses to be addressed by this intercomparison study.

- One 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:
 1. 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).
 2. 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 Teflon 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 following 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 here. 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, we anticipate a range of precision from less than 10% to about 30%.

A detailed list of hypotheses is given in the Statistical Analysis section. The detailed hypotheses primarily address.

Sampler Types and Rationale

Chemical speciation samplers have been developed and manufactured by three different manufacturers under the National PM Sampler procurement, the need for which was described under 40 CFR, Part 58, Appendix C. The three samplers are the Reference Ambient Air Sampler (RAAS) developed by Andersen, Mass Aerosol Speciation Sampler (MASS) developed by University Research Glassware (URG), and Spiral Ambient Speciation Sampler (SASS) developed by MetOne. The external peer-review committee (Koutrakis, 1998) recommended comparison of these samplers under field conditions in different areas of the country and different seasons. They also recommended comparison to samplers used previously and historically accepted as providing data of known uncertainty, and to the FRM.

Historical methods included in this study include the National Park Services' IMPROVE sampler modified to include 47 mm filters as suggested by the expert review panel (IMPROVE, Koutrakis, 1998), the Versatile Air Pollution Sampler (VAPS)(URG; four available), and the PTEMP sampler operated by the South Coast Air Quality Management District (SCAQMD) at their Rubidoux, CA site. These samplers are well characterized for collecting relatively unbiased samples suitable for chemical analysis of major PM composition with a few exceptions. Recent work suggests that a bias may exist when using nylon filters for determining sulfate concentrations in air (Sickles, 1998) as is currently employed in the IMPROVE sampler.

Two FRM samplers will be operated at each site to allow for chemical characterization of the collected sample similar to that being obtained by the chemical speciation samplers. One FRM will collect aerosol samples on Teflon filters for mass and elements by XRF while the other FRM will use quartz-fiber filters for determination of ions (SO_4^- , NO_3^- , and NH_4^+). The FRM should provide a suitable reference for stable species, such as many of the trace metals and sulfate. The historical samplers, in particular the VAPS should provide a reference for labile compounds (nitrate ion, ammonium ion, and organic carbon) as it uses denuders and reactive filter backup filters thus minimizing the potential loss of these species when using only Teflon filters. While the VAPS uses similar technology to the chemical speciation samplers, it has been used and evaluated in numerous studies over the last decade, and thus, provides a reference to numerous other databases. The PTEMP sampler, only operated at Rubidoux, also falls into this category.

Sampler Descriptions - The Chemical Speciation Samplers.

Design of the three chemical speciation samplers for the National PM Network can be found in the EPA chemical speciation guidance document (EPA, 1998). The draft of the guidance document, as of the date of this program plan, outlines the general design of these samplers as envisioned for the PM network; although they are not likely the final designs to be implemented. Specific designs of the samplers for this intercomparison are given below. In general, each sampler draws air at a specified flow rate through a size selective inlet with a 50% collection efficiency (cutpoint) of 2.5 μm . As recommended by the expert peer-review panel (Koutrakis, 1998), the efficiency of collection (slope and cutpoint) for each sampler should closely resemble that of the FRM. Described below are the three samplers provided to us by URG, Met-One, and Andersen.

Reference Ambient Air Sampler (RAAS) developed by Andersen Instruments

A schematic flow diagram of the Andersen RAAS is shown in Figure 1. It consists of a size selective inlet followed by two cyclone fractionators. These cyclones are used to remove particles greater than 2.5 micrometers. The flow is then split into four channels. The first channel (labeled 1 in Figure 1) is used to estimate atmospheric concentrations of particulate organic and elemental carbon (OC/EC). After passing through the cyclone and manifold the PM is collected on a baked (to lower background OC) quartz-fiber filter. The flow rate in this channel is 7.3 Lpm. Due to the current uncertainty in using organic denuders and the desire to leave research oriented approaches to more careful examination, organic denuders will not be used during Phase I of this field test, with a few exceptions as described below. In the second channel (labeled 2 in Figure 1), particulate matter is collected on a Teflon filter for analysis of mass, and elements using XRF. The flow rate for channel 2 is 16.7 Lpm. The third channel (labeled 3 in Figure 1) also uses a Teflon filter, but this filter is extracted in water and the extract is analyzed for sulfate, nitrate, and ammonium ions by ion chromatography (IC). The last channel (labeled 4 in Figure 1) is used to obtain a nearly unbiased estimate of fine particle nitrate by removing acidic gases (e.g., HNO_3) from the air stream using a Mg denuder and collecting aerosol nitrate on the reactive Nylasorb (nylon) backup filter. The filter is extracted in IC eluent and analyzed by IC for nitrate. In all channels, critical orifices control the flow and the flow rates are monitored using calibrated rotameters.

Spiral Ambient Speciation Sampler (SASS) developed by MetOne

The Met-One SASS has five channels as illustrated in Figure 2. Each channel contains a spiral impactor designed to give a 50% cut-point at 2.5 micrometers with a slope similar to the FRM. The first channel (labeled 1 in Figure 2) contains a Teflon filter that will be analyzed for mass and elements by XRF. The second channel (labeled 2 in Figure 2) also uses a Teflon filter to collect PM. The filter is extracted in water and the extract is analyzed for sulfate, nitrate, and ammonium using IC. A MgO coated Al honeycomb denuder is placed in the third channel (labeled 3 in Figure 2) behind the spiral impactor. This denuder is used to remove acidic gases (e.g., HNO_3) from the sampled air stream and is followed by a Nylon filter that will be analyzed for nitrate by IC. As in the RAAS sampler the denuder/reactive filter pair is used to obtain a nearly unbiased estimate of aerosol nitrate. The fourth channel (labeled 4 in Figure 2) contains two baked quartz-fiber filters located behind the spiral impactor. The first quartz-fiber filter will be analyzed for OC/EC by thermal-optical reflectance, while the second quartz-fiber filter will be archived. The fifth channel (labeled 5 in Figure 2) will also include 2 baked quartz-fiber filters, however, they will be preceded by a carbon black honeycomb denuder. This denuder is used to remove semi-volatile organic compounds that may interfere with the OC measurement. Testing of the carbon black denuder is not directly part of this intercomparison, and was included because of its uniqueness, having not been used before, and because the MetOne sampler has the extra fifth channel. The flow rate through each channel is nominally 6.7 Lpm and is controlled by a critical orifice. The flow rate in this instrument is monitored using calibrated mass flow meters.

Mass Aerosol Speciation Sampler (MASS) developed by University Research Glassware (URG)

The URG MASS sampler is shown in Figure 3. This sampler consists of two modules, each with a size selective inlet and a WINS impactor to obtain a PM_{2.5} cutpoint. The first module is equipped with a Na₂CO₃ denuder before the WINS impactor but after the size selective inlet. This denuder is used to remove acidic gases much like the MgO denuders discussed above. The particles less than 2.5 micrometers are collected on a dual filter pack. The top filter is an inert Teflon filter that will be analyzed for PM_{2.5} mass and elements by XRF. The backup filter is a nylon filter that efficiently collects any nitrate that may have vaporized during sampling. Nitrate ion will be quantified using IC after extraction from the Teflon and nylon filter. The sum of nitrate measured on the Teflon plus nylon filters provides a nearly bias free estimate of fine particle nitrate. The second module contains a single filter pack containing one baked quartz-fiber filter. OC/EC will be determined by thermal-optical reflectance and IC will be utilized for the analysis of sulfate, nitrate, and ammonium ions. An organic denuder (XAD coated annular denuder) is not used here, but will be used in the next phase of the study. The flow rate through each module is nominally 16.7 Lpm.

Descriptions - Historical Samplers

Historical samplers include the IMPROVE, VAPS, FRM, and PTEMP samplers, the latter being operated only at Rubidoux as part of a SCAQMD study.

IMPROVE Sampler

Detailed descriptions of the IMPROVE sampler can be found in Eldred et al. (1998). A schematic diagram of the IMPROVE is given in Figure 4. In general, the IMPROVE sampler consists of several modules each of which is dedicated to collecting a series of related chemical components of the atmospheric aerosol. Each module consists of a size selective inlet, a cyclone to provide a PM_{2.5} size cutpoint based on the specified flow rate, filter media for sample collection, a critical orifice that provides the proper flow rate for the desired size cutoff, and a vacuum pump to produce the flow. IMPROVE samplers consist of up to four parallel modules, and a common controller as described in Eldred et al. (1998). The first module (labeled 1 in Figure 4) collects PM on a Teflon filter, which will be analyzed for PM_{2.5} mass and elements by XRF. The second module includes a Na₂CO₃ denuder before the PM_{2.5} cyclone to remove acidic gases (e.g., HNO₃) followed by the cyclone and a nylon filter. This nylon filter is extracted in water and the extract is analyzed for sulfate, nitrate, and ammonium ion by IC. The third module (labeled 3 in Figure 4) collects PM on a baked quartz-fiber filter that is analyzed for OC/EC using the thermal-optical method.

Versatile Air Pollution Sampler

The VAPS sampler is shown in Figure 5. A PM_{2.5} cutpoint is obtained using a size selective impactor followed by a virtual impactor with a PM_{2.5} cutpoint. The coarse particles follow the minor flow (3 Lpm) and are collected on a Teflon filter from which coarse (PM₁₀-PM_{2.5}) particles mass can be obtained. The fine (< PM_{2.5}) particle flow (30 Lpm) is split evenly between two channels. One channel (labeled 1 in Figure 5) contains a Na₂CO₃ denuder followed by Teflon/nylon filter pack as described above. The Teflon filter will be analyzed for mass by gravimetric analysis and for elements

by XRF. The Na_2CO_3 denuder will be extracted and analyzed for nitrate to give an estimate of ambient nitric acid concentrations. The second channel (labeled 2 in Figure 5), contains an XAD coated annular denuder, designed specifically for the VAPS (Gundel, personal communication) to remove gas phase semi-volatile organic compounds that might be collected by the quartz-fiber filter that follows the denuder. The quartz-fiber filter will be analyzed for OC/EC by the thermal-optical method. Filters are returned to the laboratory for chemical analysis with other filters from the study.

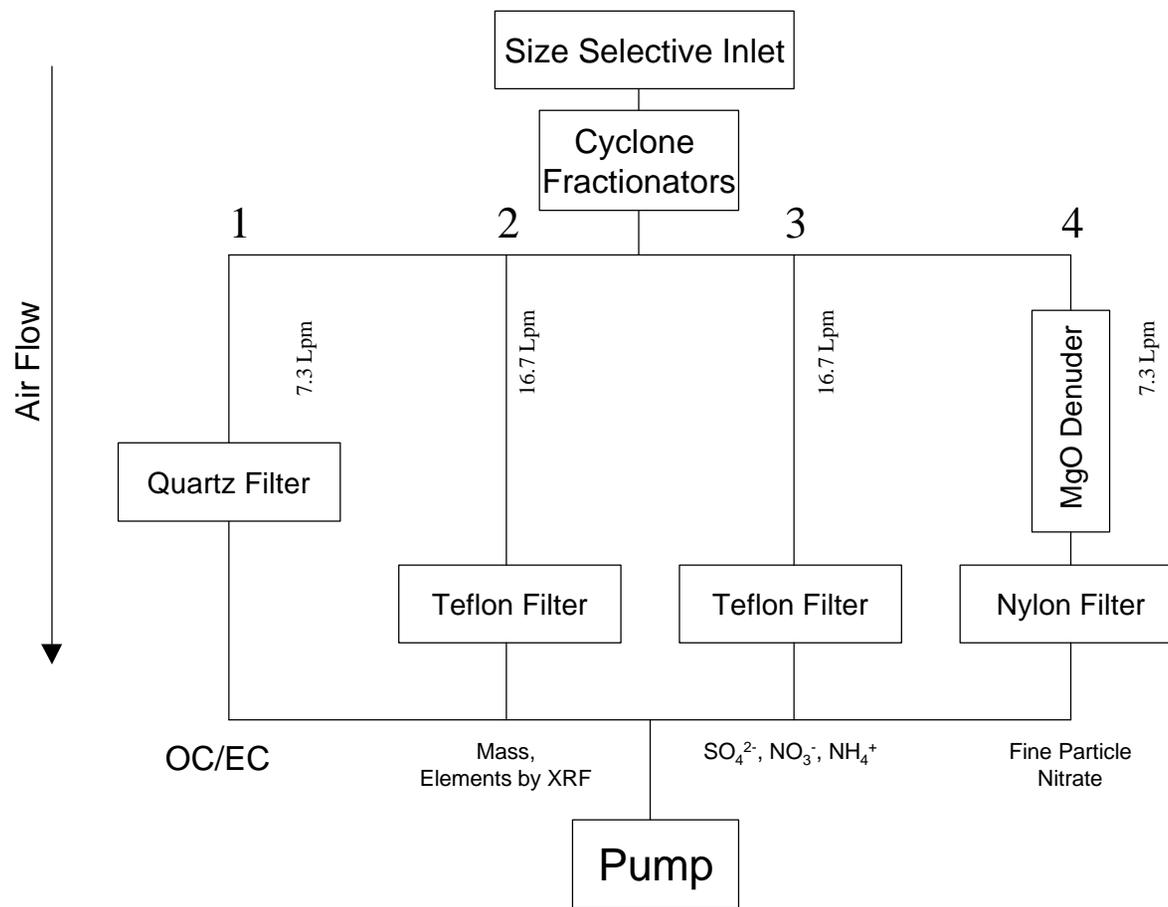
Federal Reference Method

The experimental design of the two FRM samplers schematically illustrated in Figure 6. Two FRM samplers will be used at each site to obtain chemical characterization of the collected aerosol in a manner similar to the other samplers. One FRM will use a Teflon filter to obtain $\text{PM}_{2.5}$ mass by gravimetric analysis. This same filter will be analyzed for elements by XRF. The second FRM will use a baked quartz-fiber filter that will be analyzed for OC/EC by thermal-optical reflectance and for sulfate, nitrate, and ammonium ions by IC. As mentioned above, the FRM is the reference method for $\text{PM}_{2.5}$ mass and should provide a suitable reference for non-volatile species, such as sulfate and many of the trace elements determined by XRF. The semi-volatile species, such as ammonium nitrate and some of the organic species will be obtained with less bias by the VAPS sampler and in Rubidoux by the PTEMP sampler. Thus, the VAPS will provide a reference for semi-volatile species.

SCAQMD PTEMP Sampler

The PTEMP sampler is quite similar to the Andersen RAAS, as both were based on the design of the Caltech Gray Box sampler (Solomon 1989). Air is drawn through an inlet and a $\text{PM}_{2.5}$ cyclone to obtain the desired cut-point. Air is split into several sample streams, with a fraction of the air passing through denuders and into filter packs or directly into filter packs. Details of the design can be found in SCAQMD (1996).

Figure 1. The Andersen RAAS Sampler



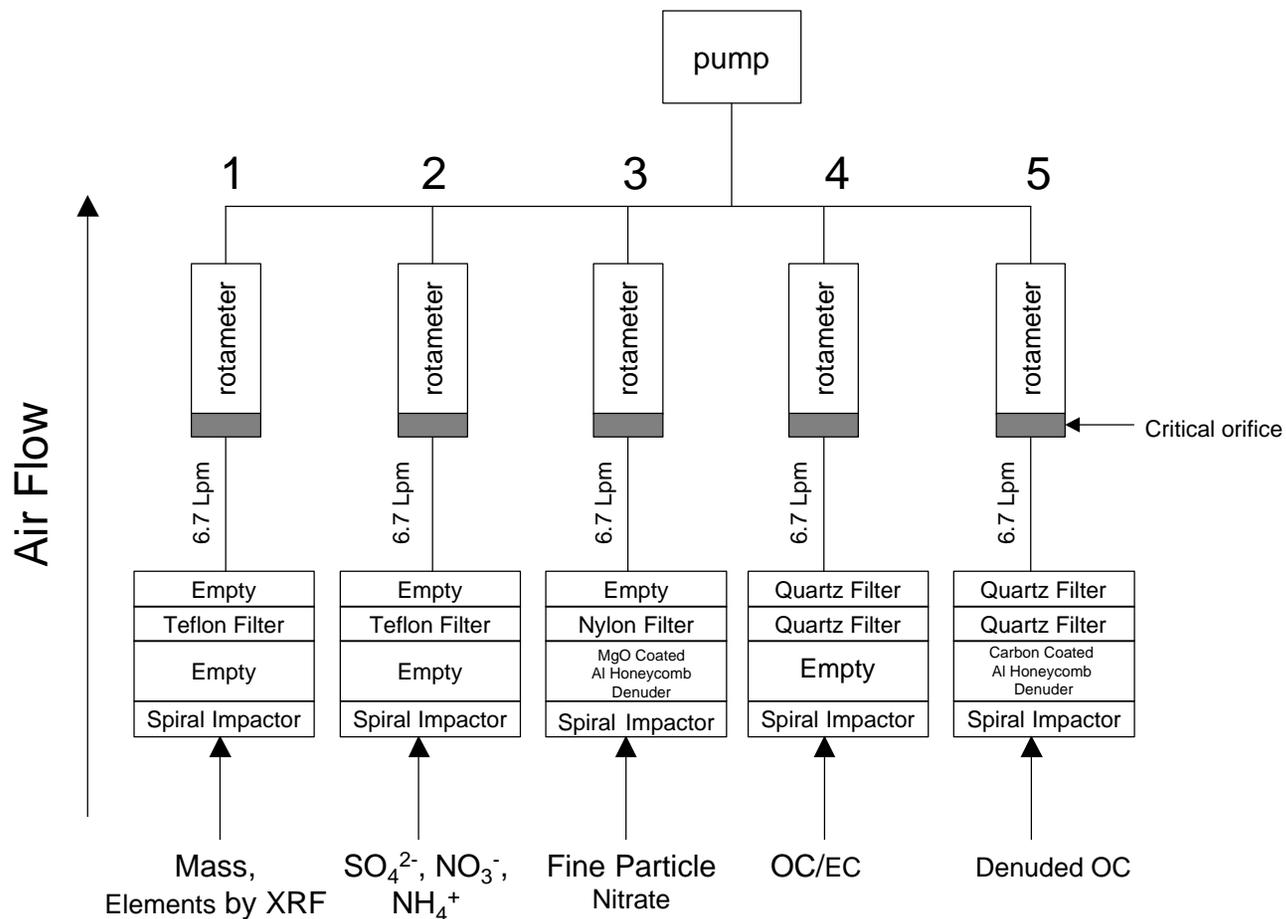


Figure 2. The Met One SASS Sampler

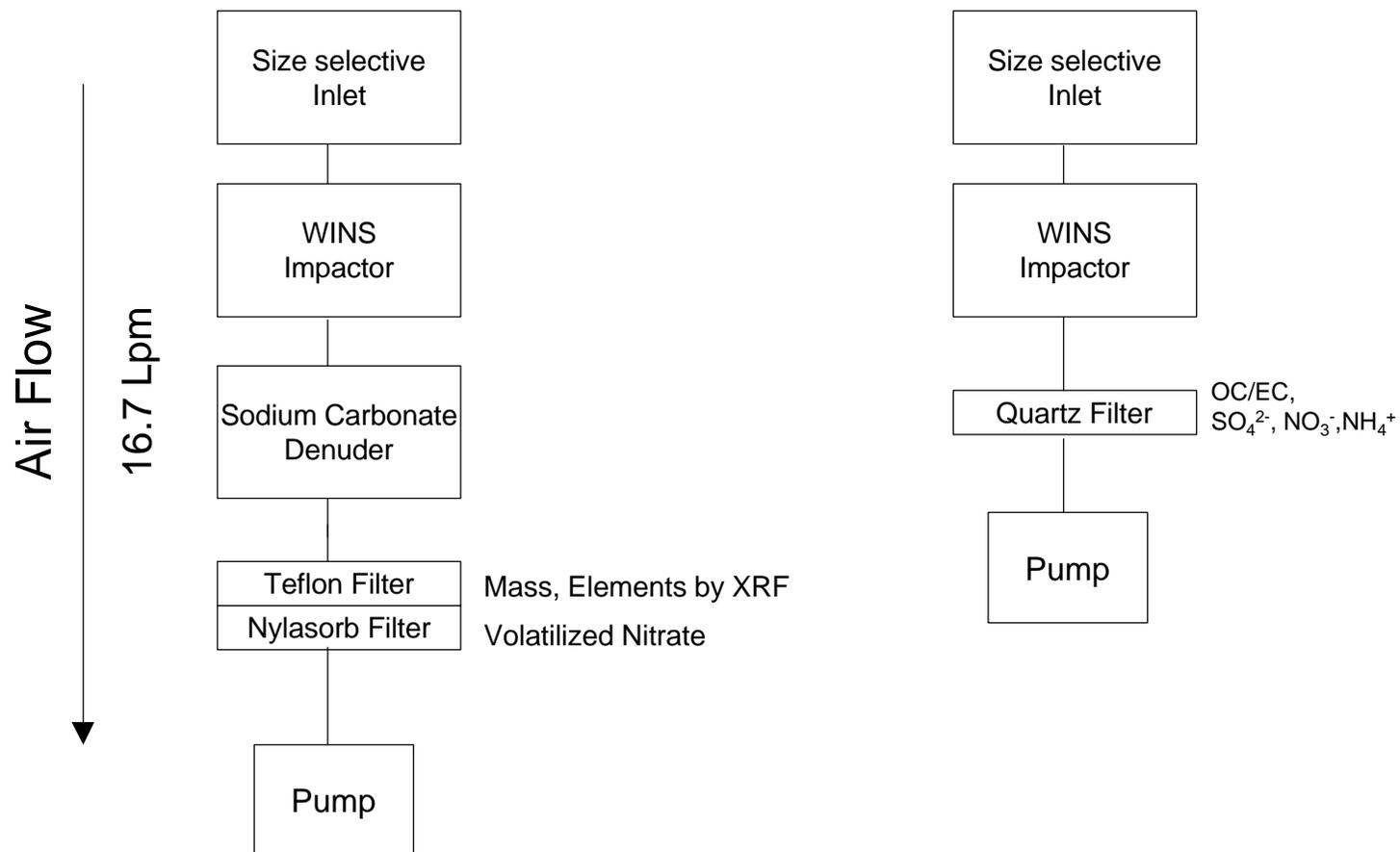


Figure 3. The URG MASS Sampler

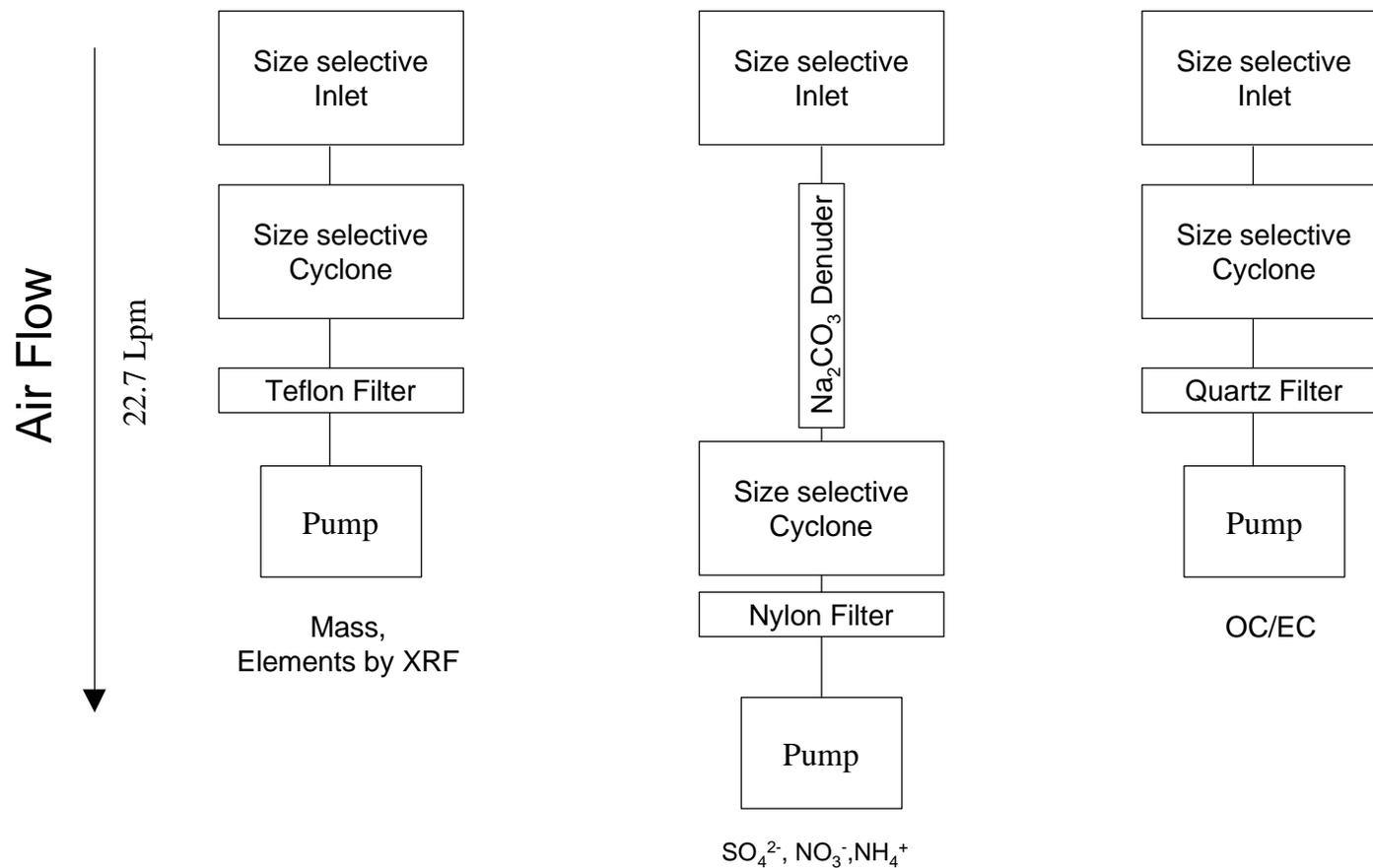


Figure 4. The IMPROVE Sampler

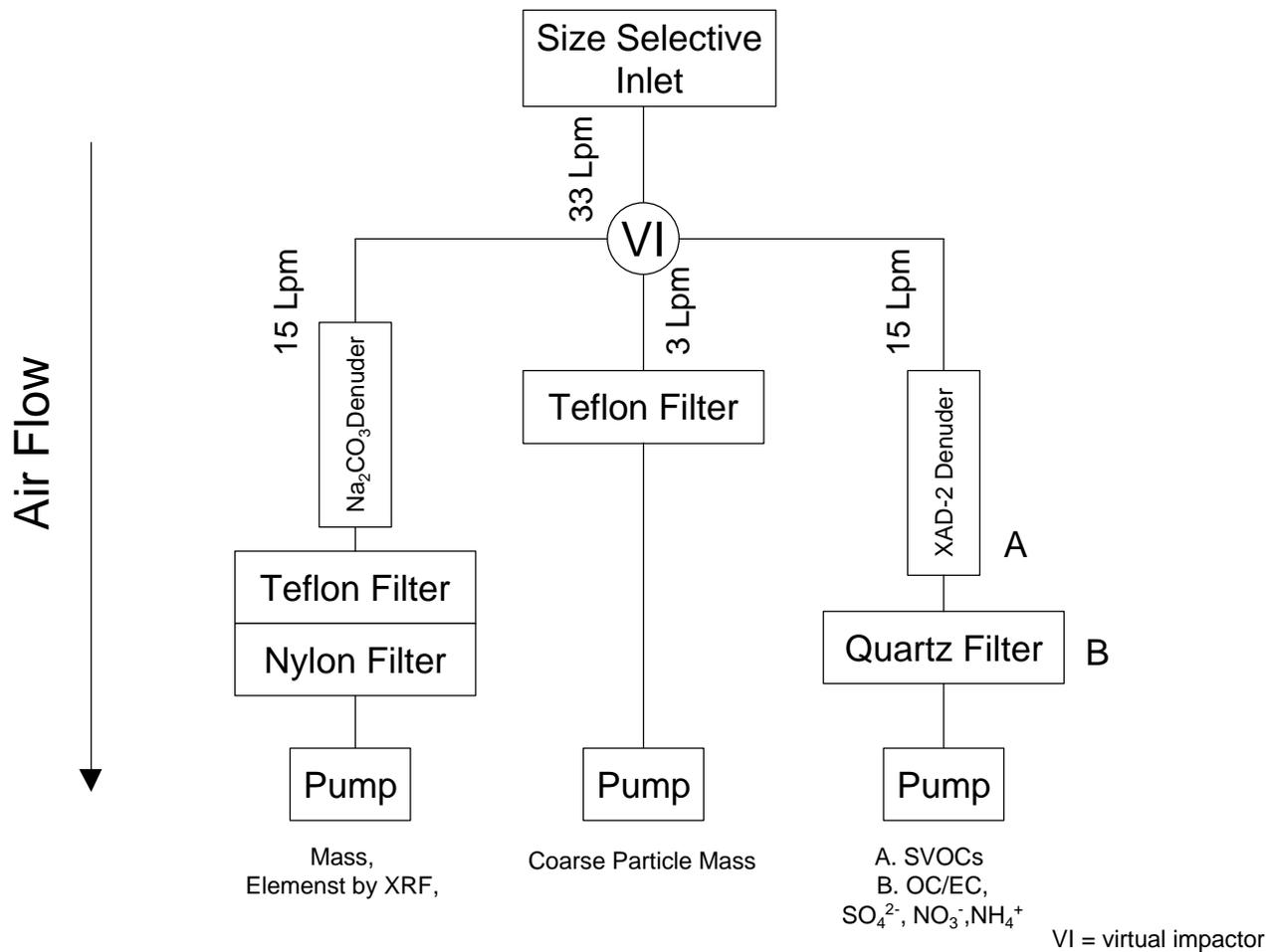


Figure 5. The VAPS Sampler

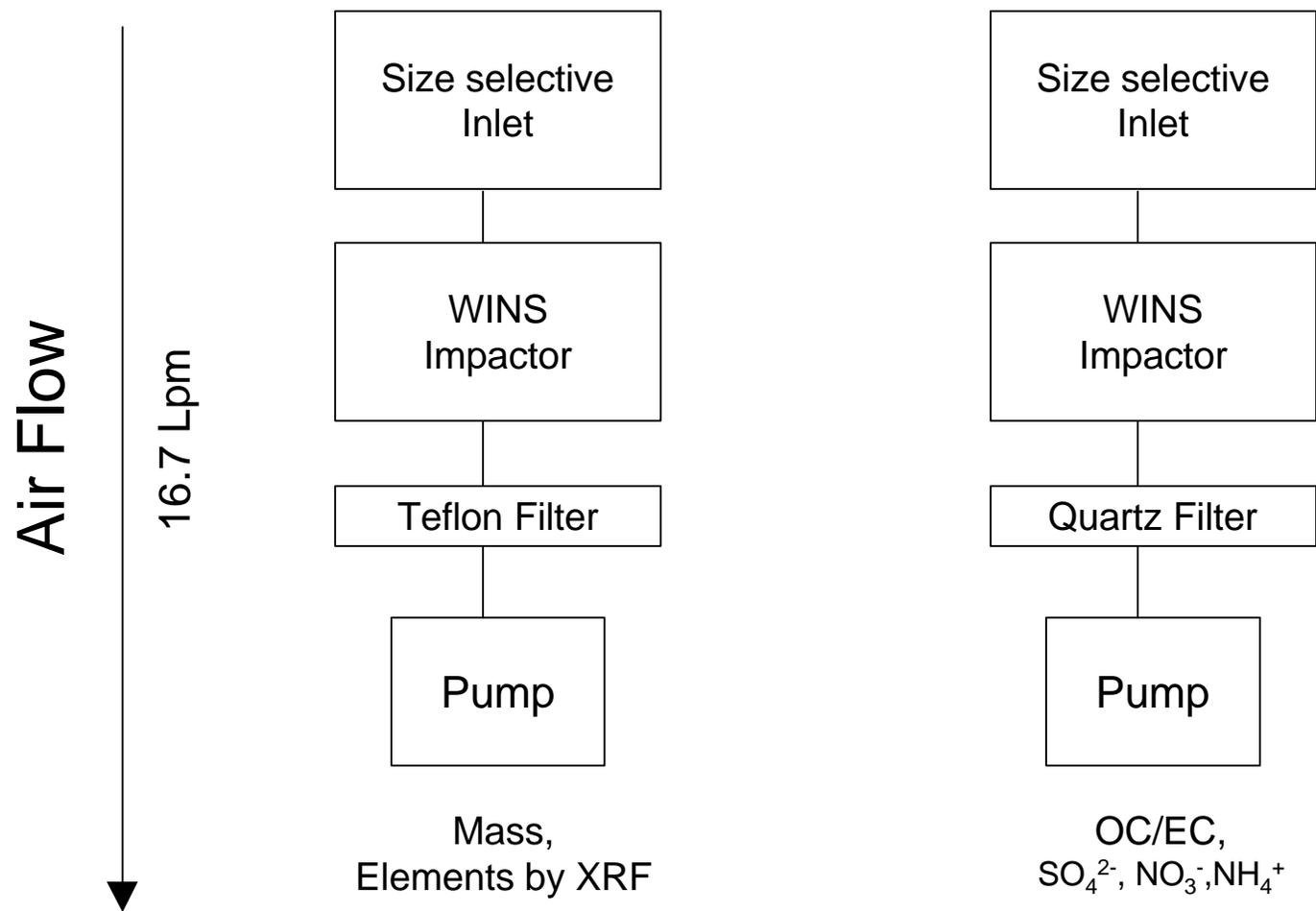


Figure 6. The Federal Reference Method Samplers

Chemical Speciation and Chemical Analysis

The chemical components of PM_{2.5} measured in this study will be the same as those specified for the National Network (EPA, 1998) and recommended by the expert peer-review panel (Koutrakis, 1998). Chemical characterization will include mass, sulfate, nitrate, and ammonium ions, elements (Na through Pb) by XRF, and OC/EC. Appropriate filter media will be used to allow for chemical analysis by routine methods as described in EPA (1998), Koutrakis (1998), and Chow (1995). As described above, these media combined with appropriate denuders should minimize sampling artifacts. The field study described here, however, will not involve comparisons to independent certified methods that would allow for an estimate of accuracy. However, comparison to the historical samplers (VAPS and FRM) will provide for a comparison to samplers that have been evaluated under a number of conditions. Differences in nitrate losses and possibly losses (negative artifact) or gains (positive artifacts) of SVOCs can be initially evaluated as a result of this intercomparison.

Chemical analysis of the aerosol on the collected filters will be by routine methods as described in EPA (1998) and Chow (1995). Figures 1-6 illustrate the experimental design for each sample and show which analytes will be determined on which filters for each sampler. Appendix A summarizes the chemical analysis methods. Detailed standard operating procedures (SOPs) are being prepared and will be followed for all analyses. In general, PM_{2.5} mass will be determined gravimetrically on Teflon filters. Elements (Na – Pb) will be determined on the same filter as PM_{2.5} mass by XRF. Anions (sulfate and nitrate), and ammonium ion will be determined from aerosol collected on several different filter media (Teflon, quartz-fiber, or nylon) and quantified using ion chromatography. In some cases, only nitrate will be determined on the nylon filters. Organic and elemental carbon (OC/EC) will be determined on the quartz-fiber filters using thermal-optical reflectance (TOR).

A special study will be conducted to evaluate the reliability of using the Teflon filter located behind the MgO or Na₂CO₃ denuder for determining mass gravimetrically, elements by XRF (vacuum and atmospheric pressure), and ions by ion chromatography, as is the original approach with the URG MASS speciation sampler and with the VAPS. The concern is the potential loss of nitrate and semi-volatile organic material from the Teflon filter during either vacuum or atmospheric pressure XRF. To evaluate this, Teflon filters assigned for elemental analysis will first be analyzed using the atmospheric pressure XRF available at ORD (Lewis, personal communication). A subset of 40 of these filters will be sent to a laboratory for analysis by vacuum XRF. Nitrate ion will then be determined in the remaining aerosol on the filters analyzed by vacuum XRF. The latter will be compared to nitrate ion determined on filters that have not undergone XRF analysis either on the same sampler using results from quartz-fiber filters or from Teflon filters collected on a collocated sampler. As well, nitrate and sulfate will be determined on the quartz-fiber filter located behind the organic denuder to determine ion analysis on the quartz-fiber filters is a suitable substitute for the determination of nitrate and sulfate in the URG and VAPS sampling systems.

Sampling Locations and Rationale

The determination of the sampling locations is based upon the following criteria. First, the statistical design requires testing each sampler under different chemical atmospheres and varying environmental conditions. Secondly, locations are chosen where PM sampling is ongoing with preference given to locations where PM chemical speciation sampling has occurred or will be occurring at the time of the study. Finally, sufficient infrastructure had to be available with local support to assist with filter changing and sampler operations. Four locations were chosen that meet these criteria: Philadelphia, PA, Phoenix, AZ, Rubidoux, CA, and Research Triangle Park, NC. Philadelphia represents a typical east coast situation where high sulfate and organic material are present in the aerosol, but nitrate is typically low. Phoenix represents an area with the potential for high crustal material, which typically is the dominant material above 2.5 μm , but with a tail in the less than 2.5 μm size range. Phoenix also has a strong nitrate and organic material component. Rubidoux represents an area with very high nitrate, moderate organic material, low sulfate, and relatively low crustal material. The RTP site is for sampler performance and evaluation studies as well as providing a site with particulate matter levels near the expected lower limit of detection for these samplers.

Of the four sites, Rubidoux will be the prime site because it will likely provide the most stringent test of the samplers for examining collection efficiencies of nitrate and semi-volatile condensed organic compounds, will have a full complement of PM, gaseous, and meteorological sampling equipment, including full chemical speciation using the SCAQMD's PTEMP sampler, and the characteristics of the air at Rubidoux has been well characterized by many studies over the last decade. Two full sets of samplers will be collocated at Rubidoux to obtain precision estimates. Table 1 outlines the existing sampler equipment located at Rubidoux, CA. Table 2 lists the equipment that is expected to be in place at Phoenix, AZ. As can be seen, these two sites will be well equipped to support this study with both additional PM measurements, meteorological measurements (the most important of which are relative humidity and temperature), and supporting gas phase measurements, such as ozone, nitrogen oxides, and sulfur oxides. The Philadelphia site will operate a PM10 sampler and collect meteorological data during the study. At RTP, samplers are being installed at a new NERL sampling platform. We anticipate basic surface meteorology, criteria gases, and PM2.5 mass by the FRM.

These sites represent Phase I of the program to evaluate the chemical speciation monitors due to study limitations. For example, we are missing the high sulfate season on the east coast and are not sampling in areas with either high biogenic organic material or high wood smoke emissions. Finally, the highest season for crustal material in Phoenix is during the summer, thus, crustal material will be a lower fraction of PM than desired. Phase II if resources are available will attempt to intercompare the samplers under the just mentioned conditions.

Table 1. Measurements made at Rubidoux, CA

Species	Measurement Method	Duration/Frequency ¹
PM _{2.5} PM ₁₀ Mass and Chemistry	Sierra Anderson Dichotomous Samplers	2, 6, and 24 hours, C
PM _{2.5} Elemental Carbon	Magee Scientific aethalometer with a Harvard Impactor PM _{2.5} inlet	5 minute average, C
Light scattering	Optec nephelometer	1 hour average, C
PM _{2.5} EC/OC	Rupprecht & Patashnick Total Carbon Analyzer	1 hour average, C
PM ₁₀ Mass	Rupprecht & Patashnick PM ₁₀ Federal Equivalent Method TEOM	1 hour average, C
Methane/NMHC	TEI hydrocarbon analyzer	1 hour average, C
NO _x /NO _y	TEI NO _x /NO _y analyzers	1 hour average, C
O ₃	One Dasibi ozone analyzer	1 hour average, C
CO	TEI CO analyzer	1 hour average, C
NO,NO ₂ ,NO _x	TEI NO _x analyzer	1 hour average, C
Wind Speed	AGL	1 hour average, C
Wind Direction	AGL	1 hour average, C
Standard Deviation of Wind Direction	AGL	1 hour average, C
Air Temperature	2 meters AGL, nephelometer height	1 hour average, C
Relative Humidity	2 meters AGL, nephelometer height	1 hour average, C
Delta Temperature		C

¹ O6-one in six days; C-continuous; D-Daily; OD-Every other day.

Table 2. Measurements Made at Phoenix, AZ

Species	Measurement Method	Duration/Frequency ²
PM _{2.5} PM ₁₀ Mass and Chemistry	Sierra Anderson Dichotomous Samplers	2, 6, and 24 hours/O6,D
PM _{2.5} Elemental Carbon	Magee Scientific aethalometer with a Harvard Impactor PM _{2.5} inlet	5 minute average/C
Light scattering	Optec nephelometer	1 hour average/C
PM _{2.5} EC/OC	Rupprecht & Patashnick Total Carbon Analyzer	1 hour average/C
PM ₁₀ Mass	Rupprecht & Patashnick PM ₁₀ Federal Equivalent Method TEOM	1 hour average/C
Methane/NMHC	TEI hydrocarbon analyzer	1 hour average/C
NO _x /NO _y	TEI NO _x /NO _y analyzers	1 hour average/C
O ₃	One Dasibi ozone analyzer	1 hour average/C
CO	TEI CO analyzer	1 hour average/C
NO,NO ₂ ,NO _x	TEI NO _x analyzer	1 hour average/C
Wind Speed	AGL	1 hour average/C
Wind Direction	AGL	1 hour average/C
Standard Deviation of Wind Direction	AGL	1 hour average/C
Air Temperature	2 meters AGL, nephelometer height	1 hour average/C
Relative Humidity	2 meters AGL, nephelometer height	1 hour average/C
Delta Temperature		1 hour average/C

² O6-one in six days; C-continuous; D-Daily; OD-Every other day.

Sampling Schedule

OAQPS requested a draft report of results from this intercomparison by March 1, 1999. However, this assumed that samplers would be here on or before October 15, 1998. With current delays, assuming that the outstanding samplers are delivered early the week of Nov. 9, 1998, a draft report will be delivered to OAQPS on April 2, 1999. Any further delays in delivery of the samplers will result in a further delay of this intercomparison and of the final report.

With the above assumption, we anticipate being in the field in early December. Prior to field installation, samplers are under going a detailed systems audit at RTP. Also during that period, field management personnel will be trained on the detailed operation of the samplers. Next, the samplers will be shipped to the field, installed, daily operators will be trained, and the systems will undergo systems and performance audits by the ORD field managers and local agency staff. We will sample on an every other day sampling frequency at all sites except Rubidoux, which will be 1 in three. The less frequent schedule at Rubidoux allows for sampling on the same schedule as the PTEMP sampler operated by the SCAQMD. The goal, based on the statistical design is to collect 15 successful sample sets, where most if not all samplers are operating simultaneously. The above schedule should allow us to meet this goal, as we have planned for the collection of up to 20 days over the two-month period from early December through the end of January. The ability to collect samples every other day will depend on local site operators' (contractors, state, or district personnel) schedule. The final data archive would not be due to EPA until March 1, 1999, assuming an early December sampling start date. This should allow for sufficient time to prepare a draft report by April 2, 1999, although internal ORD review may need to occur at the same time as the OAQPS review.

To meet the every other day sampling schedule, filters and holders will be shipped overnight to the contractor immediately after collection according to the schedule illustrated in Table 3. Filters, the XAD denuder in the VAPS, and all Na_2CO_3 denuders will be shipped in coolers at reduced temperatures (with blue ice) and with a max/min thermometer. Three full sets of filter holders and denuders will be available for this purpose. All samples will be collected for 24-hr sampling periods. Filters and denuders that need to be changed will be installed during the morning of Day 1 and sampled until the morning of Day 2, operating for 24 hours. This should provide sufficient time for filters to be changed on all samplers at one site. During the morning of Day 2 the filters are removed, log sheets annotated, and the filters shipped overnight to the laboratory where filters will be removed from their holders, the holders cleaned, loaded with new filters, and then shipped back to the field on day three. The filters arrive in the field on day four and are installed for use the morning of Day 5 to begin sampling at midnight of day 6. The process then continues. The second set of filters is shipped to the field on Day 2 to sample on Day 3. The process continues as with the first set of filters.

Study Implementation**Overall Program Schedule**

Table 3 summarizes the overall schedule for this study. The schedule is driven by two criteria: 1) a draft report is due to OAQPS by early June, 1999 and 2) all five sets of the three chemical speciation samplers and the IMPROVE sampler will be delivered to ORD no later than November 10, 1998. This includes delivery of spare parts and extra filter holders to allow for every-other-day sampling. These two criteria uniquely define the schedule for the program and dictate that sampling must be performed simultaneously at the four locations chosen for this study. This time frame is challenging and further delays in the delivery of the samplers will likely result in delay of the final report beyond early April, 1999. The statistical design requires the collection of 15 valid samples on all samplers simultaneously at a given site. To help ensure this 20 sample sets will be collected at each site.

The current schedule has sampling beginning in early December and ending at the end of January. This schedule requires sampling every-other-day, including weekends, but finishes the sampling portion of the program by the end of January, after which the samplers will likely be sent to Seattle to collect PM during periods with high wood smoke emissions. If this schedule is maintained, all chemical analysis should be completed by mid-February 1999 with Level II data delivered to EPA as specified by March 15, 1999. EPA will perform statistical analysis on the data and prepare a draft report for internal review by April 30, 1999. After addressing internal review comments, a draft final report will be delivered to OAQPS on May 25, 1999 for review and implementation as needed. This is a rigorous and challenging schedule to maintain, especially during the holidays. The EPA project managers will keep OAQPS closely informed of the status of the project and immediately notify OAQPS staff of any further delays. This schedule is predicated on the basis that the samplers will be delivered to EPA/ORD/NERL by November 1, 1998. Delays in the sampler delivery date may further delay study and submission of the draft report.

Preliminary Evaluation and Training

Once samplers have been received at EPA in Research Triangle Park, they will be configured for use in the field for this study and undergo a full shakedown, which will be overseen by Mr. Gemmill of EPA/NERL. It is expected that one representative from each manufacturer will be available to ensure proper assembly of their samplers and to train RTP personnel. The shakedown audit will include, for example, running each sampler for two-12 to 24 hour periods to ensure the samplers are turning on and off as expected, flow rate checks, flow control checks, leak checks, etc. EPA and contractor personnel will be trained to change filter holders and denuders as needed. Contractor and EPA personnel will be trained on how to change filters, clean filter holders and impactors as needed, and how to re-coat denuder tubes. Standard operating procedures (SOP) (see Appendix B) will be made available from the manufacturers when the samplers are delivered to RTP. SOPs for field and laboratory efforts are being prepared by the contractor and will be delivered one week before field sampling begins. A list of expected SOPs is given in Table 4. All parties involved in operating the samplers will review the SOPs.

Table 3. Overall Study Schedule.

Date	Deliverable
1998	
November 10	Standard operating procedures received from the 3 chemical speciation sampler manufacturers and for the IMPROVE and VAPS samplers
October 1-Nov. 20	Sites prepared for sampler installation. Power and platforms installed as needed to accommodate all samplers (see Tables 1 and 2 for listing of samplers at each site).
Nov 1 - 30	Samplers will undergo an evaluation and RTP field personnel will be trained on installation, operation, and quality control
Nov 12-24	External review by the expert peer-review panel on chemical speciation.
Nov 20-Dec 10	Samplers shipped to sampling sites and local operators trained.
Dec 8-Dec 12	Systems and performance audits performed with help from local agency (Rubidoux and Phoenix)
Dec 14	First day of sampling. (Rubidoux and Phoenix)
1999	
Jan 4-Jan 5	Systems and performance audits performed with help from local agency (Phoenix and Philadelphia)
Jan 6	First day of sampling (Philadelphia and RTP)
Jan.1-4	Systems and performance audits performed with help from local agency.(optional) Chemical analysis of first half of samples should be started.
March 1	Last day of sampling. Systems and performance audits performed with help of local agency.
March 2-5	Decommission sites.
March 20	Chemical analyses complete.
April 15	Level II data delivered to EPA for all chemical analyses.
April 15-May 1	EPA review data and begins initial statistical analysis ¹
May 1-May-15	All final statistics prepared, including plots, tables, and figures
May 15-May 30	Prepare report and submit to internal NERL review group for comments
June 15	Address comments from internal review group
June 25	Provide OAQPS with draft report.

¹. Initial results are forwarded to OAQPS at this point or earlier.

Table 4. List of Standard Operating Procedures for Field and Laboratory Efforts During the Chemical Speciation Monitor Evaluation Study.

Field Related SOPs

SOP	Prepared By	Status	Short Version for Field
Spiral Ambient Speciation Sampler	MetOne	Delivered	In Progress
Reference Ambient Air Sampler	Andersen	In Progress	Unknown
Mass Aerosol Speciation Sampler	URG Corp.	In Progress	Unknown
IMPROVE Sampler	UC Davis	Delivered ¹	RTI to Prepare
Versatile Air Pollution Sample	RTI	In Progress	RTI to Prepare
PM2.5 Federal Reference Method	RTI	In Progress	RTI to Prepare
Filter Pack and Cassette Handling in the Field	RTI	In Progress	RTI to Prepare
Denuder Handling and Shipping in the Field	RTI	In Progress	RTI to Prepare
Receiving, Laboratory and Field	RTI	In Progress	RTI to Prepare
Shipping at Reduced Temperatures	RTI	In Progress	RTI to Prepare

Laboratory Related SOPs

SOP	Prepared By	Status	Comments
Filter Pack and Cassette Handling in the Lab	RTI	In Progress	
Denuder Preparation – Na ₂ CO ₃	RTI	In Progress	
Denuder Extraction – Na ₂ CO ₃	RTI	In Progress	
Denuder Preparation – MgO	RTI	In Progress	
Denuder Preparation – XAD	RTI	In Progress	
Denuder Regeneration – XAD	RTI	In Progress	
Denuder Extraction – XAD	RTI	In Progress	
PUF Cartridge Cleaning and Preparation	RTI	In Progress	
Filter Preparation – Nylasorb (nylon)	RTI	In Progress	
Filter Preparation – Teflon	RTI	In Progress	
Filter Preparation – Quartz-Fiber	RTI	In Progress	
Acceptance Testing of Filters	RTI	In Progress	
Filter Sectioning Procedures	RTI	In Progress	
Filter Extraction – Nylasorb	RTI	In Progress	
Filter Extraction -- Teflon	RTI	In Progress	
Filter Extraction – Quartz-Fiber	RTI	In Progress	
Mass by Gravimetric Analysis	RTI	Complete	Federal Register for FRM
Anions by Ion Chromatography	RTI	Draft Complete	
Cations by Ion Chromatography	RTI	Draft Complete	
XRF – Atmospheric Pressure	Mantech/NERL	Complete	
XRF – Under Vacuum	DRI/Reno	Complete	
Thermal-Optical Reflectance (TOR)	DRI/Reno	Complete	
Thermal-Optical Transmittance (TOT)	Sunset Labs	In Progress	
Data Validation	RTI	In Progress	

¹ SOP is not complete. RTI will prepare one for the field operators.

Filter and Denuder Preparation

Several of the filters require pretreatment to lower blank levels. For example, nylon filters must be cleaned before use to ensure consistently low blank levels, while quartz-fiber filters used for OC/EC analysis are baked for several hours (Chow, 1995). Table 5 lists the filters by sampler type and indicates general filter preparation needs. Denuders must be coated initially, cleaned or refurbished, and recoated as needed. As described in Table 5, MgO denuders only require the initial coating as they are believed to have sufficient capacity and can not be extracted for chemical analysis. The Na₂CO₃ coated denuder, must be cleaned and re-coated after every use. In the VAPS, this denuder will be extracted and analyzed for HNO₃. The XAD denuders, must be refurbished after every sampling period, and re-coated after every tenth sampling period.

Site Installation and Decommissioning

Samplers will be installed at each site as follows. All sites will have one of each of the three chemical speciation samplers, one IMPROVE, one VAPS, and one set of two FRM samplers. Rubidoux will have a collocated second set of all samplers except the VAPS sampler. EPA personnel will install the samplers at all but the RTP site. Systems and performance audits will be conducted on each sampler by the EPA personnel and in conjunction with local operators, as described below. After the study, EPA personnel will perform a second system and performance audits of the samplers and decommissioning of the sites.

Sampler Operation and Filter Shipping and Storage

Samplers will be operated according to the SOPs as given for each sampler in Appendix B. Samplers will operate for 24-hr periods every-other-day except at Rubidoux to operate on the same schedule as the PTEMP sampler. This will allow time for filters and holders to be shipped to the contractor for exchange, thus, removing site-to-site variability for filter changing. Filters will be shipped in coolers at reduced temperature with a max/min thermometer. At a minimum, each cooler should contain sufficient blue ice, sealed in plastic bags, or some other closed system to keep the filters cool for 24-hours. Battery operated coolers are another option. At the field site, the filters should be stored before and after sampling at reduced temperatures in a refrigerator, especially after sample collection. Except for equilibration of filters for mass determination, filters with collected aerosol should be stored in sealed petri dishes at reduced temperatures and preferably at or below freezing.

Table 5. Experimental Design Including Filter and Denuder Preparation.

Sampler	Filter Type (Channel)	Denuder Type	Analysis	Filter and Denuder Preparation
Andersen RAAS	Teflon (2)		(2) Mass and elements ⁵	Filters have to be equilibrated before weighing
	Teflon (3)		(3) ions ⁶	Filters are wet with ethanol before extraction
	Nylon (4)	MgO	Fine particle NO ₃	Nylon filters must be cleaned before use and extracted in IC eluent MgO denuders are not changed or cleaned during the study
	Quartz (1)		OC/EC	Quartz filters must be baked before use
Met-One SASS	Teflon (1)		(1) Mass and elements	Filters have to be equilibrated before weighing
	Teflon (2)		(2) ions	Filters are wet with ethanol before extraction
	Nylon (3)	MgO	Fine particle NO ₃	Nylon filters must be cleaned before use and extracted in IC eluent MgO denuders are not changed or cleaned during the study
	Quartz (4)		OC/EC	Quartz filters must be baked before use
	Quartz (5)	Elemental Carbon	OC/EC, SVOCs from denuder	Quartz filters must be baked before use Carbon denuder needs to be heat treated every 7 samples
URG MASS	Teflon		Mass and elements	Filters have to be equilibrated before weighing
	Nylon	Na ₂ CO ₃	Volatilized nitrate	Nylon filters must be cleaned before use and are extracted in IC eluent Na ₂ CO ₃ denuders must be cleaned and re-coated daily
	Quartz		OC/EC, ions	Quartz filters must be before use Filter will be split in half to allow for ion analysis
IMPROVE	Teflon		Mass and elements	Filters have to be equilibrated before weighing
	Nylon	Na ₂ CO ₃	Volatilized nitrate	Nylon filters must be cleaned before use and are extracted in water since NH ₄ ⁺ will also be analyzed in the extract Na ₂ CO ₃ denuders must be cleaned and re-coated daily
	Quartz		OC/EC	Quartz filters must be baked before use
VAPS	Teflon	Na ₂ CO ₃	Mass and elements Denuder for HNO ₃	Filters have to be equilibrated before weighing Na ₂ CO ₃ denuders are extracted and re-coated daily
	Nylon	Na ₂ CO ₃	Volatilized nitrate	Nylon filters must be cleaned before use. Nylon is backup filter in a Teflon/nylon filter pack
	Quartz	XAD-4	Filter for OC/EC, ions Denuder for SVOCs	Quartz filters must be baked before use XAD denuders must be rinsed daily, re-coated every 10 samples
FRM	Teflon		Mass and elements	Filters have to be equilibrated before weighing
	Quartz		Ions and OC/EC	Quartz filters must be baked before use Filter will be split in half to allow for ion analysis

5. Elements refer to those obtained from XRF analysis, potential Na to Pb.

6. Ions include nitrate, sulfate and ammonium.

Chemical Analysis

Listed below is a summary of the analytical methods to be used to determine the chemical composition of the aerosol collected on Teflon, quartz-fiber, and nylon filters. SOPs for filter preparation and handling, denuder preparation, and handling, filter extraction, and analytical methods are given in Appendix B of this report. A more detailed summary of the analytical methods than given here is given in Appendix A.

PM_{2.5} mass, will be determined gravimetrically on Teflon filters using a microbalance (see Appendix B). These same filters will be analyzed for elements from Na to Pb by atmospheric pressure X-ray fluorescence (see Appendix B). In this method, the filter is open to the atmosphere, but surrounded by a sheath of He gas. Secondary x-rays are used as the excitation source resulting in virtually no heating of the filter or collected sample. Quantification of XRF spectra are obtained by comparing to standards of known concentration as described in the SOP. Atmospheric concentrations are obtained from the volume of air sampled.

Atmospheric pressure XRF, with secondary ion excitation will likely minimize loss of volatile species during XRF analysis, e.g., nitrate and condensed SVOCs, thus, these filters might be able to be analyzed for nitrate, sulfate, and ammonium at a later date, or archived for other uses (e.g., QC check on final mass). However, most analytical laboratories use vacuum XRF, which would likely result in a significant loss of volatile species from the filter and limit its use for other analyses. Therefore, determining the effect of vacuum XRF on volatile species is important for two reasons. First, the MASS sampler, as specified from the manufacturer uses the same filter to obtain mass, elements by XRF, and ions. If volatile species, i.e., nitrate and ammonium, are lost during vacuum XRF then the subsequent determination of those species will be biased by the amount lost. Secondly, the FRM sampler in the compliance network is being used only for mass determination. If vacuum XRF does not bias the nitrate, ammonium, and organic determinations, then these filters can be archived and, if needed re-weighed at a later time, or analyzed for sulfate, nitrate, and ammonium to provide a more detailed chemical composition of the collected aerosol from the FRM sampler. The alternative would be requiring atmospheric pressure XRF analysis of all Teflon filters or not using the filters for further chemical analysis. To examine the potential loss of volatile species from the collected Teflon filter during vacuum XRF (see SOPs and Appendix B), 40 filters will be analyzed by vacuum XRF, after atmospheric XRF analysis, and then analyzed for sulfate, nitrate, and ammonium by extraction and IC analysis as described below. These ions will be compared to their concentrations collected by the same sampler and by collocated samplers.

As just described, analysis of Teflon filters by atmospheric pressure XRF may also result in the loss of volatile species due to loss of nitrate and ammonium from the phase equilibrium shifting to the gas phase as He passes over the sample. Anions (sulfate and nitrate) will be determined by ion chromatography (IC) (see Appendix B). Anion and ammonium ion concentrations will be determined in the extract from Teflon filters or quartz-fiber filters as illustrated in Figures 1-3 and 5-6 that show the experimental design for each sampler. For the IMPROVE sampler, anions and ammonium will be obtained from extracting the nylon filters. Volatilized nitrate will be determined in the extract from the nylon filters located behind the Teflon filter used for anion analysis in the URG and VAPS samplers. Anions also will be determined from a section of the quartz-fiber filter in the URG chemical speciation, VAPS, and FRM samplers, for comparison to anions determined from extracts of Teflon filters. This will help to ensure that nitrate and sulfate collected on the quartz-fiber filter can be used for anion determination if nitrate and ammonium are lost from the Teflon filter during XRF.

Teflon filters will be wetted with 50 l ethanol and then extracted in water or IC eluent according to the SOP listed in Appendix B. If the filter also is to be used for analysis of ammonium ion analysis then the filter will be extracted in water. Quartz-fiber filters will be extracted in water. Nylon filters will be extracted in the IC eluent used for anion analysis (see Appendix B). Use of eluent minimizes the water dip associated with anion analysis that could interfere with the determination of chloride ion. However, chloride ion is not being determined in this intercomparison study. Standards will be run according to the procedures outlined in the SOP (Appendix B) and used to quantify the concentrations of the anions in the extract. Atmospheric concentrations will be obtained based on the amount of filter used, volume of eluent, and volume of air sampled.

Cations (ammonium ion) will be determined by ion chromatography (see Appendix B). Ammonium ion will be determined in the extract from Teflon, quartz-fiber, or nylon filters as described above for anions. Teflon filters will be wetted with 50 l of ethanol and extracted in either distilled water (DI water) or IC eluent, according to the SOP found in Appendix B. Standards will be run according to the procedures outlined in the SOP (Appendix B) and use to quantify the concentrations of the anions in the extract. Atmospheric concentrations will be obtained based on the amount of filter used, volume of eluent, and the volume of air sampled.

Organic and elemental carbon collected on baked quartz-fiber filters will be determined by the thermal/optical reflectance method (see SOP). In this method, a portion of the quartz-fiber filter is heated first in He to remove organic material and then in He with 2% oxygen to determine elemental carbon. Optical reflectance of the sample is monitored to correct the OC/EC analysis for possible charring during the highest temperature step in 100% He. The volatilized carbon is converted to methane and measured by an FID. Concentrations are determined by comparison to a known standard. Atmospheric concentrations are obtained based on the amount of filter used and the volume of air sampled.

As described above, some of the filters are used for more than one analysis or the analytical method itself requires only a section of the filter. For example, Teflon filters for anion and cation analysis are split in half so that each half can be extracted using the appropriate solution. Quartz-fiber filters are sectioned and only a small section (about 1 cm²) is used for analysis. As well, in the case of the URG chemical speciation sampler a section will be used for ion analysis. The SOP for sample sectioning is found in Appendix B.

Quality Assurance/Quality Control (QA/QC)

Field QA/QC

Quality assurance will consist of system and performance audits by local district or state audit personnel at the request of EPA, if resources are available. If not, EPA will provide these audits. Initial QA audits of the samplers will be performed prior to the first sample if possible, or as quickly after the initiation of the program as possible. A second set of system and performance audits will be performed in the middle of the program, between the 8th and 10th sampling periods. A third set of audits will be performed after the last sample, but before decommissioning of the samplers either by EPA personnel or local district or state personnel. System audits will check installation of the samplers, site setting, site operations and operators, and custody management. Performance audits will check flow rates, check for vacuum leaks, and other performance characteristics of the samplers. Quality control will consist of checking flow rates before and after each sample on every filter unless automatically logged by the sampler, maintaining appropriate operations logs, checking filter holders and denuders prior to and after each sampling period, and other items as specified on the data log sheets.

Laboratory QA/QC

Laboratory systems and performance audits will be conducted for species according to schedules already in place in the laboratories. Results will be reported to EPA staff in the final report, unless results fall outside of normal laboratory operations.

Personnel

EPA, local agency, and contractor personnel will be utilized for the field portion of the project, while only contractors perform laboratory operations. EPA personnel will be responsible for training field technicians, sampler installation, initial QC checks, overall management, and decommissioning of the sites, except at the RTP site where the contractors will take primary responsibility. Approximately 700 hours of the field portion of this project out of about 1800 hours will be performed by EPA staff, about 625 by local site operators, and the remainder by contractors. Besides chemical analysis, contractors will be responsible for tracking filters (from receipt of the new filter to final value reported in data archive), changing filters, cleaning filter holders and other items, preparing and maintaining denuders, chemical analysis, data management, data quality assurance, and delivery of the final data archive. Other items may arise and this list is not meant to be comprehensive, but to summarize personnel for major tasks. Local staff (state or local agency) will be under supervision of the local management.

Contingencies

It has been assumed in this plan that site operations will be provided through in-kind support by either state or local agencies. This has been confirmed for Rubidoux and Phoenix. Two contingencies have been developed for the other sites. The first, which likely will not increase the budget, is to pay local site operators a small fee for changing filters (about \$2,500 for the study). The second approach, which likely will increase the budget, is to have the main contractor for the study provide on-site operators. It has also been assumed that QA will be performed by state and local agencies as in-kind support or by EPA staff. If a contractor perform these tasks, the budget will likely increase as well.

Spare parts for the samplers are being obtained prior to the start of the study (excluding pumps, circuit boards, and similar equipment). One of each of the chemical speciation samplers (the retrofitted first articles) will be available if needed. Arrangements will be made with the vendors to supply major parts overnight if failures occur.

Statistical Analysis

Statistical Hypotheses Being Tested

As described above in the introduction, the primary objective of this study is to determine if there are differences among the three chemical speciation monitors for their estimation of the concentrations of the chemical components of PM_{2.5} mass. Comparisons also will be made to two historical samplers and to the FRM using these samplers as a relative reference.

There are two major questions to be addressed by this intercomparison study.

- § How do the chemical components as determined by the FRM compare to those measured by the chemical speciation monitors or can FRM mass be reconstructed within expected uncertainties from the sum of the chemical components as measured by the chemical speciation monitors, and
- § How well do the measured concentrations from the various speciation samplers agree? This can be considered in two parts:
 1. The first is associated with examining the differences among the samplers, without regard to the cause of the differences, if they exist. This will be addressed through analysis of variance (ANOVA).
 2. The second part will examine the causes of the differences, if they exist. Some are expected due to the different methods employed.
- § A third set of hypotheses deals with the potential effect of different analytical methods on measured concentration of the chemical components of PM_{2.5}. These include the effect of vacuum XRF vs. atmospheric pressure XRF on nitrate concentrations measured on Teflon filters and the effect of thermal optical reflectance vs. thermal optical transmittance on OC/EC concentrations.

All of the 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 following 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 (one site, one time of the year, one set of atmospheric conditions), it will provide a first cut estimate of the precision needed for the statistical analysis to be performed here. If for example, the precision is estimated at 50%, then determining differences among samplers will not be as informative as if the precision were say 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, we anticipate a range of precision from less than 10% to about 30%.

In the following discussion, the phrase “speciation samplers” includes the Andersen RAAS, the URG MASS, the Met-One SASS, the IMPROVE, and the VAPS.

The following hypotheses are related to reconstructing the measured FRM mass. For each of these hypotheses, the concentrations, on a species-by-species basis, from each of the speciation samplers is compared to the respective concentration from the FRM. The concentrations from the speciation samplers are not compared to each other. The specific hypotheses are:

1. PM_{2.5} mass concentrations on the FRM by gravimetric method on the Teflon filter compared to PM_{2.5} mass as measured by the chemical speciation monitors. The hypothesis is that the mass concentration from each of the speciation samplers is not statistically different from the mass on the FRM filter. This is the starting point. The next eight hypotheses delve further into understanding why the mass concentrations do or do not compare favorably.
2. PM_{2.5} elements or groups of elements on the FRM Teflon filter as determined by XRF are compared to metals on the Teflon filters in the speciation samplers. The hypothesis is that there is no statistical difference between the concentrations from each of the speciation samplers to that from the FRM. These concentrations should be comparable since these species are stable.
3. PM_{2.5} sulfate on the FRM quartz filter is compared to sulfate on the Teflon (RAAS, SASS), quartz (MASS, VAPS), or nylon (IMPROVE) filters in the speciation samplers. The hypothesis is that there is no difference between the concentrations from each of the speciation samplers to that from the FRM, with the possible exception of the IMPROVE. These concentrations should be comparable since sulfate is a stable species.
4. PM_{2.5} ammonium on the FRM quartz filter compared to ammonium ion on the Teflon (RAAS, SASS), quartz (MASS, VAPS), or nylon (IMPROVE) filters in the speciation samplers. The hypothesis is that there is no difference between the concentrations from each of the speciation samplers to that from the FRM. These concentrations may not be comparable since ammonium is volatile when in the form of ammonium nitrate.
5. PM_{2.5} nitrate on FRM quartz filter is compared to nitrate on the Teflon (RAAS, SASS), quartz (MASS, VAPS), or nylon (IMPROVE) filters in the speciation samplers. The hypothesis is that there is no difference between the concentrations from each of the speciation samplers to that from the FRM. These concentrations should be comparable since the collection of nitrate on these filters should all be biased by the loss of nitrate due to volatilization, with the exception of the IMPROVE.

6. PM_{2.5} nitrate on the FRM quartz filter is compared to nitrate on the nylon (RAAS, SASS, IMPROVE), or quartz+nylon (MASS, VAPS) filters in the speciation samplers. The hypothesis is that the nitrate from each of the speciation samplers is greater than or equal to the nitrate on the FRM Teflon filter, due to negative artifacts in the FRM. This addresses questions about the amount of nitrate volatilized from the FRM Teflon filter.
7. PM_{2.5} elemental carbon (EC) on the FRM quartz filter is compared to EC on the quartz filters from the chemical speciation samplers. The hypothesis is that there is no difference between the concentrations from each of the speciation samplers to that from the FRM. These concentrations should be comparable since elemental carbon is stable.
8. PM_{2.5} organic carbon (OC) on the FRM quartz filter is compared to OC on the quartz (MASS, RAAS, SASS, IMPROVE) filters in the speciation samplers. The hypothesis is that there is no difference between the concentrations from each of the speciation samplers (except the VAPS) to that of the FRM. These concentrations should be comparable since as designed they all potentially suffer from negative or positive artifacts, except the VAPS that is operating with an XAD denuder.
9. PM_{2.5} OC on the FRM quartz filter is compared to OC on the quartz filter from the VAPS speciation sampler and from channel 5 on the SASS sampler. The hypothesis is that OC on the FRM will be greater the OC collected by the VAPS or SASS denuded channels if there are positive or less than the VAPS and SASS denuded channels if there are negative artifacts. No difference would be inconclusive.

The following hypotheses compare the concentrations of the chemical components measured on the chemical speciation samplers to address why there are differences among measured concentrations, if they exist. For each of these hypotheses, only the concentrations from the speciation samplers are compared, excluding the FRM, except for the first hypothesis, which will include the FRM in the analysis.

1. PM_{2.5} mass and chemical composition as determined according to the manufacturer's guidelines. The hypothesis is that all species of interest are comparable among the chemical speciation samplers when concentrations are determined according to manufacturer's guidelines. This will be tested using analysis of variance.
2. PM_{2.5} mass concentrations by gravimetric method on Teflon filters are compared among the samplers. The hypothesis is that there is no difference in these masses.
3. PM_{2.5} elements (individually or in groups) from the Teflon filters as measured by XRF are compared among the samplers. The hypothesis is that there is no difference in these concentrations as these elements are stable during sampling and analysis.
4. PM_{2.5} nitrate concentrations from the nylon (RAAS, SASS, IMPROVE) or Teflon+nylon (MASS, VAPS) filters are compared among the samplers. The hypothesis is that there is no difference in these concentrations.

5. PM_{2.5} sulfate from the Teflon (RAAS, SASS), quartz (MASS, VAPS), or nylon (IMPROVE) filters are compared among the samplers. The hypothesis is that there is no difference in sulfate concentrations as sulfate is stable during sampling and analysis. We will also look at sulfate estimated from XRF sulfur ($S \times 3$ equal to sulfate) to see how well XRF sulfur estimates sulfur determined by IC from both Teflon or quartz filters.
6. PM_{2.5} organic and elemental carbon from the quartz filters where no denuder is used will be examined relative to each other. Since channel 5 of the RAAS and VAPS use denuders, they will not be included in this hypothesis. The hypothesis is that the concentrations of OC and EC are the same provided no denuder is employed.
7. PM_{2.5} organic and elemental carbon from quartz filters including speciation samplers where a denuder is used is compared among the samplers. The hypothesis is that samplers that use denuders (VAPS and channel 5 of the SASS) will have lower concentrations since the potential for positive artifact due to organic vapors has been minimized. Nothing can be said about negative artifacts.
8. PM_{2.5} ammonium from the Teflon (RAAS, SASS), quartz (MASS, VAPS), or nylon (IMPROVE) filters are compared among the samplers. The hypothesis is that the concentrations of ammonium are the same for all speciation samplers as all potentially suffer from negative artifacts.
9. Ammonium nitrate equilibrium is a function of temperature and relative humidity and thus, nitrate and HNO₃ concentrations will be compared as a function of temperature and RH to determine if these factors bias sample collection. The hypothesis is that there is not difference in the samplers as a function of temperature or RH.
10. Crustal related elements are typically associated with particles greater than 2.5 μm AD, however, differences in the inlet efficiency or slope may result in different concentrations of crustal related material being measured by these samplers. The hypotheses is that the crustal related material as determined from summing the oxides of Fe, Ca, Si, Mg, and Ti are not statistically different among the samplers. If differences are observed relate these differences to the coarse particle mass as measured by the VAPS or by other collocated PM₁₀ monitors. Wind speed may also be a variable of interest in this analysis.
11. Compared the sum of the mass (accounting for missing elements O, H) among the different samplers. The hypothesis is that there is no difference among the samplers for the sum of the mass relative to the actual measured mass. This to evaluate differences in how well these samplers reproduce the sum of the mass within each sampler, among each sampler, and to the FRM.

Several tests will be done to examine the affect of different analytical methods on the concentration of the species measured. These include the effect of vacuum XRF or atmospheric XRF on nitrate concentrations measured on the filter after XRF analysis and the use of TOR vs. TOT for OC/EC analysis.

- § Vacuum vs. atmospheric pressure XRF and its affect on nitrate concentrations measured on the Teflon filter after XRF analysis. The hypothesis is two fold. First, there will be a greater loss of nitrate from Teflon filters after vacuum XRF than after atmospheric pressure XRF. Secondly, losses that occur during atmospheric pressure are minimized, such that nitrate measured after atmospheric pressure XRF is not different than nitrate measured on a Teflon filter that has not undergone XRF analysis. It is important to understand the magnitude of the loss of nitrate from Teflon filters after vacuum or atmospheric XRF because the proposed design of the URG sampler has ion analysis occurring after XRF analysis. There is also great potential for the FRM Teflon filter to be used for XRF analysis and ion analysis after mass determination to obtain additional speciation data at FRM sites.
- § Examine difference between OC and EC as measured by TOR and TOT. The hypothesis is that these two methods are statistically not different from each other for determining OC and EC from quartz filters. However, differences have been noted, especially with samples collected in areas with high wood smoke emissions. A better test of this will come from filters collected in Phase II of this study, where the samplers will be operated in an area of high wood smoke emissions and samples collected on quartz filters and on quartz filters located behind and XAD denuder.

For OAQPS, it is imperative that the experimental and statistical design be powerful enough to detect differences if they exist and not to conclude differences exist when they do not. Thus the design must have small Type I and Type II error rates. A Type I error will occur if we conclude that some of the samplers differ even though in truth they are the same. A Type II error will occur if we conclude that the samplers are the same, when in truth they differ.

Finally, the samplers will be evaluated in terms of their operational performance or practicality use of the samplers in the field, that is, reliability, ruggedness, ease of use, and maintenance requirements. Field operators will be asked to maintain detailed logs of their operational performance and they will be interviewed after the study regarding practicality of the samplers for field use.

Number of Locations (Sites) and Number of Samplers at Each

As shown in Table 6, samples will be collected at four locations using six types of samplers at each location. One sampler of each type will be operated at three of the locations and duplicates of each sampler will be operated at one location (Rubidoux), with the exception of the VAPS sampler. Samplers have been described earlier.

Analytes for Each Sampler

Table 7 shows the analytes that will be measured by each type of sampler. In general, but differing somewhat by sampler, Teflon filters will be analyzed for mass and elements by XRF or for ions (sulfate, nitrate, and ammonium ions), quartz-fiber filters will be analyzed for OC/EC and/or ions, nylon filters will be analyzed for nitrate or all three ions, as in the case for the IMPROVE sampler. Only two denuders will be extracted and analyzed. One is the Na₂CO₃ coated annular denuder in the VAPS and the other is the XAD coated denuder, also in the VAPS. The extract from the Na₂CO₃ coated denuder will be analyzed for nitrate by IC to provide an estimate of nitric acid concentrations observed during the study. The extract from the XAD denuder will be analyzed by GC-MS as part of an internal NERL research project, to provide an estimate of svocs concentrations observed during the study.

Pre-Statistical Analysis Data Validation Procedures

A visual scan will be done on each data set from each location to identify anomalous values. The ancillary data associated with each anomalous value (e.g., QA/QC documentation, meteorological data from site, etc.) will be examined to determine if there is a scientifically defensible reason to identify it as invalid. Values identified as invalid will be excluded from the statistical analyses, but those that cannot be established as invalid will be included.

All data will be screened to identify values less than five times the method (sampling plus analysis) detection limit (MDL). Values less than 5 x MDL will be excluded from the statistical analysis.

Table 6. Sampling Scheme For Speciation Sampler Intercomparison.

Location	Sampling Systems							Days	
	Met One	MASS	RAAS	IMPROVE	FRM-T	FRM-Q	VAPS	Min	Max
Rubidoux, CA	2	2	2	2	2	2	1	15	20
Phoenix, AZ	1	1	1	1	1	1	1	15	20
Philadelphia, PA	1	1	1	1	1	1	1	15	20
RTP, NC	1	1	1	1	1	1	1	15	20

Table 7. Analyte Listing for Speciation Sampler Intercomparison

Analytical Method	Analyte (Concentration Units)	Sampling Systems						
		Met One	MASS	RAAS	IMPROVE	FRM-T	FRM-Q	VAPS
Gravimetric	Total Mass	X	X	X	X	X	-	X
Ion Chromatography	SO ₄ , Cl, NH ₄ , NO ₃	X	X	X	X	-	X	X
Thermal/Optical Ref. Method	OC/EC	X	X	X	X	-	X	X
Atmospheric Pressure XRF	S, Al, Si, Ti, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, Ba, Pb, Groupings of metals, etc.,	X	X	X	X	X	-	X

Statistical Analysis

Results for each sampler across all locations will be combined on an analyte by analyte basis and an ANOVA will then be applied to each analyte using the following linear model to confirm that the samplers are equivalent statistically.

$$y_{ijk} = u + D_i + L_j + S_k + DL_{ij} + DS_{ik} + LS_{jk} + DLS_{ijk}$$

where:

- y = Analyte
- D_i = Days with associated degrees of freedom equal to $D - 1$.
- L_j = Locations with associated degrees of freedom of $L - 1$.
- S_k = Samplers with associated degrees of freedom of $S - 1$. (The duplicate data from Rubidoux will be averaged to give one value per day per sampler/analyte.)
- DL_{ij} = The interaction between days and locations. This interaction term allows us to test the hypothesis that the differences between sites (locations) are constant from day to day.
- DS_{ik} = The interaction between days and samplers. This interaction term allows us to test the hypothesis that the differences between samplers are constant from day to day.
- LS_{jk} = The interaction between locations and samplers. This interaction term allows us to test the hypothesis that the differences between samplers are constant from location to location.
- DLS_{ijk} = Since there is duplication at only one site (Rubidoux), the three way interaction term will be used to estimate overall experimental error. NOTE: The Rubidoux duplicate sampling results will provide a estimate of sampler repeatability (precision) at one site. We expect to compare the Rubidoux results to the three-way interaction term via an F-test to provide a robust estimate of the reasonableness of using the three-way interaction term to approximate overall precision of each sampler.

Results from samplers identified as statistically different from the others will be examined to determine if differences are significant at a truly meaningful level. If a sampler's values are found to be meaningfully different from the other samplers, the interaction terms from the ANOVA will be examined to determine if the difference is location specific. If differences are observed a series of comparisons, as described in the hypotheses, will be conducted using the student's t-Test or some other method of comparison.

Statistical power calculations for Speciation Sampler Intercomparison

If the minimum number of valid and complete sampling sets is achieved at each location there will be 15 sets of data per analyte per site ($N = 15$) and a total of 60 sets ($N = 60$) across all locations. Figures 7 and 8 show power curves for each analyte across all locations (Figure 7) and for each location (Figure 8). These power curves are based on a non-central F-distribution.

These power curves allow us to estimate the likelihood that we will be able to detect a real difference between samplers at the $\alpha = 0.05$ significance level as a function of the number of valid sample sets (N in Figures 7 and 8) and the minimum range between two sampler means (in units of the method standard deviation (DELTA in Figures 7 and 8). For example, Figure 7 shows that with just 15 sample sets at each location we have an 80% chance of detecting a true difference of 30% of the standard deviation ($\text{DELTA} = 0.3$) at the $\alpha = 0.05$ significance level between samplers for each analyte. Also, Figure 8 shows that if the differences between the samplers are location-specific, we still have an 80% chance of detecting a true difference of 55% of the standard deviation at the $\alpha = 0.05$ significance level between samplers for each analyte, if we have 15 valid sample sets at that location.

Data Reporting Format

The concentrations for each analyte will be compiled as a flat ASCII file organized as follows:

- 1) Format
ASCII text file with defined columns and rows.

- 2) Site ID's:
1 = Rubidoux
2 = Phoenix
3 = Philadelphia
4 = Research Triangle Park

- 3) Sampler ID's:
FRM - Teflon = FRM-T
FRM - Quartz = FRM-Q
VAPS = VAPS
Met One-SASS = MET
URG-MASS = URG
Andersen RAAS = AND
Improve = IMP

4) Analytes (mass/m³)

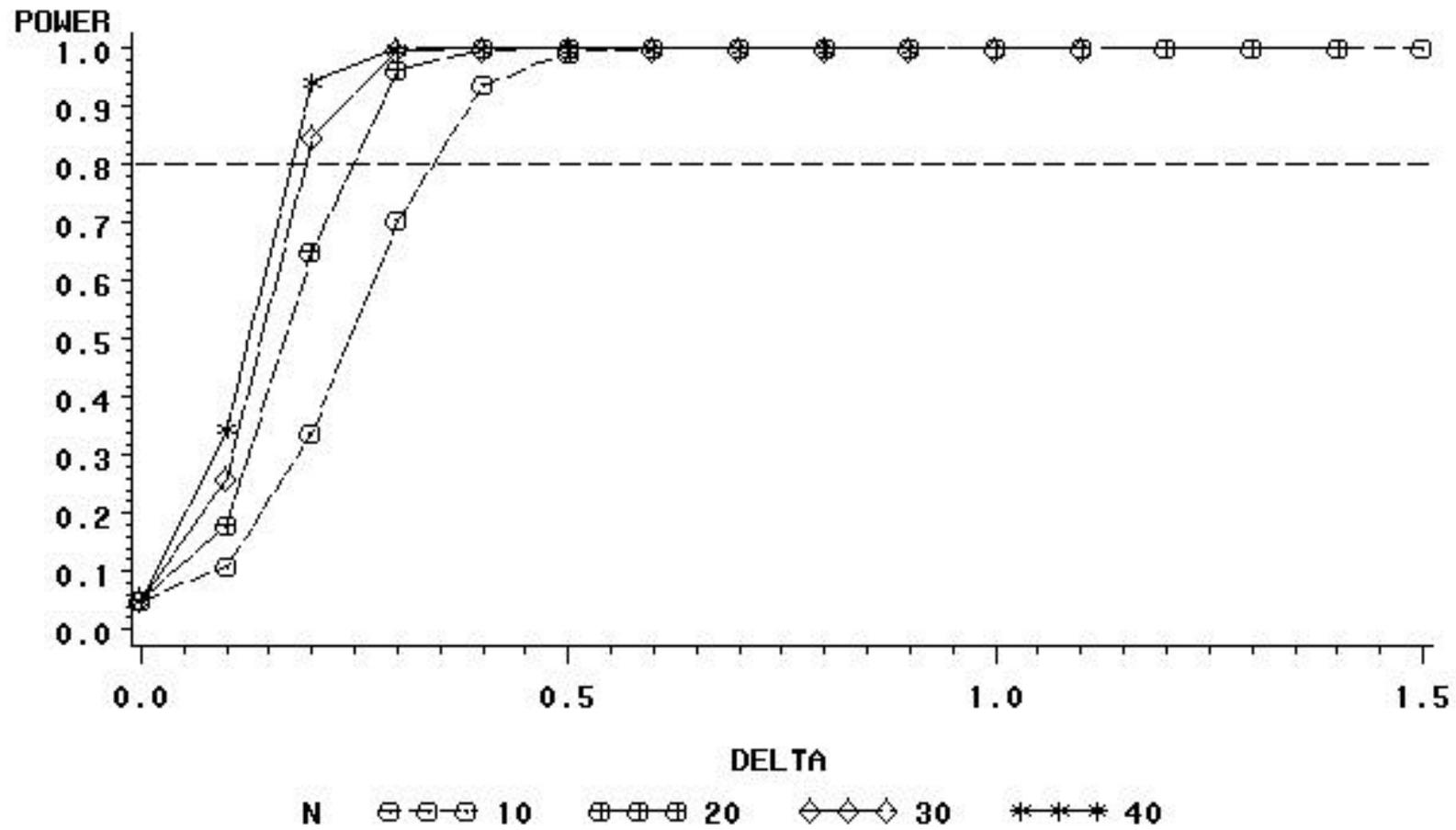
C-1	=	PM2.5
C-2	=	SO ₄
C-3	=	NO ₃
C-4	=	NH ₄
C-5	=	OC
C-6	=	EC
C-7	=	S-XRF
C-8.Cn	=	Individual metals – XRF

5) Reporting Duplicate Sampler Results (Rubidoux)

Identify as "Repeat 1" and "Repeat 2".

6) MDL for Total Method (Sampling Plus Analysis)

The total method MDL for each sampler/analyte combination should be reported in units of mass/ (nominal) volume of air sampled. For these calculations, it will be acceptable to use MDL for the analyte (as reported by the analytical laboratories) in combination with the nominal volume of air collected by the sampler over a 24-hour sampling period.



e 7. Power curves for each analyte across all locations.

Figur

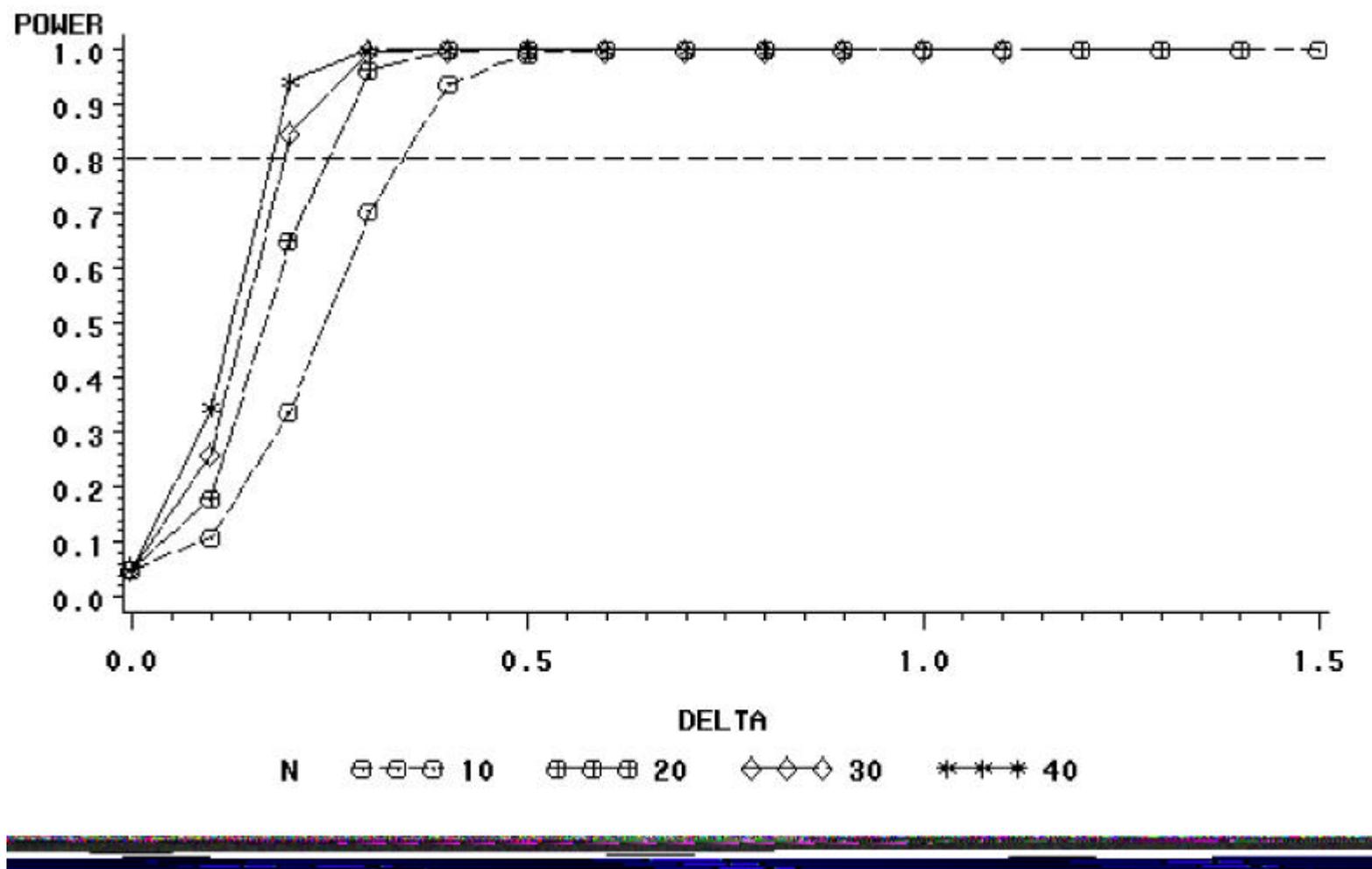


Figure 8. Power curves for each analyte for each location.

References

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Appendix A

Sample Analysis Methods for Chemical Speciation

from

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

DRAFT

13 July 1998

US 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

7.0 SAMPLE ANALYSIS METHODS

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

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

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

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

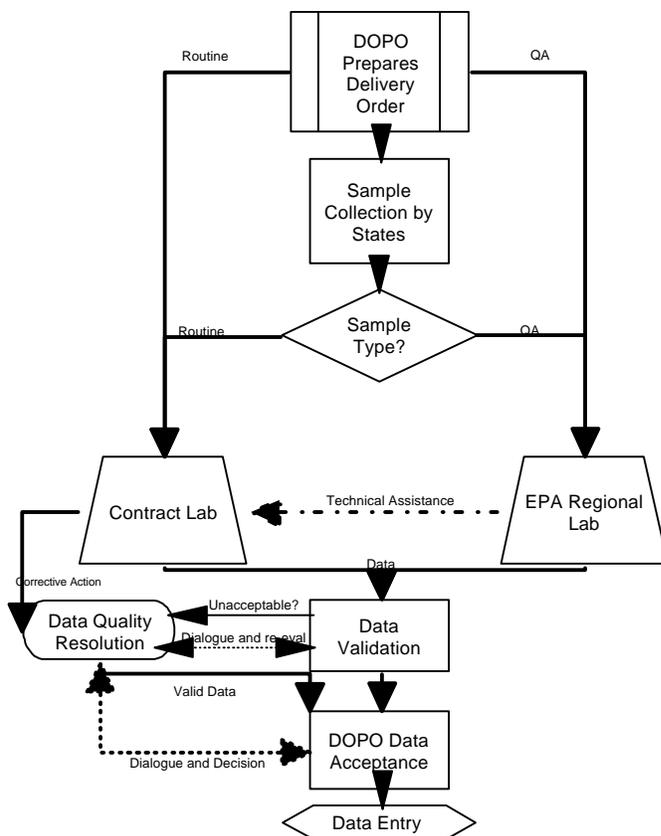


Figure 1. Flow Diagram of the Sample Analysis Delivery Order Process

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

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

7.1 Elemental Analysis

Energy dispersive X-ray fluorescence (EDXRF) is the analytical method of choice to characterize the elemental composition of the aerosol deposits on PTFE filters for the PM_{2.5} NAMS chemical speciation program. Interest in elemental composition is commonly derived from concerns about health effects and the utility of these elements to trace the sources of suspended particles or source characterization. Since sample filters often contain very small amounts of particle deposits, preference is given to methods that can accommodate small sample sizes and require little or no sample preparation or operator time after the samples are placed into the analyzer. X-ray fluorescence (XRF) meets

these needs and leaves the sample intact after analysis so it can be submitted for additional examinations by other methods as needed. To obtain the greatest efficiency and sensitivity, XRF typically places the filters in a vacuum which causes volatile compounds (nitrates and organics) to evaporate. Volatilization will not be an issue for the NAMS since PTFE filters will not be subsequently analyzed for volatile species.

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

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

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

The sensitivity of this method is on the order of few ng/m₃ for 24-hour samples (flow rates of 10-20 liters per minute). Nonetheless, quite often environmental samples have elemental measurements below the detection limit of this method. Thus, analytical uncertainties can have a significant impact on the quality of the data analysis such as for source apportionment studies. It should be mentioned that, during the analysis using XRF, the sample is introduced into a chamber that is evacuated and the sample is slightly heated due to the absorption of X-rays or protons. As a result, species that can volatilize such as ammonium nitrate and certain organic compounds can be lost during the analysis. This volatilization is important if the Teflon⁷ filter is to be subjected to subsequent analyses.

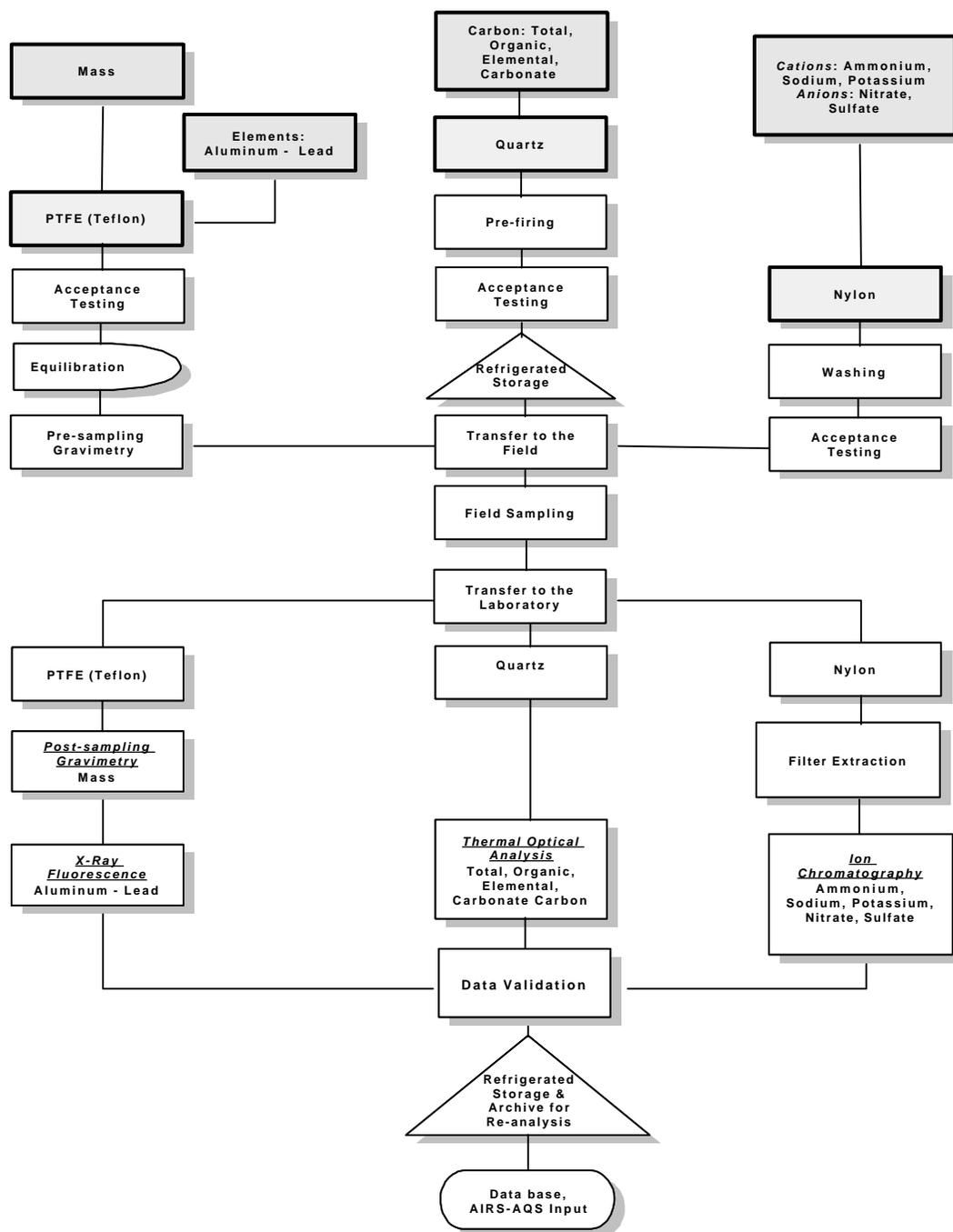


Figure 2. Flow Diagram of Filter Processing and Analysis Activities for the NAMS

7.2 Ion Analysis

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

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

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

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

In IC, the sample extract passes through an ion-exchange column which separates the ions for individual quantification, usually by a electroconductivity detector. The anions are separated when passed through a resin consisting of polymer beads coated with quaternary ammonium active sites. The separation is a result of the different affinities of the anions for these sites. After separation and prior to detection, the column effluent and anions enter a suppressor column where the cations are exchanged for H^+ ions. Species are then detected as their acids by a conductivity meter. The ions are identified by their elution/retention times and are quantified by the conductivity peak area or peak height. The IC is especially desirable for particulate samples because it provides results for several ions with a single analysis, low detection limits, and uses a small portion of the filter extract with low detection limits.

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

7.3 Particulate Organic Speciation

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

7.3.1 Carbon Analysis

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

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

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

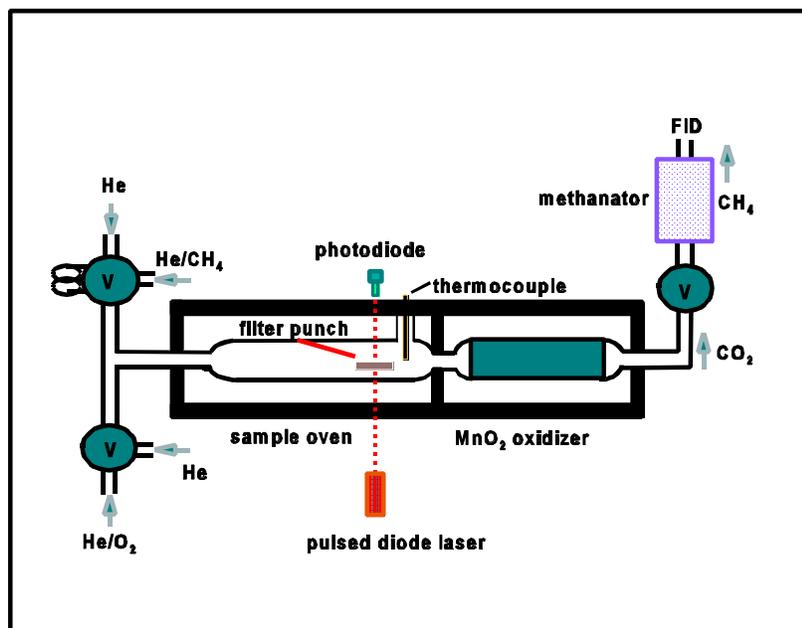


Figure 3. Schematic of the Thermal-optical Analyzer Evaluated by NIOSH

Thermal-optical analyzers operate by liberating carbon compounds under different temperature and oxidation environments. A small portion (or punch) is taken from a quartz-fiber filter sample and placed in the sample oven. The oven is purged with helium and the temperature is then stepped to a preset value. Volatilized compounds are converted to carbon dioxide (CO₂) in an oxidizer oven (MnO₂ at 870C or higher), the CO₂ is subsequently reduced to methane (CH₄) in a methanator (nickel-impregnated firebrick heated to ~550C in a stream of hydrogen), and CH₄ is quantified by a flame ionization detector (FID). In the second part of the analysis, an oxygen-helium mix is introduced and the remaining carbon is removed through combustion and quantified in the same manner. A schematic of the thermal-optical analyzer evaluated by NIOSH researchers is shown in Figure 7-3; an example of the instrument's output, called a "thermogram," is given in Figure 7-4.

In NIOSH Method 5040, the sample oven is purged with helium and the temperature is stepped (to 250, 500, 650 and 850C) to volatilize the organic and carbonate-source carbon. It is critical to ensure that trace oxygen is not present during the first part of the analysis. Potential sources of oxygen include leaks and inadequate helium gas purification. If present, trace oxygen will cause organic carbon to be overestimated and elemental carbon correspondingly underestimated. In the second part of the analysis, the temperature is lowered, a 2% oxygen/98% helium mix is introduced, and the temperature is then stepped to a maximum of 940C. At the end of the analysis, a calibration gas standard (CH₄) is injected. Correction for pyrolysis is made by continuously monitoring the filter transmittance throughout the analysis. The point at which the filter transmittance returns to its original value is defined as the split between organic and elemental carbon. Designation of the split in this manner allows assignment of pyrolyzed organic carbon to the organic fraction.

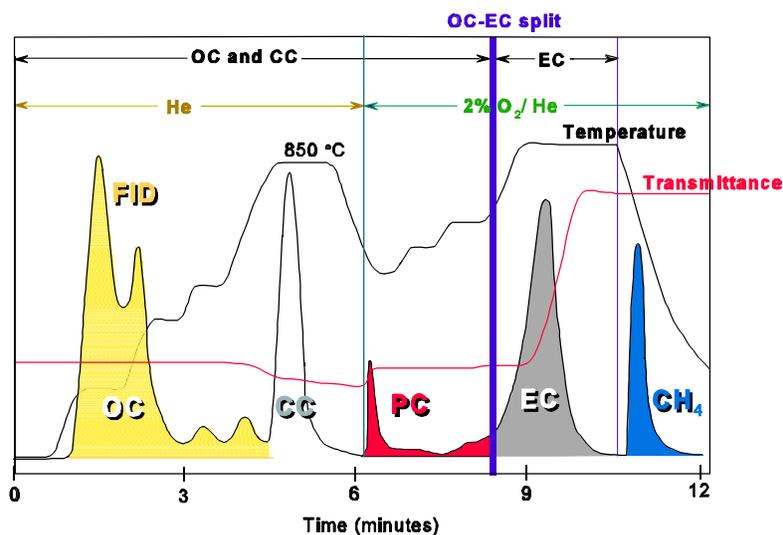


Figure 4.. Sample Output of Thermal-Optical Method Showing Different Forms of Carbon

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

It is important to remember that elemental and organic carbon have meaning only in the operational sense. That is, results reflect the method used and the appropriateness of a method depends on its purpose. Operational methods differ from those used for specific, identifiable analytes (e.g., sulfate or sulfur), where a well-defined entity is quantified and laboratory standards are available for its determination. Because elemental and organic carbon are defined operationally, the details of the measurement method must be rigorously prescribed.

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

7.3.2 Semi-volatile Organic Aerosols

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

The collection of particulate organic matter can be accomplished using particulate sampling instruments equipped with quartz fiber or Teflon⁷-impregnated glass fiber filters. However, since many organic compounds are distributed between the gas and particle phases, additional sampling techniques are required to measure the particle phase semi-volatile organics. This methodology is susceptible to negative (desorption of semi-volatile compounds from the particles on the filters) and positive (adsorption of gases by the filter material) artifacts. Considerable experimental and theoretical effort has been expended to understand and correct for these vaporization and condensation effects. Denuder technology has been employed to provide a less artifact-encumbered approach for accurate determination of semi-volatile species because the gas phase is removed prior to the particulate phase. A sorbent or denuder after the filter may also be employed to collect any semi-volatile material desorbed from the filter.

For quantitation of individual organic compounds the denuder, filter, and sorbent is extracted individually with a suitable organic solvent (or a combination of solvents). The extract is then analyzed by gas chromatography (GC) combined with mass spectrometry (MS) or with other specific detectors. Combined GC/Fourier transform infrared (FTIR)/MS techniques or high performance liquid chromatography (HPLC)/MS techniques are also used.

Appendix B

Standard Operating Procedures

Chemical Speciation Monitor Intercomparison Study

To be included prior to initiation of sampling program.