

RECOMMENDATIONS OF THE EXPERT PANEL ON THE EPA PM_{2.5} CHEMICAL SPECIATION NETWORK

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Speciation Expert Panel

The expert panel met on May 12-13 in Seattle, WA, to review the EPA's guidance document on the speciation network. Members of the panel are: Drs. John Cooper, Tom Cahill, Lara Gundel, John Ondov, Robert Stevens, and Petros Koutrakis. Other participants in this meeting included the EPA Speciation Workgroup and several members of the EPA staff and representatives from several states. Below is a summary of the important (expert panel and working group) recommendations.

Objectives:

The panel supports the EPA's effort to establish a comprehensive speciation network which will enable the states and the EPA to develop and evaluate particle control strategies. The EPA intends to establish about 300 monitoring sites with the primary purpose of determining key components of PM_{2.5}. About 50 of these sites will be designated as species trends sites (STS) with the primary objective of defining long-term concentration trends of major and key PM_{2.5} species. As such, the species measured, as well as the sampling and analysis methods, need to be defined precisely. The primary objective of the remaining 250 sites is to provide state and local agencies with speciated PM_{2.5} data which will help them develop effective SIPs. The species measured at these SIP assistance sites (SAS), as well as the sampling and analysis methods, are not expected to be similar at all of the sites. PM_{2.5} species data collected as part of the proposed network may be used to meet other secondary objectives, such as providing data on fine particle composition to health effects and visibility studies. Because of the large number of trend sites, the speciation network can provide exposure information for a large fraction of the U.S. population. This is a great opportunity to support large particle epidemiological and risk assessment studies; however, it should be stressed that the network will be designed in order to meet its primary objectives presented above.

As discussed below, the speciation network will utilize state-of-the-art sampling and analysis techniques to measure the most important constituents of fine particulate matter in a cost-effective way. In addition, as new methodologies evolve, it will be possible to incorporate them into the network. While the EPA and the expert panel will provide guidance about the necessary analytes to be measured, the states may choose to include additional ones. These decisions will be based upon the availability of human, equipment, and monetary resources. In addition, it is anticipated that future epidemiological and toxicological studies will provide better information about the chemical, physical, and biological properties of fine mass responsible for the particle health effects already identified by epidemiologic studies. As a result, both the expert panel and the working group have agreed that the target analytes should be modified as new scientific information on particle health effects becomes available. While one of the main assets of the proposed speciation

network is its flexibility, the panel recognizes the challenge of sustaining the focus and the quality of the network as it evolves. Therefore, the panel feels that the continuous involvement of the EPA and the working group will be imperative for the success of the network.

Monitoring Strategy:

Because the speciation network should focus on the quality of the air that people breathe, most of the trend sites should be located within large urban areas. Considering that the majority of the IMPROVE network sites are located in rural and semi-rural environments, the two networks will compliment each other. Together, the speciation and the IMPROVE networks will provide a good balance of measurements between urban and rural environments.

It is important to keep in mind that the majority of fine particulate matter consists of secondary particles, a large fraction of which are generated outside the boundaries of the impacted states (especially true for Eastern U.S.). In addition, results from previous studies suggest that particle concentrations are relatively uniform and correlated throughout large metropolitan areas, and on subregional and regional scales. As such, the speciation network should investigate types of sources and their global emissions, rather than focusing on chasing hot spots. We believe that the states and the EPA have learned a lot from the ozone attainment problem, which is to some extent similar to fine particles. Essentially, the data from the speciation network should enable the EPA and the scientific community in general to identify the major sources of fine particles and their impact on the different U.S. regions, and to evaluate the impact of the different particle emission control strategies. Of course, there are exceptions, mostly in the western U.S. where emissions from local sources, such as wood burning or vehicles under certain meteorological and topographical conditions, can have an important impact on the local air quality. In this case, states will have to focus on local sources and conduct spatial monitoring.

The speciation network should not seek to establish a spatial distribution of concentrations throughout the entire U.S. because this effort would be expensive and unnecessary. Instead, it should focus on the most important air sheds responsible for transporting fine particles to areas in which large populations are exposed. For instance identification of particle sources impacting a large Northeastern metropolitan environment (e.g. New York) and investigation of source/receptor relationships it may be sufficient to develop sound and cost effective control strategies for the entire Northeastern US. We believe that the value of a network depends to a great extent on the quality, rather than the quantity, of information it provides. For this reason, site selection, target analytes, selection of sampling and analysis techniques, and sampling frequency are very important for the success of the network, as discussed below.

Finally, we agree with the EPA's one-atmosphere approach. An investigation of relationships between particulate and gaseous concentrations is very critical to our understanding of the sources, transport, fate, and health effects of these pollutants. Therefore, an attempt should be made to co-locate the speciation sites with PAM sites or other monitoring sites which measure gaseous air pollutants (ozone, carbon monoxide, nitrogen oxides, sulfur dioxide, and volatile

organic compounds).

Sampling frequency:

The panel was concerned about the frequency of the 24-hour measurements at the trend sites. Based on our experience with particle data, we believe that the every six-day measurements will not be sufficient to determine accurate yearly average concentrations necessary for trends analysis. This can be shown easily by calculating and comparing yearly average concentrations using every day, every other day, every third, and up to every sixth day data. For instance, analysis of the Philadelphia, PA, fine and coarse mass data showed that maximum errors for every sixth day versus every day sampling were: 9, 9, and 12% for $PM_{2.5}$, PM_{10} and $PM_{10-2.5}$, respectively (preliminary analysis conducted by Dr. William Wilson of the EPA). Furthermore, analysis of the Phoenix, AZ, elemental data showed significant errors for a number of important tracer elements such as: V, (50%); Mn, (13%); Ni, (35%); Cu, (21%); Zn, (15%); As, (14%); Se, (16%); and Pb, (10%). This analysis suggests that it may be statistically impossible to determine pollutant trends which are on the order of a few percent per decade, with only every sixth day sampling.

In addition, the data from the trend sites also may not be adequate for exposure and epidemiological studies, since time series analysis of mortality and morbidity data require every day or at least every other day particle measurements. Moreover, collecting only fifty to sixty samples per year per site may not be sufficient for conducting source apportionment studies or investigating relationships between concentrations and meteorological parameters. Therefore, the panel recommends increasing the sampling frequency to every third day (for the approximately 50 trends sites). This schedule will be compatible with that of both the IMPROVE and the FRM sites. The increase of the frequency from every sixth day to every third day for the remaining 250 planned speciation sites can be accomplished by:

1. Decreasing the number of spatial sites, or
2. Using continuous and semi-continuous methods. To date, methods for nitrate, sulfate, and elemental carbon exist, but these methods need to be improved in order to be adequate for routine measurements. This will happen if there is a market for these monitors. Use of continuous methods most likely will reduce sampling and analysis costs and will render the network more cost-effective. It also will generate information on the diurnal variability of concentrations which may be very useful for source apportionment and exposure assessment studies.

The collection of week-long samples was also considered, but the panel felt that this is not a viable solution because of the loss of information on temporal variability. This information is very important for the implementation of the daily standard, source apportionment studies, longitudinal epidemiological investigations, and health effects studies in general. Also, because it is very important for the speciation network to obtain information which is comparable to that of the

compliance monitoring network for fine particle mass, the sampling duration should be at most 24 hours to correspond to the Federal Reference Method (FRM) for the fine particle mass. A further disadvantage of week-long sampling, beyond loss of information on temporal variability, is the potential of compromising the sample integrity because of the long sampling durations.

Target Analytes and Analytical Methods:

The main objectives of the speciation data analysis will be:

1. To identify and quantify the most important components of fine particle mass. This information will be used to establish trends of the major components of fine particle mass and to determine their relationship to the different control strategies.
2. To perform mass balance closure for quality control purposes. The sum of the most important fine particle mass components, such as sulfate, nitrate, ammonium, elemental and organic carbon, and elements should be less or equal to the mass determined from the gravimetric analysis; however, this may not be true when the gravimetric method underestimates semivolatile species (such as nitrate or organic compounds), which can be quantitatively determined by the speciation methods (such as nitrate).
3. To conduct qualitative source apportionment studies. The panel recognizes the limitation of the currently-available source apportionment tools for the following reasons: the lack of robust source tracers; the lack of accurate source fingerprints (most of the available ones are too old and need to be updated); the co-linearity of pollutant concentrations; the non-linear relationship between source emissions and concentrations at the receptor; and the large fraction of secondary aerosols. As a result, the speciation information can only be used to determine the relative contribution of the different source types (e.g., vehicular emissions, power plants), rather than associating concentrations at the receptor to a specific sources (e.g., power plant A versus B). Source-receptor relationships will be studied as part of the Supersite network or the EPA/NARSTO particle centers.
4. To provide data about the chemical composition of fine particle mass to health effects studies, including exposure and risk assessment, and epidemiological and toxicological investigations.

Based on the considerations listed above, the expert panel and the working group recommended that the speciation network include measurements of ions, elements, and carbon, as discussed below:

Ions. Ionic species such as sulfate, nitrate, and ammonium can represent a large fraction of fine particulate matter, thus their analysis is critical in order to meet the data analysis objectives

presented above. These three ions will be measured at all speciation sites (base analytes). The analysis of other important ions such as hydrogen, chloride, potassium, and sodium will be optional (optional analytes) and will be included depending upon the site location and the availability of resources.

- **Sulfate.** Sulfate is one of the most robust species of particulate matter because it remains stable during and after sampling. Sulfate should be collected on Teflon filters and aqueous extracts of these filters will be analyzed using ion chromatography. This analytical method is both sensitive and accurate, it is also labor intensive and the instrumentation requires frequent maintenance. Particulate sulfur also is routinely analyzed using X-Ray fluorescence (XRF). Measurements of collocated samples by ion chromatography and XRF are usually highly correlated. The typical mass ratio of [(sulfate by IC)/(sulfur by XRF)] is about 3, which indicates that almost all of the fine particle sulfur is in the form of sulfate. Therefore, routine comparisons should be made between the sulfate concentrations determined using ion chromatography and sulfur concentrations obtained from XRF or PIXE analysis for QC purposes. Furthermore, continuous monitoring of particle sulfate is possible using the flame ionization method (Hunzicker, et al., 1978). According to this method, sulfur species are combusted in a hydrogen flame in order to create excited sulfur dimers. An intercomparison between this method and conventional filter samples analyzed by ion chromatography showed favorable agreement (Suh, et al., 1994). In addition, sulfate can be measured using a chemiluminescence analyzer Benner and Stedman, 1989). According to this method, particulate sulfur species are converted to SO in a hydrogen flame. Subsequently, SO reacts with O₃ to produce an excited state of SO₂. Both continuous methods use a denuder to remove sulfur dioxide prior to particulate sulfur measurement. It should be mentioned that both continuous methods assume that all particulate sulfur is present in the form of sulfate. This assumption is generally true for typical ambient atmospheres.
- **Nitrate.** Accurate measurements of nitrate require the removal of gas phase nitric acid prior to particle collection. They also require the collection of nitrate on a filter medium, such as a nylon filter, which binds nitric acid molecules produced during the volatilization of the collected particulate ammonium nitrate. Removal of the gaseous nitric acid can be achieved by using diffusion denuders coated with alkaline substances (e.g., sodium carbonate) or (unanodized) aluminum inlets. Previous methods which have used Teflon or glass fiber filters are negatively biased due to the ammonium nitrate loss during and after sampling. The equilibrium between particle ammonium nitrate, gaseous ammonia, and nitric acid can be perturbed by changes in relative humidity and temperature. Loss of ammonium nitrate also can be caused by the presence of ammonium bisulfate and similar incompletely neutralized forms of sulfuric acid collected on the filter media (Koutrakis, et al., 1992). Nitrate, as well as other semi-volatile compounds, can be lost after sampling during shipping and storage. To date, there is no agreement among the different studies regarding the extent of nitrate loss. This disagreement stems from the fact that these results correspond to a variety of locations, meteorological conditions, and sampling

methods. Therefore, the nitrate sampler should include a nitric acid denuder and a nylon filter. If the speciation sampler relies upon metallic denuders which will be used for long periods of time (e.g., more than a couple of weeks, as with the IMPROVE network), the capacity of these denuders should be determined through laboratory and field studies. Nylon filters are slightly alkaline and can collect nitrate quantitatively. Aqueous extracts of the Nylon filters can be analyzed using ion chromatography or colorimetric methods to determine the nitrate concentration. As with sulfate, ion chromatography is the method of choice. Finally, a few nitrate continuous monitors are under development. These methods convert nitrate to NO, which can subsequently be quantified using a chemiluminescent NO_x analyzer; however, these methods are still at the experimental stage and probably will not be ready when the speciation network commences.

- **Ammonium.** Aqueous extracts of the Teflon filters will be used to determine ammonium concentrations. Ion chromatography is the recommended analytical method for ammonium. Ammonium sulfate salts are very stable, so ammonium loss during sample collection and storage is negligible; however, ammonium nitrate, which is an important constituent of fine particle mass, is unstable and can volatilize during both sample collection and storage. The extent of dissociation of ammonium nitrate depends on many parameters, including temperature, relative humidity, and face velocity for the collecting filter. Thus, one would expect that current sampling techniques underestimate ammonium concentrations due to the volatilization of ammonium nitrate, but fine particle mass contains many acidic compounds. Consequently, a fraction of volatilized ammonium (in the form of ammonia) can be retained on the Teflon filter by reacting with the acid compounds. Therefore, it is reasonable to assume that ammonium loss is less than the nitrate loss.
- **Hydrogen ion.** Particle strong acidity (hydrogen ion) is mostly associated with sulfate species and it can be present at high concentrations in the Northeastern U.S. environments during the summer season. Denuder/filter pack techniques have been used to measure particle acidity and other ionic species (Koutrakis, et al., 1992). The samplers consist of three components: (1) a PM_{2.5} inertial impactor to remove coarse particles (which are generally alkaline and would consequently neutralize the fine particle strong acidity collected on the sample filter); (2) a diffusion denuder to remove gaseous ammonia from the air sample; and (3) a Teflon filter to collect fine particles. The fine particles subsequently are extracted using an aqueous solution of dilute perchloric acid. The hydrogen ion concentration is measured using a pH meter equipped with a semi-microelectrode. The acid aerosol sample must be protected from ammonia neutralization during transport, storage and analysis. Because hydrogen ion measurement requires such special care, it is quite labor intensive; however, because hydrogen ion is an important indicator of atmospheric acidity, it should be measured at least at several Eastern sites (both urban and rural environments). It is expected that the use of an ammonia denuder may result in lower ammonium concentrations, as compared to those which will be obtained using any of the candidate speciation methods. Therefore, in order to provide

consistent ammonium measurements between all sites, it is recommended that a separate sampler be used for the sampling of particle strong acidity.

- **Chloride.** Aqueous extracts of Teflon filters can be analyzed using ion chromatography to determine chloride concentrations. Although chloride can be an important constituent of fine particulate matter in coastal environments, there have been only a few studies which have measured this species to date. One of the reasons is that many precautions must be taken during filter preparation, sampling, transport, and analysis to minimize chloride contamination of the samples. Otherwise, both laboratory and field blanks will be highly variable, and sample precision too poor, for quantitative results. The states impacted by oceanic aerosols may decide to measure chloride if resources are available.
- **Potassium and sodium.** These two cations can be used to trace wood burning and ocean sources, respectively. Similarly, for the rest of the ions, aqueous extracts of Teflon filters can be analyzed using ion chromatography to determine the concentrations of potassium and sodium, but, as with chloride, sodium blanks also may be highly variable, unless special precautions are taken.

Elements. Elemental analysis of aerosol samples is very important because it can be very helpful in identifying particle sources, and in determining the contribution of the soil and ocean sources to fine mass. Also, the contribution of trace metal salts (oxides, nitrates, and sulfates) can be determined, but typically this is expected to be negligible. To date, several analytical methods have been used to determine the elemental composition of the particulate matter. These methods include: X-Ray Fluorescence (XRF), Proton Induced X-Ray Emission (PIXE), Instrumental Neutron Activation Analysis (INAA), Atomic Emission Spectrophotometry (AES), Inductively Coupled Plasma (ICP) equipped with atomic emission spectroscopy (ICP-AES) or mass spectroscopy (ICP-MS). From these methods XRF and PIXE are the most widely used because they require no sample preparation. In contrast, both AES and ICP methods require filter extraction of the filter sample using strong acidic solutions in order to achieve sample dissolution; however, because ambient particles are complex, it is difficult to dissolve them completely regardless the strength of the solvent, thus reducing the accuracy of the analysis. Also, extraction is a very time consuming and expensive process. Nonetheless, AES is used occasionally for the analysis of sodium and magnesium, which cannot be analyzed by either XRF or PIXE methods. ICP-AES and ICP-MS can be used to analyze a large spectrum of elements with detection limits suitable for aerosol samples; however, as with AES, these methods require sample extraction and are destructive. ICP-MS also can be used for isotope analysis. Although INAA is a non-destructive method, the sample must be folded and sealed in plastic. Because the sample is bombarded by gamma rays, it becomes radioactive. Indeed, this makes it difficult to use the sample for further analysis. Finally, INAA cannot be used for the analysis of certain important elements, including lead and silicon.

XRF (Dzubay and Stevens, 1975; Jaklevic, et al., 1977) and PIXE (Cahill, et al., 1990) have been used extensively in the analysis of ambient aerosols because they are non-destructive, have multi-

element capabilities, and are relatively low cost. These methods are usually performed on Teflon filters for approximately forty elements (from sodium to uranium); however, for typical atmospheres, the analysis is meaningful only for half of these elements, including aluminum, silicon, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, nickel, copper, zinc, arsenic, selenium, bromine, cadmium, and lead. The sensitivity of these methods is on the order of few ng/m³ for 24-hour samples (flow rates of 10-20 liters per minute). Because these detection limits are quite low, XRF and PIXE analysis provide meaningful information for typical samples. Nonetheless, quite often environmental samples have elemental measurements below the detection limit of the methods. Thus, analytical uncertainties can have a significant impact on the quality of the data analysis such as for source apportionment studies. Since particle concentrations are expected to decrease due to the implementation of the new PM NAAQS, XRF and PIXE may not be sensitive enough. It should be mentioned that, during the analysis using these methods, 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.

To date, there are no continuous measurement techniques for the quantitative elemental analysis of ambient aerosols. Currently, some research efforts are under way, but it may take at least three to five years before new monitoring techniques will appear. These techniques should be very useful for the generating the quality of data sets needed for more comprehensive source apportionment studies.

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

Carbonaceous particles are commonly collected on a series of two quartz filters. Presumably, the first collects all of the particle phase carbon (elemental and organic) and a very small fraction of gas phase organic carbon. Likewise, the second quartz filter is supposed to collect only the same small fraction of gas phase organic carbon as collected by the first filter. Therefore, the concentration or particle phase organic carbon is calculated by subtracting the amount of organic

carbon on the second from that of the first stage; however, this assumption does not take into account particle phase organic carbon that can volatilize from the first filter and gets collected by the second quartz filter. When this volatilization occurs, it results in underestimation of particle phase organic carbon.

As part of the speciation network, the U.S. EPA is planning to use a PM_{2.5} impactor followed by two-quartz filters to collect organic carbon. Although this approach has been used by the IMPROVE network, this method is questionable. Eatough, et al. (1989) and Tang, et al. (1994) concluded that desorption of organic gases from particles on the first quartz filter was the dominant sampling artifact (negative artifact), while Turpin, et al. (1994) suggested that organic gases can be collected by the quartz-filter (positive artifact). Turpin, et al., found that adsorbed organic gases represent up to 50% of the organic carbon measured on quartz filters in southern California. This study suggested that: 1) organic gas absorption (positive bias) was much larger than organic particle volatilization (negative bias); 2) as sample durations increase, the fraction of the adsorption bias decreases because the filter becomes saturated; and 3) the magnitude of the bias depends on the composition of the organic gases and particles present in the air sample. For these reasons, we currently do not know to what extent the use of the second quartz filter improves the accuracy of the organic carbon measurements. Therefore, we recommend analysis only of the first quartz filter in order to reduce analytical costs.

There is a great need to develop bias-free particle organic carbon sampling techniques. The diffusion denuder approach may be a sound approach to overcome the problems mentioned above. According to this sampling technique, gaseous organic compounds are removed using an activated carbon or XAD coated diffusion denuder. Subsequently, the particle-phase organic carbon can be collected downstream of the denuder using a series of two-quartz filters. The first filter collects particle phase organic carbon, while the second collects the organic carbon volatilized from the first quartz filter. The total particle carbon concentration is determined by adding the concentrations of the first and second filter, respectively. To achieve maximum accuracy, the denuder must collect close to 100% of all gas phase organic compounds, and the second filter must collect all of the volatilized organics coming off of the first filter. Multi-channel activated carbon denuder or XAD systems also have great potential, but they need to be developed and tested further. A series of laboratory tests must be conducted to determine the capacity and efficiency of these denuders as a function of temperature, relative humidity and type of organic compound. Prior to the successful completion of these tests, the panel recommends that no denuder be used.

Filter transmission analysis has been used to measure elemental carbon. There also are several thermal methods for the analysis of elemental and organic carbon. These methods include: thermal/optical reflectance, thermal/optical transmission, and thermal manganese oxidation. All of these methods use temperature ramping to separate organic from elemental carbon; however, their results differ depending upon the particle composition. All thermal methods measure carbon and thus have to multiply the carbon concentration by an average factor of 1.4 to estimate total organic compound mass concentrations. This factor comes from an old

study and is expected to vary with location and season, and usually may be higher than 1.4 as discussed in a recent paper by Andrews, et al. (1998). Therefore, organic compound concentrations may be higher than those reported by previous studies.

Continuous elemental carbon concentrations can be estimated from light absorption measurements. The Aethalometer is the most commonly used instrument (Hansen and Rosen, 1990). It also is assumed that all light absorbing material is elemental carbon and that its light absorption coefficient remains constant for different sources; however, this assumption has not yet been thoroughly validated. There are a few studies that have shown a good agreement between Aethalometer data and thermal analysis methods (Allen, et al., 1998), but more studies need to be conducted in order to examine the relationship of light absorption versus elemental carbon as a function of ambient aerosol composition.

An *in-situ* thermal/optical carbon analyzer has been developed by Turpin and Huntzicker (1991). According to this method, particles are collected on quartz-fiber. Organic carbon is volatilized by heating the filter at 650°C in a helium atmosphere. This volatilized organic carbon is then converted to carbon dioxide, which is subsequently reduced to methane, which is measured using a flame ionization detector. Elemental carbon is measured by lowering the temperature to 350°C in the presence of oxygen. The evolved carbon dioxide is reduced to methane and is measured by the flame ionization detector. During volatilization of the organic carbon, light transmission through the filter is measured in order to make a correction for charring, which is caused by pyrolysis of the organics. In order to take account of collection of gas phase organic carbon by the first quartz filter, an identical quartz filter is placed downstream. A continuous organic/elemental carbon analyzer is commercially available. This monitor is based on the collection of particles on a impaction surface. Subsequently, the surface is heated at two different temperatures in order to measure the concentration of organic and elemental carbon. Although this method can provide information about the temporal variability of carbon concentrations, the accuracy is questionable for three reasons: 1) they only collect particles above 0.15µm, which can result in a negative bias because a large mass fraction of particles containing carbon can have a diameter below this size; 2) during the thermal ramping, organic carbon can be pyrolyzed; since there is no pyrolysis correction, a negative bias for organic carbon and in a positive bias for elemental carbon is likely; and 3) the sample is collected under a vacuum over the one to three hour collection period, so some semi-volatile organic carbon may volatilize before the analysis cycle begins. The extent of these biases will depend on the composition and size distribution of the carbonaceous particles. To reduce the costs of elemental and organic carbon analysis the states may chose to use continuous monitors and this may be a reasonable decision; however, these continuous methods should be validated prior to their implementation.

In summary, organic compounds can represent a large fraction of fine particle mass. Also, organic compound speciation can provide a great deal of information regarding the sources and formation processes of carbonaceous particles. Identification of individual organic compounds is the subject of many ongoing research efforts, yet this goal is beyond the scope of the speciation required for this program. Similarly, promising novel approaches for reduction of artifacts due to

sampling of semi-volatile compounds (C_{sv}) are not yet ready for routine deployment; however, research directions suggest that current and future technological developments will permit both extensive quantification of individual compounds and accurate differentiation of semi-volatile gas and particulate phase organic carbon. Therefore, speciation of individual organics and accurate differentiation of C_{sv} from C_t is optional and will be done depending upon the availability of funding and human resources (optional analytes). Although speciation is desirable, it is not easy to perform because there is no single analytical method that can be used to analyze all classes of organics. It may be more cost-effective to develop inexpensive methods that allow for the measurement of specific characteristic groups of organic compounds. Attempting to obtain comprehensive spatial and temporal patterns on hundreds of organic compounds may not be a cost-effective strategy; however, the lumping approaches have not developed yet thus their implementation to the speciation network is not possible yet.

Other Properties:

Other physical or chemical properties of fine particles will be measured depending upon the availability of resources and the sources impacting the specific site or region. Parameters, such as particle size and number, particle morphology, particle number, organic compound speciation, etc., can be very useful in our effort to identify and quantify particle sources. Because measurement of some of these parameters may be costly, especially for the organic particle speciation and the morphological analysis, it may be advantageous to perform analysis only for a subset of samples. The sample selection could be based on different criteria, such as fine particle mass levels, season, concentration of organic carbon or trace elements, and meteorological parameters. Alternatively, measurement of additional particle properties could be conducted every third day (similarly to the base analytes reported above) for only one year. This may be a sound approach, since we know from limited studies that there is very little year-to-year variability in particle mass concentration and composition at a given site.

Although the selection of such additional parameters will depend on the cost, availability of resources, and the type of sources impacting the specific site, we believe that speciation of carbonaceous particles should be a top priority within the measurement research community. Organic carbon comprises a large fraction of fine particulate matter, and identification of individual organic molecules can provide a great deal of information regarding its sources and formation processes. In addition, sampling and analysis protocols already have been developed for the determination of a large number of organic compounds associated with particulate matter and further evaluation of these methods should be included in planning for the eventual implementation of detailed organic speciation with a long-term, routine chemical speciation network. These assessments are very important because of the high cost involved in collection and analysis of samples for organics. The only drawback with the organic carbon speciation analysis is its cost.

Microscopic analysis can be used to characterize both the morphology and the chemical composition of individual particles. Because these analyses are very costly and time consuming and are still at the developmental stage, they should be used only for a limited number of samples.

Although particle size distribution and total number measurements are important parameters and should be measured when feasible, it should be kept in mind that they are site- and meteorology-specific. For instance, the particle number concentrations at a given site may be strongly influenced by local sources. In addition, particle sizes depend on the relative humidity. Overall, considering the limits of the available funding, this information is less useful than that which can be obtained by measurements of chemical speciation.

Sampling Devices:

The description of the three contracted sampling devices provided by the guidance document was incomplete. For this reason, it was not possible to judge whether these methods will be adequate for the speciation network. The panel feels that EPA staff should not select a sampling device until the performance of the candidate samplers have been thoroughly tested in both laboratory and field experiments. The EPA staff commented that it is not necessary to evaluate rigorously the performance of the speciation samplers, since they will not be used for compliance monitoring; however, considering that the data from the different analyses will be used for mass closure and to make comparisons with fine particle mass measurements, it is imperative that the size cut-off characteristics of the speciation samplers be similar to those of the FRM.

To date, OAQPS has contracted three manufacturers to prepare sampling devices that can be used to collect filters for elemental, ionic, and carbon analysis. Since a large amount of data already exists from the IMPROVE network, and a large number of states are familiar with this technology, the panel recommends that a modified IMPROVE sampler be considered along with the three other sampling devices. The panel felt that there is insufficient information available at this time upon which to base a recommendation for a specific sampler; however, the panel proposes a process and general criteria that can be used to aid in sampler selection. The recommended specifications for speciation samplers are as follows:

1. The inlet cut-point and separation profile must be comparable to the WINS inlet. A number of laboratory and field tests should be conducted to demonstrate that the fine particle mass samples collected by the speciation monitor and the FRM are in good agreement (for example slope of 1 ± 0.1 and r^2 better than 0.90).
2. The sampler should use a well tested denuder technology to obtain nitrate and anion/cation measurements. The nitric acid denuder should be tested for its capacity and efficiency as a function of exposure time and relative humidity. If it is proposed that a denuder will be used for more than one sampling day, it will be important to prove that its collection efficiency does change with time.

3. The sampler needs to collect samples at face velocity and volume similar to that of the FRM PM-2.5 sampler on 46.2mm diameter filters.
4. The sampler must be reliable, rugged, and employ field-proven monitoring approaches.

Three activities should be pursued to develop the information required to make decisions among candidate samplers. Acceptance testing is needed to ensure that delivered samplers meet nominal specifications of the manufacturers. Laboratory testing is needed to check samplers' particle size selection characteristics (efficiency curves and particle losses) for comparisons to those of the FRM. Finally, field studies are needed to intercompare speciation data from the various candidate methods and other historically accepted samplers and the FRM, as well as to identify sampler practical and performance characteristics that would affect their use under routine field sampling conditions. Field studies should be conducted at a minimum of four combined locations/seasons to sample under distinctly different aerosol and meteorological conditions. These cities could be the first four speciation sites. For each study, duplicate samplers operated for a minimum of 20 sample periods (nominal 24-hour duration) are required to determine sampler precision for each sampler and between-sampler comparability. Comparability should be judged against the FRM for mass, elements (XRF), and carbon, and against the Harvard/EPA denuder filter pack sampler for ions on Teflon and nylon filters. This method is described by the EPA compendium for acid aerosol sampling.

Integration to the Other Networks:

The supersites will be important for the speciation network because they could be used to evaluate the performance of the speciation and mass samplers. Several issues related to the performance and the evolution between routine and advanced methods demand that a feedback system across supersites and routine sites be established and maintained to ensure progress in applying advanced methods routinely, and to reduce uncertainty in data trends interpretations brought about by changing methodologies. The spatial requirements for characterizing the multiple interacting spatial scales (horizontal) can not be addressed by supersites, and, in this context, routine sites can be viewed as satellites for greater spatial detail. Furthermore, the data from the speciation network will prove critical to the interpretation of the compliance network data, since they make it possible to investigate relationships between particle concentrations and particle compositions.

Data Analysis:

The idea to make the speciation data available through the Internet is an excellent one. This will make it possible to use the data for trend analysis, source apportionment, and health effects studies. In addition, the value of the data would be greatly enhanced if measurement uncertainties were included with the data base.

General Comments:

The panel was impressed with the progress already made in this effort, such as in the communication efforts with the states about this initiative, the documentation prepared for sampling and analysis techniques, and the arrangements made for the contracts with manufacturers. Also, the panel was very satisfied with the willingness of the EPA to expand the list of analytes and to introduce new technologies when necessary and feasible. The panel feels that the EPA's commitment will be of paramount importance for the success of this Network. We suggest that the EPA staff from both OAQPS and ORD be permanently assigned to oversee the network, provide guidance to the states about all of the scientific issues related to sampling, analysis quality assurance, and data analysis, and work together with the states and the scientific community. We have observed a good deal of enthusiasm about this network and we want to make sure that a core of EPA staff will be assigned permanently to this initiative for the years to come. Otherwise, this network could end up becoming a very expensive undertaking with limited value to the EPA's overall strategy to protect the public from fine particle exposures.

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