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Monitoring of particulate matter outdoors

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Abstract

Recent studies of the size and composition of atmospheric particulate matter (PM) have demonstrated the usefulness of separating atmospheric PM into its fine and coarse components. The need to measure the mass and composition of fine and coarse PM separately has been emphasized by research in exposure, epidemiology, and toxicology of atmospheric PM. This paper provides a background on the size distribution and properties of PM relevant to the differences between fine and coarse particles. Various decisions that must be made when deciding how to separate, collect, and measure PM are discussed. Techniques for monitoring fine and coarse particles, including the US Federal Reference Method for $PM_{2.5}$ and several techniques for $PM_{10-2.5}$, are presented. Problems encountered in collecting semivolatile PM and in weighing atmospheric PM collected on a filter are described. Continuous monitoring methods for PM mass and for PM components (carbon, nitrate, and sulfate) are described and brief descriptions are given of analytical techniques for the chemical characterization of collected PM. This information should be especially useful for environmental workers familiar with monitoring methods for total suspended particles or PM_{10} but who will need to measure $PM_{2.5}$ and $PM_{10-2.5}$ in the future.

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Keywords: Particulate matter; Fine particles; Coarse particles; Monitoring methods; Chemical analysis; Semivolatile PM

Contents

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1. Introduction

Atmospheric particles originate from a variety of sources and possess a range of morphological, chemical, physical, and thermodynamic properties. Examples include combustion-generated particles such as diesel soot or fly ash, photochemically produced particles such as those found in urban haze, salt particles formed from sea spray, and soil-like particles from resuspended dust. Some particles are liquid; some are solid; others contain a solid core surrounded by liquid. Atmospheric particles contain inorganic ions, metallic compounds, elemental carbon (EC), organic compounds, and crustal compounds. Some atmospheric particles are hygroscopic and contain particle-bound water. The organic fraction is especially complex, containing hundreds of organic compounds. Primary particles are emitted directly from sources. Secondary particles are formed from gases through chemical reactions in the atmosphere involving atmospheric oxygen (O_2) and water vapor (H_2O); reactive species such as ozone (O_3); radicals such as the hydroxyl ($^{\cdot}OH$) and nitrate ($^{\cdot}NO_3$) radicals; and pollutants such as sulfur dioxide (SO_2), nitrogen oxides (NO_x), and organic gases from natural and anthropogenic sources. The particle formation process includes nucleation of particles from low-vapor pressure gases emitted from sources or formed in the atmosphere, condensation of low-vapor pressure gases on existing particles, and coagulation of particles. Thus, any given particle may contain particulate matter (PM) from many sources.

Atmospheric particles often are not spherical and have a range of densities. Therefore, their diameters are often described by an "equivalent" diameter (i.e., the diameter of a unit density sphere that would have the same physical behavior as the particle in question). The aerodynamic diameter, important for particle transport, removal, collection, and respiratory tract deposition, is defined as the diameter of a spherical particle with a density of 1 g/cm^3 but with a settling velocity equal to that of the particle in question. Particles with the same physical size and shape but different densities will have different aerodynamic diameters. Detailed definitions of the various sizes and their relationships are given in standard aerosol textbooks, e.g., Friedlander (1977); Reist (1984), and Seinfeld and Pandis (1998). Older particle counting studies used optical particle counters to cover the range of 0.3–30 μm diameter. Diameters of particles below 0.5 μm were measured as mobility diameters. The particle diameters used in size distribution graphs from these studies are usually given as physical diameters rather than aerodynamic diameters. Size distribution studies using impactors give direct measurements of the aerodynamic diameter. In recent years, aerodynamic particle sizers have been used to give a direct measurement of the aerodynamic diameter in the range of approximately 0.7–10 μm. A variety of electrical mobility analyzers are used to measure the mobility diameter of particles from 2–5 nm to approximately 0.5 μm (McMurry, 1999). In this paper, D_p will be used for physical diameter and D_a for aerodynamic diameter.

1.1. Definitions of particle size fractions

The distribution of particles with respect to size is an important physical parameter governing their behavior. Because atmospheric particles cover several orders of magnitude in particle size, size distributions often are expressed in terms of the logarithm of the particle diameter on the X-axis and the measured differential concentration on the Y-axis: $\Delta V/\Delta(\log D_p) =$ the volume of particles per cm^3 of air having diameters in the size range from $\log D_p$ to $\log(D_p + \Delta D_p)$. If $\Delta V/\Delta(\log D_p)$ is plotted on a linear scale, the volume of particles between D_p and $D_p + \Delta D_p$ is proportional to the area under the curve of $\Delta V/\Delta(\log D_p)$ versus $\log D_p$. Similar considerations apply to distributions of number, surface area, and mass. It has been found that atmospheric aerosol size distributions frequently may be approximated by a sum of log–normal distributions corresponding to the various modes or fractions. When approximated by a function, the distributions are usually given as $dV/d(\log D_p)$ rather than $\Delta V/\Delta(\log D_p)$.

The aerosol community uses four different approaches or conventions in the classification of particles by size: (1) modes, based on the observed size distributions and formation mechanisms; (2) cutpoint, usually based on the 50% cutpoint of the specific sampling device; (3) occupational sizes, based on the entrance into various compartments of the respiratory system; and (4) legally specified, regulatory sizes for air quality standards. These terms will be defined in the subsequent discussions.

1.1.1. Modal

The modal classification, first proposed by Whitby (1978), is shown in Fig. 1. The nuclei mode can be seen clearly in the volume distribution only in traffic or near traffic or other sources of nuclei mode particles. The observed modal structure is frequently approximated by several log–normal distributions. Definitions of terms used to describe size distributions in modal terms are given below.

> *Coarse mode:* The distribution of particles with diameters mostly greater than the minimum in the particle mass distribution, which generally occurs between 1 and 3 μm. These particles are usually mechanically generated (e.g., from wind erosion of crustal material).
>
> *Fine mode:* The distribution of particles with diameters mostly smaller than the minimum in the particle mass distribution, which generally occurs between 1 and 3 μm. These particles are generated in combustion or formed from gases. The fine mode includes the accumulation mode and the nuclei mode.
>
> *Nuclei mode:* That portion of the fine particle fraction with diameters below about 0.1 μm. The nuclei mode can be observed as a separate mode in mass or volume distributions only in clean or remote areas or near sources of new particle formation by nucleation. Toxicologists use ultrafine to refer to particles, including those generated in the laboratory, that are in the nuclei-mode size range. Aerosol physicists and material scientists tend to use nanoparticles to refer to particles in this size range generated in the laboratory.

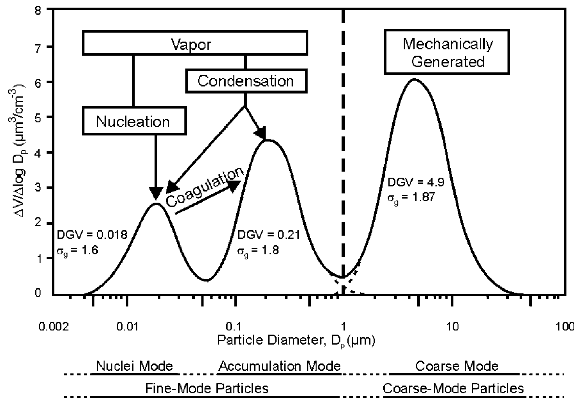

Fig. 1. Volume size distribution, measured in traffic, showing fine-mode and coarse-mode particles and the nuclei and accumulation modes within the fine-particle mode. DGV (geometric mean diameter by volume, equivalent to volume median diameter) and σ_g (geometric standard deviation) are shown for each mode. Also shown are transformation and growth mechanisms (e.g., nucleation, condensation, and coagulation) (adapted from Wilson and Suh, 1997).

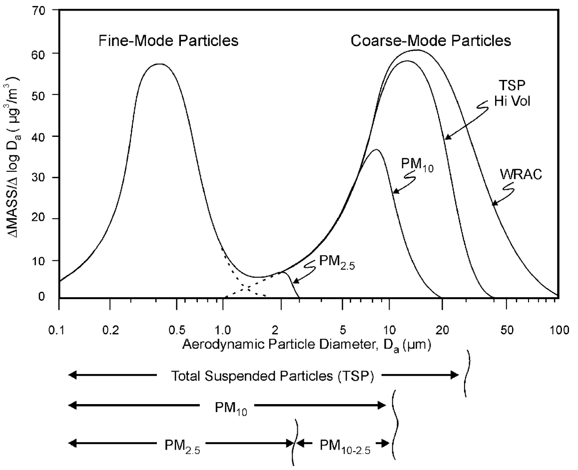

Fig. 2. An idealized distribution of ambient PM showing fine-mode particles and coarse-mode particles and the fractions collected by size-selective samplers (adapted from Wilson and Suh, 1997).

> *Accumulation mode:* That portion of the fine particle fraction with diameters above about 0.1 μm. Accumulation-mode particles normally do not grow into the coarse mode. Nuclei-mode particles grow by coagulation (two particles combining to form one) or by condensation (low-equilibrium vapor pressure gas molecules condensing on a particle) and "accumulate" in this size range.

Over the years, the terms fine and coarse, as applied to particle sizes, have lost the precise meaning given in Whitby's (1978) definition. In any given article, therefore, the meaning of fine and coarse, unless defined, must be inferred from the author's usage. In particular, $PM_{2.5}$ and fine-mode particles are not equivalent. In this document, the term mode is used with fine and coarse when it is desired to specify the distribution of fine-mode particles or coarse-mode particles as shown in Figs. 1 and 2.

1.1.2. Sampler cutpoint

Another set of definitions of particle size fractions arises from considerations of size-selective sampling. Size-selective sampling refers to the collection of particles below or within a specified aerodynamic size range, usually defined by the upper 50% cutpoint size, and has arisen in an effort to measure particle size fractions with some special significance (e.g., health, visibility, source apportionment, etc.). Dichotomous samplers split the particles into smaller and larger fractions that may be collected on separate filters. Cascade impactors use multiple size cuts to obtain a distribution of size cuts for mass or chemical composition measurements. One-filter samplers with a variety of upper size cuts have also been used.

1.1.3. Occupational health size cuts

The occupational health community has defined size fractions for use in the protection of human health. This convention classifies particles into inhalable, thoracic, and respirable particles according to their upper size cuts. However, these size fractions may also be characterized in terms of their entrance into various compartments of the respiratory system. Thus, inhalable particles enter the respiratory tract, including the head airways. Thoracic particles travel past the larynx and reach the lung airways and the gas-exchange regions of the lung. Respirable particles are a subset of thoracic particles that are more likely to reach the gas-exchange region of the lung. In the past, exact definitions of these terms have varied among organizations. As of 1993 a unified set of definitions was adopted by the American Conference of Governmental Industrial Hygienists ACGIH (1994), the International Standards Organization (ISO), and the European Standardization Committee (CEN). The curves which define inhalable particulate matter (IPM), thoracic particulate matter (TPM), and respirable particulate matter (RPM) are shown in Fig. 3.

1.1.4. Regulatory size cuts

In 1987, the US National Ambient Air Quality Standards (NAAQS) for PM were revised to use PM_{10},

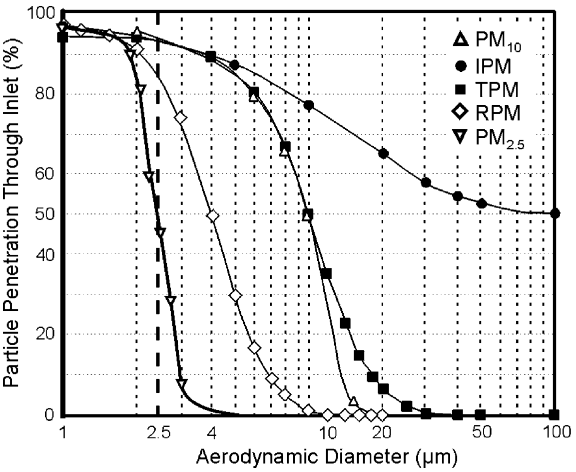

Fig. 3. Specified particle penetration (size-cut curves) through an ideal (no-particle-loss) inlet for five different size-selective sampling criteria. Regulatory size cuts are defined in the Code of Federal Regulations: $PM_{2.5}$ Code of Federal Regulations (2001a), PM_{10} Code of Federal Regulations (2001b). $PM_{2.5}$ is also defined in the Federal Register (1997, 1998). Size-cut curves for IPM, TPM and RPM size cuts are computed from definitions given by American Conference of Governmental and Industrial Hygienists, ACGIH (1994).

rather than total suspended particulate (TSP) matter, as the indicator for the NAAQS for PM (Federal Register, 1987). The use of PM_{10} as an indicator is an example of size-selective sampling based on a regulatory size cut (Federal Register, 1987). The selection of PM_{10} as an indicator was based on health considerations and was intended to focus regulatory concern on those particles small enough to enter the thoracic region. The $PM_{2.5}$ standard, set in 1997, is also an example of size-selective sampling based on a regulatory size cut (Federal Register, 1997). The $PM_{2.5}$ standard was based primarily on epidemiological studies using concentrations measured with $PM_{2.5}$ samplers as an exposure index. However, the $PM_{2.5}$ sampler was not designed to collect respirable particles. It was designed to collect fine-mode particles because of their different sources (Whitby et al., 1974). Thus, the need to attain a $PM_{2.5}$ standard will increase regulatory concern with the sources of fine-mode particles.

Prior to 1997, the indicator for the NAAQS for PM was TSP matter. TSP is defined by the design of the High Volume Sampler (hivol) which collects all of the fine particles but only part of the coarse particles. The upper cut off size of the hivol depends on the wind speed and direction, and may vary from 25 to 40 μm. The Wide Range Aerosol Classifier (WRAC) was designed specifically to collect the entire coarse mode (Lundgren and Burton, 1995).

1.2. Issues in the measurement of particulate matter

The decision by the US EPA to revise the standards by adding daily and yearly standards for $PM_{2.5}$ has led to a renewed interest in the measurement of atmospheric particles and also to a better understanding of the problems in developing precise and accurate measurements of particles. The 1996 Air Quality Criteria for Particulate Matter (PM AQCD) (US EPA, US Environmental Protection Agency, 1996) summarized measurement techniques for PM. Two other excellent reviews have been published in recent years by Chow (1995) and McMurry (1999). Unfortunately, it is very difficult to measure and characterize particles suspended in the atmosphere.

The US Federal Reference Methods (FRM) for $PM_{2.5}$ and PM_{10} provide relatively precise (±10%) methods for determining the mass of material remaining on a Teflon filter after equilibration. However, numerous uncertainties remain as to the relationship between the mass and composition of material remaining on the filter, as measured by the FRMs, and the mass and composition of material that exists in the atmosphere as suspended PM. The goal of a PM indicator might be to accurately measure what exists as a particle in the atmosphere. However, this is not currently possible, in part because of the difficulty of creating a reference standard for particles suspended in the atmosphere. As a result, EPA defines accuracy for PM measurements in terms of agreement of a candidate sampler with a reference sampler. Therefore, intercomparisons of samplers become very important in determining how well various samplers agree and how various design choices influence what is actually measured.

There are six general areas where choices must be made in designing an aerosol indicator. These include selection of an upper cutpoint; separation of fine-mode and coarse-mode PM; treatment of semivolatile components; treatment of pressure, temperature, and relative humidity (RH); time resolution; and how to assess the reliability of the measurement technique. In many cases choices have been made by default and with an inadequate understanding of the consequences. As a result, measurement methods developed by different organizations may give different results when sampling the same atmosphere, even though the techniques appear to be similar.

1.2.1. Upper cutpoint

The measurement technique should provide an upper cutpoint and its standard deviation that is independent of wind speed and direction (the classical high volume sampler head was unsatisfactory because of radial asymmetry). PM_{10} and thoracic PM, as shown in Fig. 3, have the same 50% cutpoint. However, the PM_{10} cut (Code of Federal Regulations, 2001a,b,c) is sharper than the thoracic cut, so thoracic PM contains some particles between 10 and 30 μm diameter that are excluded from PM_{10}. The US PM_{10} separation curve, while sharper than the thoracic curve, is probably satisfactory both for regulatory and health risk monitoring. It has the advantage of reducing the problem of maintaining the finite collection efficiency specified by the thoracic penetration curve for particles larger than 10 μm D_a (see Fig. 3). In Fig. 2, an idealized distribution is used to show the normally observed division of ambient PM into fine-mode particles and coarse-mode particles and the size fractions collected by the WRAC, TSP, PM_{10}, $PM_{2.5}$, and $PM_{10-2.5}$ samplers.

The PM_{10} upper cutpoint is defined as having a 50% collection efficiency at 10 ± 0.5 μm aerodynamic diameter. The slope of the collection efficiency curve is defined in amendments to 40 CFR, Part 53, the Code of Federal Regulations (2001c). Papers discussing PM_{10} or $PM_{2.5}$ frequently insert an explanation such as PM_x (particles less than x μm diameter) or PM_x (nominally, particles with aerodynamic diameter $\leqslant x$ μm). While these explanations may seen easier than the more nearly correct, PM_x, (particles collected with an upper 50% cutpoint of x μm aerodynamic diameter), they are not entirely correct and may be misleading because they suggest an upper 100% cutpoint of x μm. Some countries, however, use PM_{10} to refer not to samplers with a 50% cut at 10 μm D_a but samplers with 100% rejection of all particles greater than 10 μm D_a. Such samplers miss a fraction of the coarse thoracic PM. This is illustrated in Fig. 4 which shows the penetration curve of a PM_{10} sampler where PM_{10} does mean particles less than 10 μm (i.e., a penetration of zero or an exclusion of 100% for particles of 10 μm aerodynamic diameter). PM_x, as defined by EPA, refers to a sampler with a penetration curve that collects 50% of x μm particles and excludes 50% of x μm particles. It also means that some particles $>x$ are collected and not all particles $<x$ are collected.

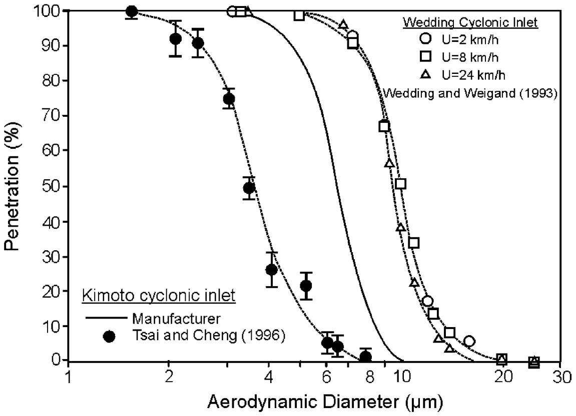

Fig. 4. Comparison of penetration curves for two PM_{10} beta-gauge samplers using cyclone inlets. The Wedding PM_{10} sampler uses the US EPA definition of PM_x as $x = 50\%$ cutpoint. The Kimoto PM_{10} defines PM_x as $x =$ the 100% cutpoint (or zero penetration) (Tsai and Cheng, 1996. Journal of Air and Waste Management Association: Comparison of two ambient beta gauge PM_{10} samplers. 46: 144. Copyright 1996. Reprinted with permission of the Air and Waste Management Association.).

1.2.2. Separation of fine-mode and coarse-mode PM

Fine-mode and coarse-mode particles differ not only in size and morphology (e.g., smooth droplets vs. rough solid particles) but also in formation mechanisms; sources; and chemical, physical, and biological properties. They also differ in terms of dosimetry (deposition in the respiratory system), toxicity, and health effects as observed by epidemiologic studies.

In an analysis reported in 1979, EPA scientists endorsed the need to measure fine and coarse particles separately (Miller et al., 1979). Based on the availability of a dichotomous sampler with a separation size of 2.5 μm, they recommended 2.5 μm as the cutpoint between fine and coarse particles. Because of the wide use of this cut point, the $PM_{2.5}$ fraction is frequently referred to as "fine" particles. However, while the $PM_{2.5}$ sample contains all of the fine particles it may, especially in dry areas or during dry conditions, collect a small fraction of the coarse particles. A PM_{10}–$PM_{2.5}$ size fraction may be obtained from a dichotomous sampler or by subtracting the mass collected by a $PM_{2.5}$ sampler from the mass collected by a PM_{10} sampler. The resulting PM_{10}–$PM_{2.5}$ mass, or $PM_{10-2.5}$, is sometimes called "coarse" particles. However, it would be more correct to call $PM_{2.5}$ an indicator of fine-mode particles (because it contains some coarse-mode particles) and $PM_{10-2.5}$ an indicator of the thoracic component of coarse-mode particles (because it excludes some coarse-mode particles below 2.5 μm and above 10 μm). It would be appropriate to call PM_{10} an indicator of thoracic particles.

At high RH, such as that found in fog and clouds, hygroscopic fine-mode particles will increase in size due to the accretion of particle-bound water. Some, originally sub-micrometer, fine-mode PM may be found with D_a above 1 μm. At very low RH, coarse-mode particles may be fragmented into smaller sizes and small amounts of coarse-mode PM may be found with D_a below 1 μm. It is desirable to separate fine-mode PM and coarse-mode PM as cleanly as possible in order to properly allocate health effects to either fine-mode PM or coarse-mode PM and to correctly determine sources by factor analysis and/or chemical mass balance. For example, sulfate in the fine-mode is associated with hydrogen and/or ammonium ions; whereas sulfate in the coarse mode is associated with basic metal ions. The sources are different, and the health effects are likely to be different. Transition metals in the coarse mode are likely to be associated with soil and tend to be less soluble than transition metals in fresh combustion particles in the fine mode.

The current practice of separating fine-mode and coarse-mode particles at 2.5 μm D_a is satisfactory for a health-based standard. However, it may not provide an adequate separation for epidemiologic studies in areas where winds cause high concentrations of wind blown soil. A possible approach that would provide a better separation of fine-mode PM and coarse-mode PM would be to dehumidify the air stream to some fixed humidity that would remove all or most particle-bound water without evaporating semivolatile components and make the cut near 1 μm D_a.

1.2.3. Semivolatile particulate matter

1.2.3.1. Treatment of semivolatile components of particulate matter. Current filtration-based mass measurements lead to significant evaporative losses, during and possibly after collection, of a variety of semivolatile components, i.e., species that exist in the atmosphere in dynamic equilibrium between the condensed phase and gas phase. Important examples include ammonium nitrate, semivolatile organic compounds, and particle-bound water. This problem is illustrated in Fig. 5.

Possible approaches that have been used to address the problem of potentially lost semivolatile components include the following which will be discussed in more detail in subsequent sections:

1. Collect/measure all components present in the atmosphere in the condensed phase except particle-bound water. (Examples: Brigham Young absorptive sampler, Harvard pressure drop monitor. Both require pre-concentration of the accumulation mode and reduction of ambient humidity.)
2. Stabilize PM at a specified temperature high enough to remove all (or almost all) particle-bound water. This results in loss of much of the semivolatile PM. (Examples: TEOM operated at 50 °C, beta gauge with heated inlet.)
3. Equilibrate collected material at fixed, near-room temperature and low RH to reduce particle-bound water. Accept loss of an unknown but possibly significant fraction of semivolatile PM. (Example: US Federal Reference Method and most filter-weighing techniques. There is also information to suggest that not all particle-bound water is removed by the equilibration process.)

The amount of semivolatile material lost is dependent upon the concentration and composition of the semivolatile components and is, therefore, also dependent on season and location. The amount of semivolatile material lost has been found to be significant in air sheds with high nitrate, wood smoke, or secondary organic aerosols.

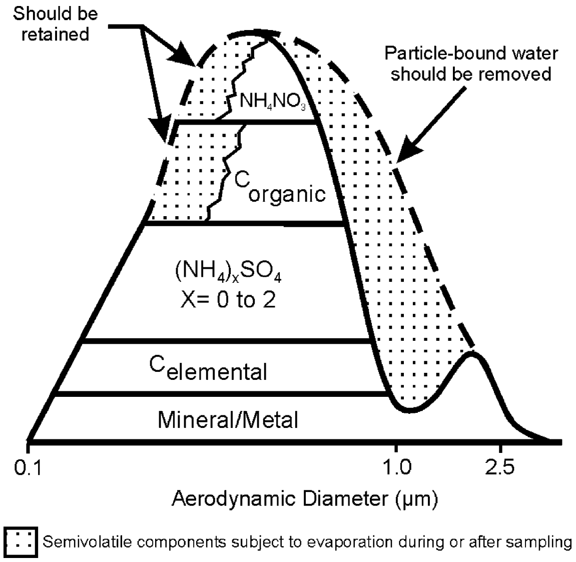

Fig. 5. Schematic showing major non-volatile and semivolatile components of $PM_{2.5}$. Semivolatile components are subject to partial to complete loss during equilibration or heating. The optimal technique would be to remove all particle-bound water but no ammonium nitrate or semivolatile organic PM.

1.2.3.2. Problems associated with semivolatile PM. It is becoming increasingly apparent that evaporation of part of the semivolatile component of PM can lead to negative sampling artifacts that significantly affect the quality of the measurement. Losses of semivolatile species, such as ammonium nitrate and many organic species, may occur during sampling, due to changes in temperature, relative humidity, or composition of the aerosol or due to pressure drop across the filter (McMurry, 1999). Gas phase organic species, both volatile and semivolatile, may adsorb onto or react with, filter media and/or collected PM, leading to a positive sampling artifact. Tsai and Cheng (1995) observed positive sulfate and nitrate artifacts on high volume PM_{10} quartz filters and attributed the artifacts to interactions between acidic gases (SO_2, HONO, and HNO_3) and both the filter media (either glass fiber or quartz) and the coarse particles collected on the filter. Volatilization losses have also been reported to occur during sample transport and storage (Chow, 1995). Evaporative losses of particulate nitrates have been investigated in laboratory and field experiments (e.g., Wang and John, 1988) and in theoretical studies (Zhang and McMurry, 1992). Volatilization losses of semivolatile organic compounds (SVOC) can also be significant (e.g., Eatough et al., 1993).

Adsorption of organic vapors onto quartz filters has also been recognized as a source of positive sampling error. Although original experiments investigating this sampling artifact were typically carried out utilizing two quartz fiber filters deployed in series, the second quartz filter can indicate both gaseous VOC adsorbed on both filters (positive) artifact and SVOC evaporated from particles on the first filter and subsequently adsorbed on the second filter (negative artifact). Unless the individual compounds are identified, the investigator does not know what to do with the loading value on the second filter (i.e., to add or subtract it from the first filter loading value).

Much progress has been made to date in the design of diffusion denuder systems for the measurement and characterization of both the particulate and gaseous phases of semivolatile compounds. Some of the recent research has focused upon reduction in the size of the denuder, optimization of the residence time in the denuder, understanding the effect of diffusion denuders on the positive quartz filter artifact, identifying changes in chemical composition that occur during sampling, determining the effects of changes in temperature and RH, and identifying possible loses by absorption in impactor coatings. The developing state of the art in which diffusion denuder technology is being applied to SVOC sampling (e.g., Eatough et al., 1993; Gundel et al., 1995), as well as for sampling of gas and particulate phase organic acids (Lawrence and Koutrakis, 1996a,b), holds promise for improving our understanding of SVOC sampling artifacts.

Particulate nitrates: It is well known that volatilization losses of particulate nitrates (e.g., Zhang and McMurry, 1992; Hering and Cass, 1999) will occur during sampling on Teflon filters. The effect on the accuracy of atmospheric particulate measurements from these volatilization losses will be even more significant for $PM_{2.5}$ than they are for PM_{10}. The FRM for $PM_{2.5}$ will suffer loss of nitrates similar to the losses experienced with other simple filter collection systems. Sampling artifacts due to the loss of particulate nitrates will represent a significant problem in areas such as southern California that experience high amounts of nitrogen species.

Hering and Cass (1999) examined the errors in $PM_{2.5}$ mass measurements due to the volatilization of particulate nitrate by looking at data from two field measurement campaigns conducted in southern California–the Southern California Air Quality Study, SCAQS (Lawson, 1990), and the 1986 CalTech study (Solomon et al., 1992). In both these studies, side-by-side sampling of $PM_{2.5}$ was conducted. One sampler collected particles directly onto a Teflon filter; the second sampler consisted of a denuder to remove gaseous nitric acid followed by a nylon filter that absorbs the HNO_3 that evaporates from ammonium nitrate. In both studies, the denuder consisted of MgO-coated glass tubes (Appel et al., 1981). Fine particulate nitrate collected on the Teflon filter was compared to fine particulate nitrate collected on the denuded nylon filter. In both studies, the $PM_{2.5}$ mass lost due to volatilization of ammonium nitrate represented a significant fraction of the total $PM_{2.5}$ mass. The fraction of mass lost was higher during summer than during fall (17% versus 9% during the SCAQS study, and 21% versus 13% during the CalTech study) (Fig. 6). In regard to percentage loss of nitrate, as opposed to percentage loss of mass discussed above, Hering and Cass (1999) found that nitrate remaining on the Teflon filter samples was on average 28% lower than that on the denuded nylon filters.

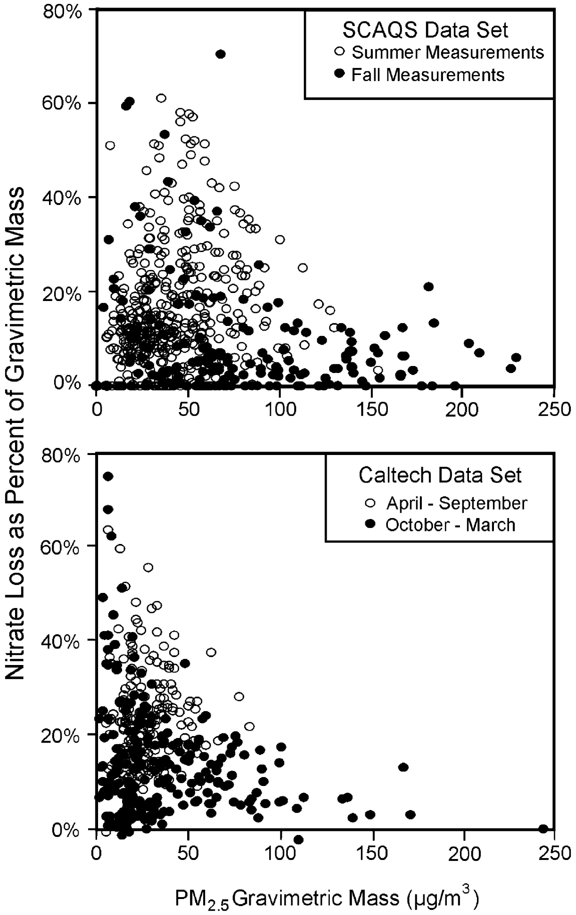

Fig. 6. Amount of ammonium nitrate volatilized from Teflon filters, expressed as a percentage of the measured $PM_{2.5}$ mass for the SCAQS and CalTech studies for spring and fall sampling periods (Hering and Cass, 1999. Journal of Air and Waste Management Association: The magnitude of bias in the measurement of $PM_{2.5}$ arising from volatilization of particulate nitrate from Teflon filters. 49:731. Reprinted with permission of the Air and Waste Management Association.).

Hering and Cass (1999) also analyzed these data by extending the evaporative model developed by Zhang and McMurry (1987). The extended model utilized by Hering and Cass (1999) takes into account dissociation of collected particulate ammonium nitrate on Teflon filters into nitric acid and ammonia via three mechanisms: scrubbing of nitric acid and ammonia in the sampler inlet [(John et al., 1988) showed that clean PM_{10} inlet surfaces serve as an effective denuder for nitric acid]; heating of the filter substrate above ambient temperature by sampling; and pressure drop across the Teflon filter. For the sampling systems modeled, the flow-induced pressure drop was measured to be less than 0.02 atmospheres, and the corresponding change in vapor pressure was 2% so losses driven by pressure drop were not considered to be significant in this work. Losses from Teflon filters were found to be higher during the summer compared to the winter, and higher during the day compared to night, and were reasonably consistent with modeled predictions.

In atmospheres with high sulfate and low ammonia, the PM tends to be acidic (NH_4HSO_4 or H_2SO_4) and nitric acid remains as a gas. In atmospheres with lower sulfate and higher ammonia, there may be sufficient ammonia to fully neutralize the H_2SO_4 and also react with HNO_3 to form NH_4NO_3 particles. Therefore, loss of nitrate will be a bigger problem in the areas where SO_2 emissions are low and ammonia emissions are high.

Semivolatile organic compounds: Although there is less information on losses of SVOC, it is known that these species can similarly be lost from Teflon filters due to volatilization and can also cause the $PM_{2.5}$ mass to be significantly underestimated. Like particulate nitrates, the FRM for $PM_{2.5}$ will suffer loss of SVOC similar to the losses experienced with other simple filter collection systems. It has been shown that attempting to correct for the losses of SVOC during sampling by deploying a second quartz filter directly behind either a quartz or Teflon filter can significantly underestimate the volatilization losses (e.g., Eatough et al., 1993). Using their multi-channel diffusion denuder sampling system (BOSS), Eatough et al. (1995) reported that, for samples collected at the South Coast Air Quality Management District sampling site at Azusa, CA, changes in the phase distribution of SVOC could result in a loss on average of 35% of the particulate organic material; the fraction of the total fine PM that this loss represents was not given. At present, there are limited data available specifically on the fraction of $PM_{2.5}$ mass lost during sampling onto Teflon filters due to volatilization of organic species and even less on the regional differences in the effects of volatilization losses of SVOC. Cui et al. (1998) found that losses of SVOC from particles in the Los Angeles Basin during the summer were greater during the day than at night. Cui et al. (1998) determined that, on average, 42% and 62% of the particulate organic material was semivolatile organic compounds lost from particles during sampling for daytime and nighttime samples, respectively.

Particle-bound water: It is generally desirable to collect and measure ammonium nitrate and semivolatile organic compounds. However, for many measurements of suspended particle mass, it is desirable to remove the particle-bound water before determining the mass. In other situations it may be important to know how much of the suspended particle's mass or volume is due to particle-bound water. The water content of PM is significant and highly variable. Moreover, there is significant hysteresis in the water adsorption–desorption pathways (Seinfeld and Pandis, 1998), further complicating the mass measurement. Figs. 7 and 8 show the change in diameter of sulfate particles as a function of RH. Fig. 7 shows the difference between deliquescence and crystallization points.

Pilinis et al. (1989) calculated the water content of atmospheric PM above and below the deliquescent point. They predicted that aerosol water content is strongly dependent upon composition and concluded from their calculations that liquid water could represent

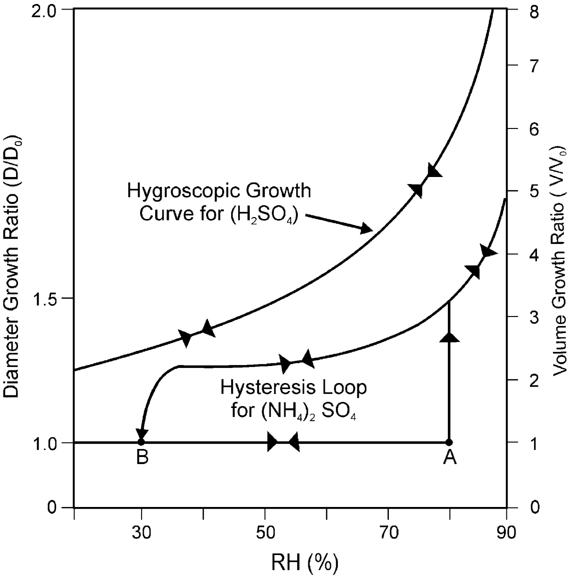

Fig. 7. Particle growth curves showing fully reversible hygroscopic growth of sulfuric acid (H_2SO_4) particles, deliquescent growth of ammonium sulfate ($(NH_4)_2SO_4$) particles at the deliquescent point (A, about 80% RH), reversible hygroscopic growth of ammonium sulfate solution droplets at RH greater than 80%, and hysteresis (the droplet remains supersaturated as the RH decreases below 80%) until the crystallization point (B, about 38% RH) is reached (adapted from National Research Council, 1993 and Tang, 1980).

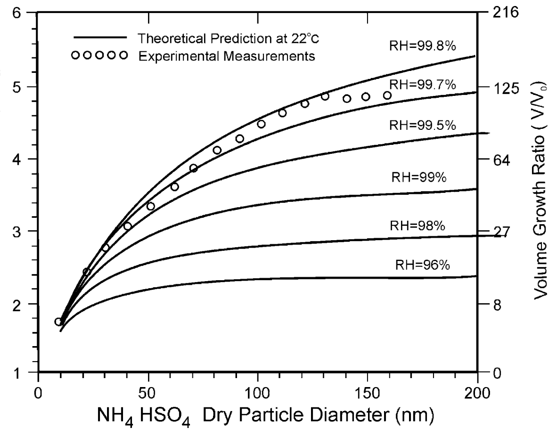

Fig. 8. Theoretical predictions and experimental measurements of growth of NH_4HSO_4 and particles at RH between 95% and 100% (Li et al., 1992. Aerosol Science and Technology: A system to measure the hygroscopicity of aerosol particles. 17:33. Copyright 1992. Reprinted with permission of the American Association for Aerosol Research.).

a significant mass fraction of aerosol concentration at relative humidities above 60%.

1.2.4. Treatment of pressure, temperature, and relative humidity

There are a variety of techniques for defining (or ignoring) the pressure, temperature, and RH during and after sampling. For example, the sample volume may be based on the mass or volumetric flow corrected to standard temperature and pressure (273 K and 1 atm) (a former EPA technique for PM_{10}), or it may based be on the volumetric flow at ambient conditions of temperature and pressure (the current EPA technique for $PM_{2.5}$ and PM_{10}).

There are also a variety of options for controlling temperature during collection. The particles may be heated enough to remove most particle-bound water (i.e., TEOM at 50 °C); the particles may be heated several degrees, just enough to prevent condensation of water in the sampling system; the particles and the sampler may be maintained near ambient temperature (±5 °C of ambient temperature is the current EPA requirement); or the particles and sampler may be maintained at constant temperature inside a heated or air conditioned shelter. There are also options for control of temperature after collection. The sample may be kept at room temperature (no control), or it may be shipped and stored at a cool temperature (4 °C is the current EPA requirement).

Consideration must also be given to RH. Changes in RH cause changes in the size of hygroscopic or deliquescent particles. Changing RH by adding or removing water vapor affects measurements of particle number, particle surface area, and particle size distribution and the amount of overlap of fine-mode and coarse-mode particles. Changing RH by intentional or inadvertent changes in temperature also affects the amount of ammonium nitrate and semivolatile organic compounds lost by evaporation. Monitoring personnel need to be aware of the various options for treatment of pressure, temperature, and RH; make appropriate selections; and document which options are used.

Studies of relationships between personal/indoor/outdoor measurements present special problems. Indoor environments are typically dryer than outdoors and may be warmer or, if air-conditioned, cooler. These differences may change particle size and the amount of volatilization of semivolatile components. Such changes between indoors and outdoors will complicate the comparison of indoor to outdoor concentrations; the modeling of personal exposure to all particles; and exposure apportionment by disaggregation of personal exposure into exposure to particles of ambient origin, exposure to particles of indoor origin, and exposure to personal activity particles.

1.2.5. Time resolution

The classic 24-h filter collection technique is being supplemented by continuous monitors for a variety of PM parameters. This process is being accelerated by the lower operational cost of continuous monitors and the availability of new continuous monitors for mass, certain chemical components, charge acceptance, and number as well as older methods based on beta attenuation or light scattering. Continuous methods are discussed in Section 1.6. A major problem in replacing 24-h filter measurements with continuous methods is that for continuous methods, particle-bound water must be removed in situ before measurement of mass. As mentioned previously, techniques that heat the PM may also remove semivolatile components. This problem may be overcome by using diffusion drying which dehumidifies without heating.

1.2.6. No way to determine accuracy

Precision and accuracy are normally used to describe the quality of a measurement. Precision is typically determined by comparison of collocated samplers or through replicate analyses while accuracy is determined through the use of traceable calibration standards. Unfortunately, no standard reference calibration material or procedure has been developed for suspended PM. Therefore, it is not possible to establish the accuracy of a PM monitoring technique. Intercomparison studies to establish the precision of identical monitors and the extent of agreement between different types of monitors are essential for establishing the reliability of PM measurements. Intercomparison studies have contributed greatly to our understanding of the problems in PM measurement. Such studies will be discussed as they apply to specific measurement problems, monitoring instruments, or analytical techniques. Measurement errors of concern in PM_{10} sampling that arise due to uncertainty tolerances in cutpoint, particle bounce and reentrainment, impactor surface overloading, and losses to sampler internal surfaces were discussed in detail in the 1996 PM AQCD (US Environmental Protection Agency, 1996). Measurement errors of concern in $PM_{2.5}$ sampling arise because of our inability to assess accuracy in an absolute sense due to a lack of primary calibration standards or procedures, because of the use of an operational definition of $PM_{2.5}$ as a surrogate for fine particles, and because of problems associated with trying to measure the mass of particles as they exist in the air rather than what remains after collection on a filter.

In response to the difficulties associated with determining the accuracy of PM measurements, the US Environmental Protection Agency has sought to make FRM measurements equivalent by specifying operating conditions and, in the case of $PM_{2.5}$ samplers, by specifying details of the sampler design. Thus, both the PM_{10} and $PM_{2.5}$ standards are defined with consistency of measurement technique rather than with the accuracy of the true mass concentration measurement in mind (McMurry, 1999). It is acknowledged in the Federal Register (1997) that "because the size and volatility of the particles making up ambient particulate matter vary over a wide range and the mass concentration of particles varies with particle size, it is difficult to define the accuracy of $PM_{2.5}$ measurements in an absolute sense..." Thus, accuracy is defined as the degree of agreement between a subject field $PM_{2.5}$ sampler and a collocated $PM_{2.5}$ reference method audit sampler (McMurry, 1999). The accurate measurement of the mass of PM suspended in the atmosphere was of concern in PM_{10} sampling and is of even greater concern for $PM_{2.5}$. As mentioned earlier, volatilization losses, during sampling or post-sampling handling, of some organics as well as ammonium nitrate can lead to a significant underestimation of the fine particulate mass concentration in some locations. Sources of error in the measurement of $PM_{2.5}$ mass suspended in the atmosphere also arise due to the adsorption of organic vapors onto collected PM, filter media, or other sampler surfaces; the neutralization of acid or basic vapors by reaction with either filter media or collected PM; and the role of particle-bound water in PM sampling.

The lack of a standard reference material or a primary calibration procedure for PM suspended in the atmosphere has prevented any evaluation of accuracy. In the last 25 years there have been advancements in the generation and classification of monodisperse aerosols, as well as in the development of electron microscopy and imaging analysis, that have contributed to the advancement in aerosol calibration (Chen, 1993). Still, one of the limitations in PM sampling and analysis remains the lack of primary calibration standards for evaluating analytical methods and for intercomparing laboratories. Klouda et al. (1996) examined the possibility of resuspending the National Institute of Standards and Technology (NIST) Standard Reference Material 1649 (Urban Dust) in air for collection on up to 320 filters simultaneously using the dust generation and collection system developed by Stanford Research International. However, the fine component cannot be resuspended with the same size distribution as existed in the atmosphere and the semivolatile component will have evaporated. Therefore, while this material is useful as a standard for composition of collected PM, it is not a suitable standard for suspended PM. Little additional work has been reported on efforts to develop an alternative standardization material.

Methods validation was discussed in the 1996 PM AQCD (US Environmental Protection Agency, 1996), and the usefulness of intercomparisons and "internal redundancy" was emphasized. For example, a number of internal consistency checks are applied to the IMPROVE network (Malm et al., 1994). These include mass balances; sulfur measurements by both proton induced X-ray emission (PIXE) and ion chromatography (IC); and comparison of organic matter by combustion (thermal/optical reflectance (TOR)) and by proton elastic scattering analysis (PESA) analysis of hydrogen. Mass balances compare the gravimetrically determined mass with the mass calculated from the sum of the major chemical components; i.e., crustal elements plus associated oxygen, organic carbon (OC), elemental carbon, sulfate, nitrate, ammonium, and hydrogen ions. Mass balances are useful validation techniques; however, they do not check for, or account for, artifacts associated with the absorption of gases during sampling or the loss of semivolatile material during sampling. The mass balance check may appear reasonable even if such artifacts are present because only the material collected on the filter is included in the balance.

1.3. PM components/parameters that need to be measured

The concentration and composition of particles need to be measured in order to determine attainment of a standard; to follow implementation of a standard; and to estimate the effects of particles on health, ecology, and radiative balance. The large variety of components of PM or PM parameters that need to be measured for various purposes are summarized in Table 1. With the exception of bioaerosol, all of these components or parameters are also of interest in studies of exposure to combustion products.

Table 1
PM components/parameters of interest for health, ecological or radiative effects; for source category apportionment studies; or for air quality validation studies

Particle number
Particle surface area
Particle size distribution
PM mass (fine-mode {$PM_{1.0}$} and coarse-mode {PM_{10-1}} mass as well as $PM_{2.5}$ and PM_{10}; non-volatile mass, Federal Reference mass, and mass including semivolatile components such as ammonium nitrate and semivolatile organic compounds but not particle-bound water)
Ions (sulfate, nitrate and ammonium)
Strong acidity (H^+)
EC
OC (total, non-volatile and semivolatile; functional groups and individual species)
Transition metals (water soluble, bioavailable, valence state)
Specific toxic elements/specific toxic organic compounds
Crustal elements
Bioaerosols
Particle refractive index (real and imaginary)
Particle density
Particle size change with changes in RH

1.4. The federal reference methods for measurement of equilibrated mass for PM_{10}, $PM_{2.5}$, and $PM_{10-2.5}$

In 1997, EPA promulgated new standards for $PM_{2.5}$ to address fine-fraction thoracic particles and retained with minor revisions the 1987 PM_{10} standards to continue to address coarse-fraction thoracic particles (Federal Register, 1997, 1998). In partial response to numerous challenges to these standards, the US Court of Appeals for the District of Columbia Circuit in *American Trucking Association vs. EPA*, 175 F. 3d 1027 (US Court of Appeals, D.C. Cir., 1999) found "ample support" for regulating coarse-fraction particles but revoked the revised PM_{10} standards (leaving in effect the 1987 PM_{10} standards) on the basis of PM_{10} being a "poorly matched indicator for coarse particulate pollution" because PM_{10} includes fine particles. Consistent with this specific aspect of the Court's ruling, which EPA did not appeal, EPA is now considering use of $PM_{10-2.5}$ as the indicator for coarse-fraction thoracic particles in conjunction with $PM_{2.5}$ standards that address fine-fraction thoracic particles. Thus, EPA is now developing a Federal Reference Method (FRM) for the measurement of $PM_{10-2.5}$.

1.4.1. PM_{10}

A FRM has been specified for measuring PM_{10} (Code of Federal Regulations, 2001b,c). The PM_{10} FRM defines performance specifications for samplers in which particles are inertially separated with a penetration efficiency of 50% at an aerodynamic diameter of 10 ± 0.5 μm. The collection efficiency increases to ≈100% for smaller particles and drops to ≈0% for larger particles. Particles are collected on filters and mass concentrations are determined gravimetrically. Instrument manufacturers are required to demonstrate through field tests a measurement precision for 24-h samples of ±5 μg/m^3 for PM_{10} concentrations below 80 μg/m^3 and within 7% for concentrations above 80 μg/m^3.

1.4.2. $PM_{2.5}$

As opposed to the performance-based FRM standard for PM_{10}, the new FRM for $PM_{2.5}$ (Code of Federal Regulations, 2001a,c) specifies certain details of the sampler design, as well as of sample handling and analysis; other aspects have performance specifications (Noble et al., 2001). The $PM_{2.5}$ FRM sampler consists of a PM_{10} inlet/impactor, a $PM_{2.5}$ impactor with an oil-soaked impaction substrate to remove particles larger than 2.5 μm D_a, and a 47-mm polytetrafluoroethylene (PTFE) filter with a particle collection efficiency greater than 99.7%. The sample duration is 24 h, during which time the sample temperature is not to exceed ambient temperatures by more than 5 °C. A schematic diagram of the $PM_{2.5}$ FRM sample collection system is shown in Fig. 9. After collection, samples are equilibrated for 24 h at temperatures in the range of 20–23 °C (±2 °C) and at relative humidities in the range of 30–40% (±5%). The equilibration tends to reduce particle-bound water and stabilizes the filter plus sample weight. Filters are weighed before and after sampling under the same temperature and RH conditions. For sampling conducted at ambient RH less than 30%, mass measurements at relative humidities down to 20% are permissible (Code of Federal Regulations, 2001a).

The PM_{10} inlet specified for the $PM_{2.5}$ FRM is modified from a previous low flow-rate PM_{10} inlet that was acceptable in both EPA-designated reference and

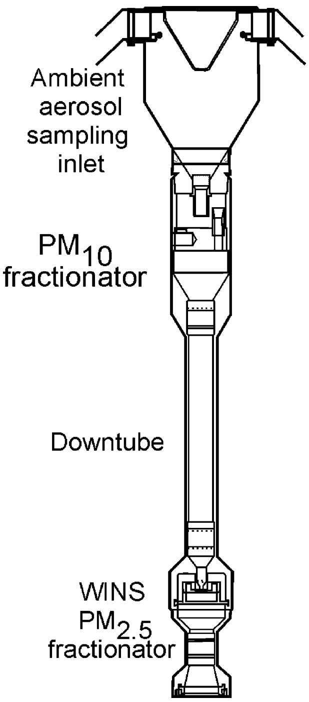

Fig. 9. Schematic diagram of the sample collection portion of the $PM_{2.5}$ FRM sampler (Noble et al., 2001. Aerosol Science and Technology: Federal reference and equivalent methods for measuring fine particulate matter. 34:459. Copyright 2001. Reprinted with permission of the American Association for Aerosol Research.).

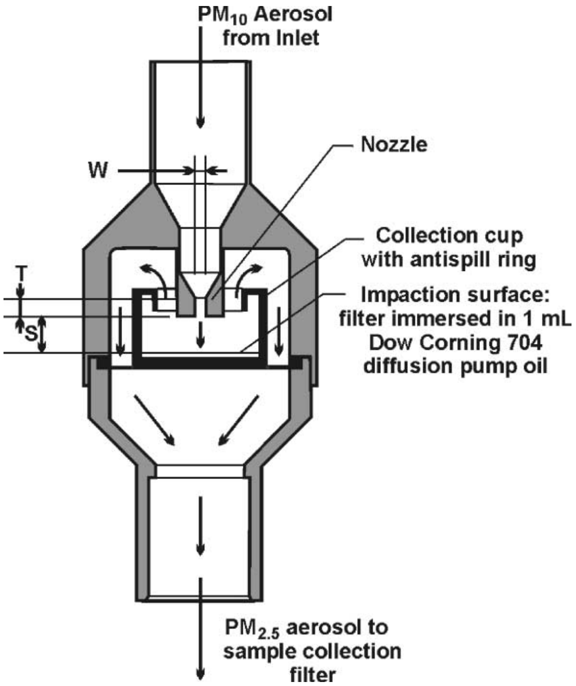

Fig. 10. Schematic view of the final design of the WINS (Peters et al., 2001a. Aerosol Science and Technology: Design and calibration of the EPA $PM_{2.5}$ Well Impactor Ninety-Six (WINS). 34:390. Copyright 2001. Reprinted with permission of the American Association for Aerosol Research.).

equivalent PM_{10} methods. The modification corrects a flaw that was reported for the previous sampler, in that under some meteorological conditions, the inlet may allow precipitation to penetrate the inlet. The modification includes a larger drain hole, a one-piece top plate, and louvers. Tolocka et al. (2001) evaluated the performance of this modified inlet in a series of wind tunnel experiments for both $PM_{2.5}$ and PM_{10} sampling. The modified inlet was found to compare very well with the original inlet, both for $PM_{2.5}$ and for PM_{10} sampling. Their results further suggest that the modified inlet can be substituted for the original inlet when it is part of a reference or equivalent method for PM_{10} (Tolocka et al., 2001). This study addressed the concern, expressed by Allen et al. (1999), that the "pie-plate" inlet required by the final version of the $PM_{2.5}$ FRM might have a different cut point than the "flat-top" inlet of the PM_{10} FRM.

WINS impactor: Design and calibration of the EPA $PM_{2.5}$ Well Impactor Ninety-Six (WINS) is given by Peters et al. (2001a). The WINS impactor was designed to be deployed downstream of the Graseby-Andersen 246B PM_{10} inlet, operating at 16.7 actual l/min. The WINS is pictured in Fig. 10. The $PM_{2.5}$ inlet consists of a single jet, round hole, with the jet exit directed toward an impaction surface that is comprised of a 37 mm diameter glass fiber filter immersed in 1 ml of low volatility diffusion pump oil (i.e., the well). Particles not having enough inertia to be removed by the impactor are captured downstream on the sample collection filter. This design was selected to minimize impactor overloading that would otherwise result in particle bounce. The oil wicks through the particulate deposit on the impactor to provide a continuously wetted surface for impaction. The penetration curve indicated a 50% cutpoint of 2.48 μm D_a with a geometric standard deviation of 1.18 (Fig. 11).

The FRM also allows for Class I, II and III equivalent methods for $PM_{2.5}$ (Code of Federal Regulations, 2001c). Class I equivalent methods use samplers with relatively small deviations from the sampler described in the FRM. Class II equivalent methods include "all other $PM_{2.5}$ methods that are based upon 24-h integrated filter samplers that are subjected to subsequent moisture equilibration and gravimetric mass analysis". Class III equivalent methods include non-filter-based methods such as beta attenuation, harmonic oscillating elements, or nephelometry (McMurry, 2000). As of July 2001, there were 11 $PM_{2.5}$ samplers designated as FRMs (Peters et al., 2001b; US EPA, 2001).

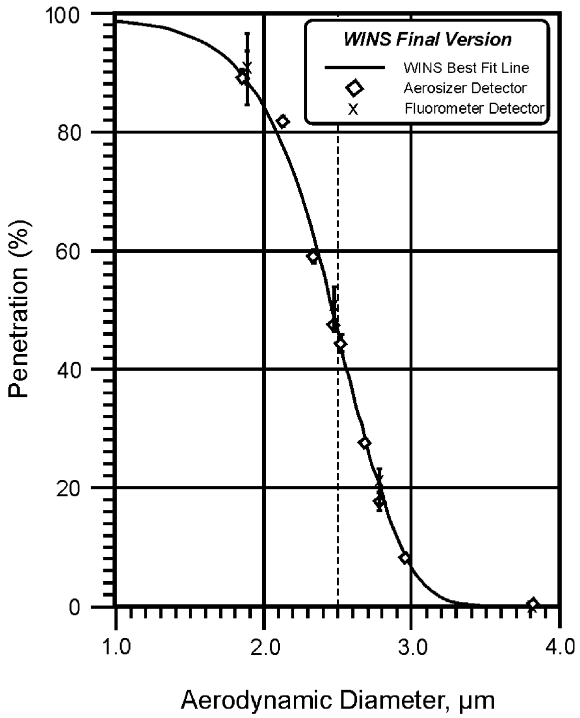

Fig. 11. Evaluation of the final version of the WINS (Peters et al., 2001a. Aerosol Science and Technology: Design and calibration of the EPA $PM_{2.5}$ Well Impactor Ninety-Six (WINS). 34:395. Copyright 2001. Reprinted with permission of the American Association for Aerosol Research.).

Since the implementation of the PM_{10} standard in 1987 (Federal Register, 1987) considerable information has accumulated on the factors that affect the quality of the data gathered from the EPA reference method for PM_{10}. These include inlet losses of coarse fraction particles (e.g., Anand et al., 1992); biases in concentrations due to differences between samplers in large particle cutpoints that are within the EPA's specified acceptable tolerances (Ranade et al., 1990); and particle bounce tolerances and reentrainment leading to as much as 30% errors (Wang and John, 1988). The sampling issues associated with cutpoint tolerances are predictable, and the particle bounce and reentrainment problems have since been dealt with voluntarily by the manufacturers by recommending operational procedures including oiling of impact surfaces and regular cleaning. The 1996 PM AQCD (US Environmental Protection Agency, 1996) concluded that the PM_{10} sampling systems can be designed such that concentration measurements are precise to ±10%. For $PM_{2.5}$, cutpoint tolerances are not expected to affect the mass concentration as much as for PM_{10} because the 2.5 μm D_a cutpoint generally occurs near a minimum in the mass distribution (e.g., Fig. 2). The $PM_{2.5}$ mass concentration will be affected by other sampling issues including gas/particle and particle/substrate interactions for sulfates and nitrates (e.g., Appel et al., 1984); volatilization losses of nitrates (Zhang and McMurry, 1992); SVOC artifacts (e.g., Eatough et al., 1993); and RH effects (e.g., Keeler et al., 1988).

1.4.3. $PM_{10-2.5}$

Measurement techniques for $PM_{10-2.5}$ are somewhat more complex than those for $PM_{2.5}$ or PM_{10} because, for $PM_{10-2.5}$, it is necessary to isolate a size fraction between an upper 50% cutpoint of 10 μm D_a and a lower 50% cutpoint of 2.5 μm D_a. The US EPA is in the process of preparing a FRM for $PM_{10-2.5}$.

1.4.3.1. The difference method. One approach to measurement of $PM_{10-2.5}$ is to make separate measurements of PM_{10} and $PM_{2.5}$ and take the difference of the resulting equilibrated masses. Errors in cutpoint, flow rate, and filter weights (both before use and after collection and equilibration of particles), and uncertainties due to loss of semivolatile components of PM must be considered for each size cut. Careful control of flow rate and equivalent treatment of PM_{10} and $PM_{2.5}$ filters in terms of pressure drop across the filter and temperature of the filter during and after collection can improve precision and accuracy. Allen et al. (1999) summarized several sampling issues to consider in measuring coarse particulate mass by difference, including the use of identical instrumentation (except cutpoints), filter media, filter face velocity, and ambient-filter temperature differences; common flow measurement devices; use of higher sampler flow rates (10 l/min minimum for 24-h sample is recommended); and avoiding excessive filter loading.

Since the difference method requires weighing two filters, the key to obtaining high precision in the coarse mass measurement is precise measurements of filter weights. Allen et al. (1999) discuss techniques for increasing the precision of the difference method by reducing errors in filter weights. These include proper temperature and humidity controls, use of a high quality microbalance, 100% replicate weighings, control of static charge, aging of new filters, weighing of a sufficient number of laboratory blank filters, and accounting for buoyancy errors caused by variability in barometric pressure. Allen et al. (1999) emphasize the necessity of replicate weighing of filters and a third weighing if the difference between the first two weights exceeds a specified minimum. Lawless et al. (2001) investigated the magnitude of uncertainties attributed to fluctuations in some of these parameters (humidity, temperature, drafts, vibration, and electrostatic charges) and recommended methods for improving their control. Koistinen et al. (1999) and Hänninen et al. (2002) give excellent discussions of the procedures developed to overcome problems associated with gravimetric measurements of $PM_{2.5}$ mass in the EXPOLIS study. They discuss factors such as corrections for buoyancy, elimination of static charge, and increases in the mass of blank filters with time. The establishment of a temperature- and humidity-controlled room required for the equilibration and weighing of filters for the FRM is expensive. Allen et al. (2001) describe a more cost-effective technique using a chamber with RH controlled at 34% RH by a saturated aqueous solution of $MgCl_2$.

Allen et al. (1999) recommend that both the coefficient of variation (CV) and the square of the correlation coefficient be included in reports of precision from collocated samplers. For a study in Boston with 27 pairs of mass data from collocated PM_{10} and $PM_{2.5}$ using standard weighing methods, they obtained a CV of 4.7% and an r^2 of 0.991 for $PM_{2.5}$, a CV of 4.4% and an r^2 of 0.994 for PM_{10}, and a CV of 15% and an r^2 of 0.88 for $PM_{10-2.5}$. By using duplicate weighings and other techniques suggested for improving precision, they obtained a CV of 1.3% and an r^2 of 0.998 for $PM_{2.5}$ in a study in Chicago with 38 collocated measurements. On the basis of the improvement in the CV for $PM_{2.5}$, they estimate that use of the recommended techniques for $PM_{10-2.5}$ by difference would yield a CV of 3.8% and an r^2 of 0.98.

This "difference" technique has been used to measure $PM_{10-2.5}$ in a number of studies. It is currently used to obtain $PM_{10-2.5}$ data in the US national monitoring program. However, EPA has not yet promulgated a FRM for $PM_{10-2.5}$.

1.4.3.2. Multi-stage impaction. A second technique involves the use of impaction to isolate the size fraction between 2.5 and 10 μm D_a. In the impaction process, the air stream is first accelerated through a small hole (nozzle) or slit. The air stream is directed so that it "impacts" on a surface. Depending on the velocity and pressure of the air stream, particles smaller than a certain size will follow the air stream around the impactor surface. Larger particles will impact on the surface. In practice, impactors have 50% cutpoints similar to those for the rejection of larger particles in $PM_{2.5}$ and PM_{10} samplers (Figs. 2 and 3).

Multi-stage impactors are used to separate particles into several size fractions for the determination of mass and chemical composition as a function of size (Wang and John, 1988; Marple et al., 1991). The major problem with the use of impactors to separate the 10–2.5 μm D_a fraction of coarse particles (thoracic coarse PM) is bounce. Coarse particles tend to be dry, solid particles. When they hit a hard surface they can bounce and be carried away with the air stream (e.g., Dzubay et al., 1976; Wesolowski et al., 1977; Rao and Whitby, 1978; Cheng and Yeh, 1979; Wang and John, 1987; John and Sethi, 1993). Various techniques have been used to reduce bounce. One technique is to use a porous substance such as a glass or quartz fiber filter (Chang et al., 1999) material or a polyurethane foam (Breum, 2000; Kavouras and Koutrakis, 2001). These techniques may result in a less precise separation and yield a sample that must be extracted before chemical analyses can be performed. Another technique is to coat the impactor with a soft wax or grease (Rao and Whitby, 1977; Turner and Hering, 1987; Pak et al., 1992). This can cause problems with weighing and chemical analyses. In addition, as the deposit of particles builds up, incoming particles may not hit the soft surface but, instead, hit a previously collected hard particle and bounce off of it. The WINS impactor discussed earlier uses a filter in a well of low volatility oil to ensure a wetted surface at all times. However, such a technique, while appropriate for removing unwanted particles, would not yield a particle sample suitable for weighing or for chemical analyses.

1.4.3.3. Virtual impaction. In an effort to alleviate the bounce problem, aerosol scientists have developed the "virtual" impactor (Loo et al., 1976; Jaklevic et al., 1981). A hole is placed in the impaction plate just below the accelerating jet. Two controlled flows allow a fraction (e.g., 10% or another predetermined fraction, typically 5–20%) of the air to go through the hole and through a filter (minor flow). A 10% minor flow gives a coarse channel enrichment factor of 10. The remaining fraction (e.g., 90% of the airflow) follows a different path and goes through a second filter (major flow). The upper cutpoint is usually set by the inlet (e.g., 10 μm D_a). The flow rates, pressures, and distance from the nozzle to the virtual impactor surface can be varied to direct particles with an D_a greater than the lower cutpoint (i.e., >2.5 μm) to go through the hole and be collected on the first filter and to direct smaller particles (i.e., <2.5 μm) to flow around the impactor to be collected on the second filter (Marple and Chien, 1980). This technique overcomes the problem of bounce. However, a fraction of the smaller particles, equal to the minor flow, will go through the virtual impaction opening with the air stream and be collected on the course particle filter. Thus, in order to determine the mass or composition of the coarse particles, it is necessary to determine the mass and composition of the fine particles and subtract the appropriate fraction from the mass or composition of the particles collected on the coarse particle filter. Virtual impactors that separate particles into two size fractions are known as dichotomous samples. Allen et al. (1999) discuss potential errors in the dichotomous sampler caused by uncertainties in the coarse mass channel enrichment factor. An example of the separation of PM into fine and coarse particles in a virtual impactor is shown in Fig. 12.

The dichotomous sampler was developed for use in the Regional Air Monitoring Study (RAMS), part of the Regional Air Pollution Study (RAPS), conducted in St. Louis, Missouri in the mid-1970s (Loo et al., 1976). Dichotomous samplers were a new concept at that time, and there was concern that particle loses might be high at cutpoint sizes below 2.5 μm D_a. In subsequent years,

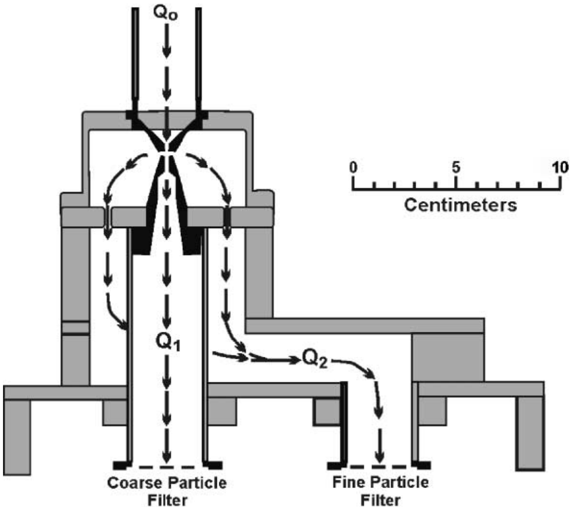

Fig. 12. Schematic diagram showing the principle of virtual impaction. The initial flow, Q_0, is split into a minor flow, Q_1, that carries the larger particles that impact into the hole and to the coarse particle filter and a major flow, Q_2, that carries the smaller particles, which can follow the airflow, to the fine particle filter (Loo and Cork, 1998. Aerosol Science and Technology: Development of high efficiency virtual impactors. 9:170. Copyright 1988. Reprinted with permission of the American Association for Aerosol Research.).

the theory of virtual impaction has advanced. Currently, virtual impactors, with rectangular slits or round holes, are used to give cutpoint sizes as low as 0.15 μm D_a and are used to concentrate coarse, accumulation, and ultrafine mode particles for use in health studies (Solomon et al., 1983; Marple et al., 1990; Sioutas et al., 1994a,b,c). Dichotomous samplers were also used in a national network to measure $PM_{2.5}$ and $PM_{10-2.5}$ in the Harvard Six City Study (Dockery et al., 1993) and the Inhalable Particulate Network (Suggs and Burton, 1983).

1.5. Speciation monitoring

The chemical composition of PM is of interest as well as the mass. In the US, chemical analyses from an approximately 300-site speciation network will be used for source category apportionment via receptor modeling of $PM_{2.5}$ (US EPA, 1999; Code of Federal Regulations, 2001d). The current samplers include at least three filters: Teflon for equilibrated mass and elemental analysis, a Nylon filter with a nitric acid denuder to collect nitrate, and a quartz fiber filter for elemental and OC (but currently without any correction for positive or negative artifacts due to adsorption of organic gases on the quartz filters or evaporation of semivolatile organic compounds from the collected particles).

1.5.1. Inorganic elemental analyses

In addition to hydrogen, carbon, oxygen, and nitrogen, the following 40 heavier elements are commonly found in ambient air samples: sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, arsenic, selenium, bromine, rubidium, strontium, yttrium, zirconium, molybdenum, palladium, silver, cadmium, indium, tin, antimony, barium, lanthanum, gold, mercury, thallium, lead, and uranium. These often indicate air pollution sources and several of them are considered to be toxic (transition metals, water-soluble metals, and metals in certain valence states (e.g., Fe(II), Fe(III), Cr(III), Cr(VI), As(III), As(V))). Measurement methods for the heavier elements include: (1) energy dispersive X-ray fluorescence (EDXRF); (2) synchrotron induced X-ray fluorescence (S-XRF); (3) proton induced X-ray emission (PIXE); (4) proton elastic scattering analysis (PESA); (5) total reflection X-ray fluorescence (TRXRF); (6) instrumental neutron activation analysis (INAA); (7) atomic absorption spectrophotometry (AAS); (8) inductively coupled plasma with atomic emission spectroscopy (ICP-AES); and (9) inductively coupled plasma with mass spectroscopy (ICP-MS). These methods differ with respect to detection limits, sample preparation, and cost (Chow, 1995). XRF and PIXE are the most commonly applied methods because they quantify more than 40 detectable elements, they are non-destructive, and they are relatively inexpensive. TRXRF and S-XRF are newer techniques with lower detection limits. AAS, ICP-AES, and ICP-MS are also appropriate for ionic measurements when the particles are extracted in deionized distilled water. PESA provides a means for measuring elements with lower atomic numbers, from hydrogen to carbon.

1.5.1.1. Energy dispersive X-ray fluorescence. EDXRF has usually been the method of choice for analysis of trace elements on filters. It is preferred over wavelength dispersive XRF because it allows fast and simultaneous analysis over the total spectrum thus allowing for the analysis of numerous elements simultaneously. EDXRF can accommodate small sample sizes and requires little sample preparation or operator time after the samples are placed into the analyzer. It also leaves the sample intact after analysis so further analysis is possible. XRF irradiates a uniform particle deposit on the surface of a membrane filter with 1–50 keV X-rays that eject inner shell electrons from the atoms of each element in the sample (Dzubay and Stevens, 1975; Jaklevic et al., 1977; Billiet et al., 1980; Potts and Webb, 1992; Piorek, 1994; Bacon et al., 1995; de Boer et al., 1995; Holynska et al., 1997; Török et al., 1998; Watson et al., 1999). 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 quantified by comparing photon counts for a sample with those obtained from thin-film standards of known concentration (Dane et al., 1996).

Emitted X-rays with energies less than ~4 keV (affecting the elements sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, and potassium) are absorbed in the filter in a thick particle deposit or even by large particles in which these elements are contained. Very thick filters also scatter much of the excitation radiation or protons, thereby lowering the signal-to-noise ratio for XRF and PIXE. For this reason, thin membrane filters with deposits in the range of 10–50 μg/cm^2 provide the best accuracy and precision for XRF and PIXE analysis (Davis et al., 1977; Dzubay and Nelson, 1975; Haupt et al., 1995).

1.5.1.2. Synchrotron induced X-ray fluorescence. S-XRF is a form of EDXRF in which the exciting X-rays are derived from a synchrotron. Bremmstrahlung X-rays are generated when energetic electrons (generally several GeV in energy) are forced by a magnetic field to make a bend in their path. The advantages of the technique are that an extremely high flux of X-rays may be obtained and that the X-rays are 100% polarized in the plane of the electron beam. The former allows for X-ray beams generally of 50–500 μm in diameter. However, the beams can be focused into X-ray microprobes with spot sizes on the order of 1 μm diameter. The X-ray polarization allows for removal of most of the background normally found under the characteristic X-ray peaks, greatly improving sensitivity compared to other XRF techniques. The primary disadvantages are the limited number of synchrotrons and that few synchrotrons have S-XRF capabilities. Thus, the technique has been relatively little used for PM and then generally for special problems such as the smoke from the Kuwaiti oil fires (Cahill et al., 1992; Reid et al., 1994). However, with the increasing availability of S-XRF facilities dedicated to PM analysis, the first of which was the Advanced Light Source at Lawrence Berkeley National Laboratory last year, the utilization of S-XRF for PM analysis is increasing.

1.5.1.3. Proton induced X-ray emission. PIXE differs from XRF analysis in the excitation source for producing fluorescence. The filter deposit is bombarded with high-energy protons to remove inner shell electrons, and the resulting characteristic X-rays are analyzed as in XRF (Johansson et al., 1970; Cahill, 1981, 1985; Zeng et al., 1993). Small accelerators, generally Van de Graaffs, generate intense beams of low energy protons, generally of a few MeV in energy. These have the ability to remove electrons from the inner shells of atoms of any element. Thus, PIXE can see a very wide range of elements in a single analysis. The cross-section for producing X-rays using protons of a few MeV in energy tends to favor lighter elements, Na through Ca, but sensitivities for equivalent PIXE and multi-wavelength XRF analysis are roughly comparable. The technique has been widely used in the US (Flocchini et al., 1976; Malm et al., 1994) and around the world as many universities have the small accelerators needed for the method. Like S-XRF, the proton beams can be focused into μm size beams, but these have been relatively little used for PM. However, the mm size beams used in both S-XRF and PIXE are well suited to analyzing the limited mass and small deposits that result from detailed PM size measurements by impactors (Perry et al., 1999).

1.5.1.4. Proton elastic scattering analysis. With the routine availability of elemental analyses for all elements sodium and heavier, organic compounds remain the major unmeasured species needed for mass balance. For programs like IMPROVE, (Malm et al., 1994) parallel filters are collected for separate OC and EC determinations. Aerosol programs that use PIXE can use PESA to directly measure hydrogen simultaneously with PIXE by scattering protons from Teflon filters that lack hydrogen (Cahill et al., 1989; Cahill et al., 1992). Generally, estimates of organic matter by carbon combustion from quartz filters and estimates of organic matter by hydrogen in PM on Teflon filters are in agreement, assuming certain assumptions about the chemical states of sulfates and nitrates are met (Malm et al., 1994; Cahill et al., 1996).

1.5.1.5. Total reflection X-ray fluorescence. One of the limitations of the EDXRF method is the minimum detection limit which may be high due to high background values (Streit et al., 2000). By implementation of X-ray optical geometries that use the total reflection of the primary radiation on flat surfaces, scattering on the substrate is reduced so that detection limits can be reduced. This is the basis for the total reflection X-ray fluorescence (TRXRF) method (Aiginger and Streli, 1997). This modification to the EDXRF technique improves detection limits and avoids the need to correct for matrix effects. Despite its apparent advantages, TRXRF has not yet become widely in use for atmospheric PM analysis but has been used in the analysis of marine PM (Stahlschmidt et al., 1997) and at a high elevation site (Streit et al., 2000). Streit et al. sampled ambient air at the High Alpine Research Station (3580 m asl) in the Bernese Alps, Switzerland, using a nine-stage, single-jet, low-pressure, cascade impactor equipped with quartz impactor plates coated with silicon oil diluted in 2-propanol. The typical sample volume for a weekly sample was 10 m^3. The quartz plates were analyzed directly by TRXRF. Streit et al. reported that the minimum detection limits, defined by the 3σ values of the blanks, ranged from 25 ng for S, decreased monotonically with increasing atomic number down to 5 pg for Rb, and decreased further after that. The use of TRXRF is expected to increase as EDXRF users become aware of the method. A relatively low-cost, add-on unit has been developed that would allow EDXRF users to test the TRXRF technique (Aiginger, 1991).

1.5.1.6. Instrumental neutron activation analysis. INAA irradiates a sample in the core of a nuclear reactor for a few minutes to several hours, depending on the elements being quantified (Dams et al., 1970; Zoller and Gordon, 1970; Nadkarni, 1975; Landsberger, 1988; Olmez, 1989; Ondov and Divita, 1993). The neutron bombardment chemically transforms many elements into radioactive isotopes. The energies of the gamma rays emitted by these isotopes identify them, and therefore their parent elements. The intensity of these gamma rays is proportional to the amount of the parent element present in the sample. Different irradiation times and cooling periods are used before counting with a germanium detector. In source apportionment studies, it is possible to use a combination of XRF and INAA to develop a relatively complete set of elemental measurements. Between these two analytical techniques, good sensitivity is possible for many elements, including most of the toxic metals of interest. In general, XRF provides better sensitivity for some metals (e.g., Ni, Pb, Cu, and Fe); whereas INAA provides better sensitivity for others (Sb, As, Cr, Co, Se, and Cd). Both methods provide similar detection limits for still other elements (V, Zn, and Mn). INAA does not quantify some of the abundant species in ambient PM such as silicon, nickel, tin, and lead. While INAA is technically non-destructive, sample preparation involves folding the sample tightly and sealing it in plastic, and the irradiation process makes the filter membrane brittle and radioactive. These factors limit the use of the sample for subsequent analyses.

1.5.1.7. Atomic absorption spectrophotometry. AAS is applied to the residue of a filter extracted in a strong solvent to dissolve the solid material; the filter or a portion of it is also dissolved during this process (Ranweiler and Moyers, 1974; Fernandez, 1989; Jackson and Mahmood, 1994; Chow et al., 2000). A few milliliters of this extract are injected into a flame where the elements are vaporized. Elements absorb light at certain wavelengths in the visible spectrum, and a light beam with wavelengths specific to the elements being measured is directed through the flame to be detected by a monochromater. The light absorbed by the flame containing the extract is compared with the absorption from known standards to quantify the elemental concentrations. AAS requires an individual analysis for each element, and a large filter or several filters are needed to obtain concentrations for a large variety of elements. AAS is a useful complement to other methods, such as XRF and PIXE, for species such as beryllium, sodium, and magnesium which are not well-quantified by these methods. Airborne particles are chemically complex and do not dissolve easily into complete solution, regardless of the strength of the solvent. There is always a possibility that insoluble residues are left behind and soluble species may co-precipitate on them or on container walls.

1.5.1.8. Inductively coupled plasma with atomic emission spectroscopy. ICP-AES introduces an extracted sample into an atmosphere of argon gas seeded with free electrons induced by high voltage from a surrounding Tesla coil (Fassel and Kinseley, 1974; McQuaker et al., 1979; Lynch et al., 1980; Harman, 1989; Tyler, 1992; Baldwin et al., 1994). The high temperatures in the induced plasma raise valence electrons above their normally stable states. When these electrons return to their stable states, a photon of light is emitted that is unique to the element that was excited. This light is detected at specified wavelengths to identify the elements in the sample. ICP-AES acquires a large number of elemental concentrations using small sample volumes with acceptable detection limits for atmospheric samples. As with AAS, this method requires complete extraction and destruction of the sample.

1.5.1.9. Inductively coupled plasma with mass spectroscopy. ICP-MS has been applied in the analysis of personal exposure samples (Tan and Horlick, 1986; Gray and Williams, 1987a,b; Nam et al., 1993; Munksgaard and Parry, 1998; Campbell and Humayun, 1999). Ion species generated from ICP and from the sample matrix can produce a significant background at certain masses, resulting in formation of polyatomic ions that can limit the ability of ICP-MS to determine some elements of interest. Cool plasma techniques have shown potential to detect elements at the ultra-trace level (Nham, 1996) and to minimize common molecular ion interferences (Sakata and Kawabata, 1994; Turner, 1994; Plantz, 1996). Detection limits of ICP-MS using a one-second scan are typically in the range of 10^{-3} ng/m^3, which is an order of magnitude lower than other elemental analysis methods. The instrument can also be set up to analyze a wide dynamic range of aerosol concentrations. Isotope analysis can also be performed with ICP-MS. Intercomparison studies need to be conducted to establish the comparability of ICP-MS with other non-destructive filter analysis methods.

1.5.2. Water-soluble ions analysis methods

The most common ions of atmospheric interest are sulfate, nitrate, ammonium, and chloride. Under certain conditions, sodium, calcium, magnesium, potassium, fluoride, and phosphate are quantifiable in ambient aerosol samples. The soluble fractions of metals such as iron, nickel, chromium, vanadium, mercury, and arsenic have been implicated as being detrimental to health.

Several simple ions, such as sodium, magnesium, potassium, and calcium can be quantified by AAS as described above. Polyatomic ions must be quantified by other methods such as IC and automated colorimetry (AC). When the aerosol deposit is suspected of being acidic, its hydrogen ion content can be determined by a pH electrode or by microtitration (Koutrakis et al., 1992). It is important to keep filters away from ammonia sources, such as human breath, to minimize neutralization of the acidic compounds.

Most ion analysis methods require that a fraction of the filter be extracted in deionized distilled water and the extract be filtered to remove insoluble residues prior to analysis. The extraction volume needs to be as small as possible, lest the solution become too dilute to detect the desired constituents at levels typical of those found in $PM_{2.5}$ or PM_{10}. The 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 compounds. Small amounts of ethanol or other wetting agents are sometimes added to the filter surface to aid the wetting of hydrophobic filter materials, such as Teflon membranes. When other analyses are to be performed on the same filter, the filter is sectioned using a precision positioning jig attached to a paper cutter.

In IC, the sample extract passes through an ion-exchange column that separates the ions in time for individual quantification, usually by a electroconductivity detector (Small et al., 1975; Mulik et al., 1976, 1977; Butler et al., 1978; Mueller et al., 1978; Rich et al., 1978; Small, 1978; Wetzel et al., 1985; Fritz, 1987; Tarter, 1987; Dasgupta, 1992; Thienpont et al., 1994; Chow and Watson, 1999). Prior to detection, the column effluent enters a suppressor column where the chemical composition of one element is altered, resulting in a matrix of low conductivity. The ions are identified by their elution/retention times and are quantified by the conductivity peak area or peak height. IC is especially desirable for particle samples because it provides results for several ions with a single analysis and because it uses a small portion of the filter extract with low detection limits. IC analyses can be automated by interfacing to an automatic sampler that can conduct unattended analysis of as many as 400 samples (Tejada et al., 1978).

Though automated data processing is usually applied to the IC output, the chromatograms are too complex for such software to detect deviations from measurement assumptions. Each chromatogram should be examined individually to verify: (1) proper operational settings, (2) correct peak shapes and integration windows, (3) peak separation, (4) correct background subtraction, and (5) quality control sample comparisons. When values for replicates differ by more than ±10% or when values for standards differ by more than ±5%, all samples before and after these quality control checks should be reanalyzed. Individual samples with unusual peak shapes, background subtractions, or operating parameters should also be reanalyzed.

Automated colorimetry (AC) applies different colorimetric analyses to small samples volumes with automatic sample throughput. The most common ions measured are ammonium, chloride, nitrate, and sulfate (Butler et al., 1978; Mueller et al., 1978; Fung et al., 1979; Pyen and Fishman, 1979). Because IC provides multi-species analysis for the anions, ammonium is most commonly measured by AC. The standard AC technique can analyze ~50 samples per hour per channel with minimal operator attention and relatively low maintenance and material costs. Several channels can be set up to simultaneously analyze several ions.

Intercomparison studies between AC and ion chromatography have been conducted by Butler et al. (1978); Mueller et al. (1978); Fung et al. (1979); and Pyen and Fishman (1979). Butler et al. (1978) found excellent agreement between sulfate and nitrate measurements by AC and IC. The accuracy of both methods is within the experimental errors, with higher blank values observed from automated colorimetric techniques. Comparable results were also obtained between the two methods by Fung et al. (1979). The choice between the two methods for sample analysis is dictated by sensitivity, scheduling, and cost constraints.

1.5.3. Carbon analysis methods

Three classes of carbon are commonly measured in ambient aerosol samples collected on quartz-fiber filters: (1) organic, volatilized, or non-light absorbing carbon; (2) elemental or light-absorbing carbon; and (3) carbonate carbon. Carbonate carbon (i.e., K_2CO_3, Na_2CO_3, $MgCO_3$, $CaCO_3$) can be determined on a separate filter section by measurement of the carbon dioxide (CO_2) evolved upon acidification (Johnson et al., 1981). Though progress has been made in the quantification of specific organic chemical compounds in suspended particles (e.g., Rogge et al., 1991), sampling and analysis methods for specific compounds have not yet evolved for use in practical monitoring situations.

Several analytical methods for the separation of organic and elemental carbon in ambient and source particulate samples have been evaluated (Cadle and Groblicki, 1982; Stevens et al., 1982). These methods include: (1) solvent extraction of the organics followed by total carbon analysis (Gordon, 1974; Grosjean, 1975; Appel et al., 1976, 1979; Daisey et al., 1981; Muhlbaier and Williams, 1982; Japar et al., 1984); (2) nitric acid digestion of the organics followed by total carbon analysis (McCarthy and Moore, 1952; Kukreja and Bove, 1976; Pimenta and Wood, 1980); (3) absorption of radiation using an integrating plate to determine EC (variations of this method include infrared absorbance (Smith et al., 1975), Raman spectroscopy (Rosen et al., 1978), and visible absorbance (Lin et al., 1973; Weiss et al., 1979; Gerber, 1982; Heintzenberg, 1982)); (4) thermal combustion including both temperature-programmed (Muhlbaier and Williams, 1982) and step-wise pyrolysis followed by oxidation using either CO_2 or methane detection (Mueller et al., 1971, 1981; Patterson, 1973; Merz, 1978; Johnson and Huntzicker, 1979; Johnson et al., 1980; Malissa, 1979; Cadle et al., 1980a,b; Heisler et al., 1980a,b; Novakov, 1981; Tanner et al., 1982; Wolff et al., 1982); and (5) a combination of thermal and optical methods (Appel et al., 1976; Dod et al., 1979; Macias et al., 1979; Cadle et al., 1980a,b; Johnson et al., 1981; Novakov, 1982; Huntzicker et al., 1982; Chow et al., 1993).

Chow and Watson (1998) summarize different carbon analysis methods along with their measurement principles. The definitions of organic and EC are operational (i.e., method dependent) and reflect the method and purpose of measurement. EC is sometimes termed “soot”, “graphitic carbon”, or “black carbon”. For studying visibility reduction, light-absorbing carbon is a more useful concept than EC. For source apportionment by receptor models, several consistent but distinct fractions of carbon in both source and receptor samples are desired, regardless of their light-absorbing or chemical properties. Differences in ratios of the carbon concentrations in these fractions form part of the source profile that distinguishes the contribution of one source from the contributions of other sources (Watson et al., 1994a).

Light-absorbing carbon is not entirely graphitic carbon because there are many organic materials which absorb light (e.g., tar, motor oil, asphalt, coffee). Even the “graphitic” black carbon in the atmosphere has only a poorly developed graphitic structure with abundant surface chemical groups. “Elemental carbon” is a poor but common description of what is measured. For example, a substance of three-bond carbon molecules (e.g., pencil lead) is black and completely absorbs light, but four-bond carbon in a diamond is completely transparent and absorbs very little light. Both are pure, EC.

Chow et al. (1993) document several variations of the thermal method for OC and EC. The thermal/optical reflectance (TOR), thermal/optical transmission (TOT), and thermal manganese oxidation (TMO) methods are most commonly used for the analysis of OC and EC in atmospheric PM. Filter transmission analysis is often performed to estimate particle light absorption which is proportional to the level of EC in the atmosphere. These methods are discussed in detail in the following subsections.

TMO method (Mueller et al., 1982; Fung, 1990) uses manganese dioxide present and in contact with the sample throughout the analysis as the oxidizing agent. Temperature is relied upon to distinguish between organic and EC. Carbon evolving at 525 °C is classified as OC, and carbon evolving at 850 °C is classified as EC. This method has been used in the SCENES (Subregional Cooperative Electric Utility, Department of Defense, National Park Services, and Environmental Protection Agency Study); (Mueller and McDade, 1986; Mueller et al., 1986; Sutherland and Bhardwaja, 1987; Watson et al., 1987) visibility network, as well as in the SCAQS (Southern California Air Quality Study) (Chow et al., 1994a,b; Watson et al., 1993, 1994a,b).

TOR method of carbon analysis developed by Huntzicker et al. (1982) has been adapted by several laboratories for the quantification of organic and EC in PM collected on quartz-fiber filters. Although the principle used by these laboratories is identical to that of Huntzicker et al. (1982), the details differ with respect to calibration standards, analysis time, temperature ramping, and volatilization/combustion temperatures.

In the most commonly applied version of the TOR method (Chow et al., 1993), a filter is submitted to volatilization at temperatures ranging from ambient to 550 °C in a pure helium atmosphere, then to combustion at temperatures between 550 and 800 °C in a 2% oxygen and 98% helium atmosphere with several temperature ramping steps. The carbon that evolves at each temperature is converted to methane and quantified with a flame ionization detector. The reflectance from the deposit side of the filter punch is monitored throughout the analysis. This reflectance usually decreases during volatilization in the helium atmosphere owing to the pyrolysis of organic material. When oxygen is added, the reflectance increases as the light absorbing carbon is combusted and removed. OC is defined as that which evolves prior to reattainment of the original reflectance, and elemental carbon is defined as that which evolves after the original reflectance has been attained. By this definition, “organic carbon” is actually OC that does not absorb light at the wavelength (632.8 nm) used and “elemental carbon” is light-absorbing carbon (Chow et al., 1993).

TOT method applies to the same thermal/optical carbon analysis method except that transmission instead of reflectance of the filter punch is measured. The National Institute for Occupational Safety and Health (NIOSH) Method 5040 for monitoring EC as a marker for particulate diesel exhaust is based upon the TOT method (Birch and Cary, 1996). The TOT OC/EC method consists of a two-stage process with the first stage being conducted in a pure helium atmosphere at temperatures of 250, 500, 650, and 850 °C for a total of 4.5 min and the second stage conducted in a 2% oxygen/98% helium mix at temperatures of 650, 750, 850, and 940 °C for 4 min. A pyrolysis base correction is made based on the transmission measurement. An example of a TOT thermogram is shown in Fig. 13.

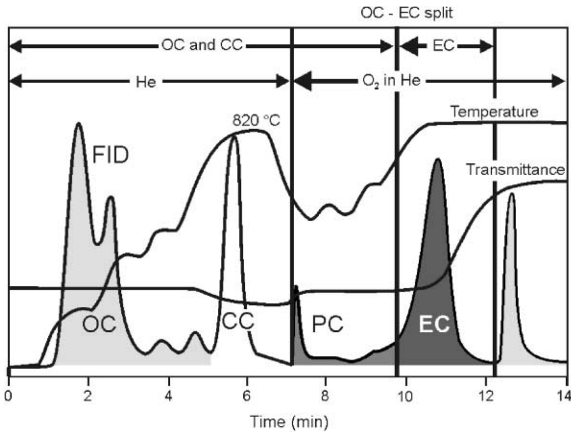

Fig. 13. Thermogram, for a sample containing rock dust (a carbonate source) and diesel exhaust, showing three traces that correspond to temperature, filter transmittance, and FID detector response. Peaks correspond to organic (OC), carbonate (CC), pyrolytic (PC), and elemental (EC) carbon. The final peak is a methane calibration peak (Birch and Cary, 1996. Aerosol Science and Technology: Elemental Carbon-based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust. 25:227. Copyright 1996. Reprinted with permission of the American Association for Aerosol Research.).

Chow et al. (1993) document several variations of the thermal (T), TOR, TOT and TMO methods for OC and EC. Comparisons among the results of the majority of these methods show that they yield comparable quantities of total carbon in aerosol samples, but the distinctions between organic and EC are quite different (Groblicki et al., 1983; Cadle and Mulawa, 1990; Countess, 1990; Hering et al., 1990; Birch, 1998; Schmid et al., 2001). TOR was consistently higher than TMO for EC, especially in woodsmoke-dominated samples where the disparity was as great as sevenfold. For the sum of organic and EC, these methods reported agreement within 5–15% for ambient and source samples (Houck et al., 1989; Kusko et al., 1989; Countess, 1990; Shah and Rau, 1991) and within 3% on carefully prepared standards. Evaluation of these methods thus is a matter of assessing how they differentiate between OC and EC. The TMO method attributes more of the total carbon to OC and less to EC than the TOR and TOT methods. None of the methods represents an ideal procedure for the separation of OC from EC.

EC can also be measured by optical absorption (OA), photoacoustic spectroscopy, and non-extractable mass (Chow et al., 1993). OA, assumed due entirely to EC, can be measured by determining light transmission through Teflon-membrane and quartz-fiber filters before and after sampling with a transmission densitometer. Informal intercomparisons among different filter transmission methods have shown high correlations of absorption but differences of up to a factor of two in absolute values (Watson et al., 1988a,b). These differences are functions of the type of filter, filter loading, the chemical and physical nature of the deposit, the wavelengths of light used, calibration standards, and light diffusing methods. At the current time, there is no agreement on which combination most accurately represents light absorption in the atmosphere. This method is applied with the knowledge that absolute differences in absorption may be found between the measurements made on Teflon-membrane and quartz-fiber filters and with respect to absolute absorption measurements made on the same samples in other laboratories.

With the limitations and precautions described above, laboratory analyses for the mass, elemental, ionic, and carbonaceous properties of suspended particles have matured to the point where they can be performed with commercially available instruments following established standard operating procedures and with traceability to common standards. Analyses of trace substances still require extraordinary precautions to obtain accurate results.

1.5.4. Organic speciation

Organic compounds are important components of PM, whether in urban, rural, or remote areas. However, routine monitoring of specific organic compounds in atmospheric PM is not yet feasible. Rogge et al. (1993a) identified and quantified over 80 individual organic compounds in the $PM_{2.5}$ fraction. However, this represented only about 10–20% of the total OC in the samples. Recent work has emphasized the characterization of individual compounds or classes of compounds that might serve as tracers of specific source categories of organic aerosol (e.g., Rogge et al., 1993a; Schauer et al., 1996). In urban and rural atmospheres, as well as in the remote troposphere, organic composition corresponding to fingerprints of plant waxes, resin residues, and long-chain hydrocarbons from petroleum residues have been found (e.g., Gagosian et al., 1982, 1987; Simoneit, 1984; Mazurek et al., 1987, 1989, 1991; Simoneit et al., 1991; Rogge et al., 1993b,c,d,e). In addition, a variety of smaller, multi-functional compounds characteristic of gas-to-particle conversion have also been observed (e.g., Finlayson-Pitts and Pitts, 1986). These compounds tend to be present in the polar fraction of ambient organic aerosol particles, having been formed from atmospheric chemical reactions of less polar precursors. A summary of sampling and analysis methods for VOC and SVOC may be found in Zielinska and Fujita (1994). Identification of the organic compounds in PM is currently an active area of research, especially in regard to understanding the chemical composition of polar organic fractions, to identifying source category tracers for use in source apportionment, and to determining which organic compounds affect human health. A discussion of current knowledge of organic speciation of PM is beyond the scope of this paper.

1.6. Continuous mass monitoring

The US EPA expects that many local environmental agencies will operate continuous PM monitors in the next few years. However, EPA has not yet provided any guidance regarding what continuous monitoring technique to use. All currently available continuous measurements of suspended particle mass share the problem of dealing with semivolatile PM components. In order not to include particle-bound water as part of the mass, the particle-bound water must be removed by heating or dehumidification. However, heating also causes loss of ammonium nitrate and semivolatile organic components. A variety of potential candidates for continuous measurement of mass or chemical components will be discussed in this section. Detailed guidance can be found in Watson et al. (1998a).

1.6.1. Tapered element oscillating microbalance

The advantages of continuous PM monitoring and the designation of the tapered element oscillating microbalance (TEOM) as an equivalent method for PM_{10} has led to the deployment of the TEOM at a number of air monitoring sites. The TEOM is also being used to measure $PM_{2.5}$. The TEOM differs from the federal reference methods for particulate mass in that it does not require equilibration of the samples at a specified temperature and RH. Moreover, the TEOM samples at a constant temperature, typically heated to some temperature higher than the ambient temperature (Meyer et al., 1995; Meyer and Rupprecht, 1996); whereas the FRM requires sampling at the ambient temperature. Thus, the TEOM may not provide data equivalent to the FRM due to losses of volatile species. Volatilization losses in the TEOM sampler can be reduced during the cooler times of the year by operating the instrument heated to 30 °C rather than the typical 50 °C and by using Nafion dryers on the inlet.

This difference in operation and the implications for fine particle measurements were examined by researchers at CSIRO Atmospheric Research in Australia (Ayers et al., 1999). That group compared 24-h mean $PM_{2.5}$ mass concentrations as determined by a TEOM and by two manual, gravimetric samplers (a low-volume filter sampler and a MOUDI sampler) in four Australian cities on 15 days in the winter half-year. The TEOM was operated at 50 °C at one location and at 35 °C at the other three locations. A systematically low TEOM response in comparison to the integrated gravimetric methods was observed. In a comprehensive study, Allen et al. (1997) reported results in which TEOM data collected at 10 urban sites in the US and Mexico were compared with 24-h integrated mass concentrations for both PM_{10} and $PM_{2.5}$. They collected a large data set that included both winter and summer seasons. Allen et al. (1997) concluded that a significant portion of PM_{10} in urban areas could be semivolatile compounds that could be lost from the heated filter in the TEOM thus leading to a systematic difference between the TEOM and the EPA FRM for PM_{10}. Moreover, they suggested that this difference is likely to be larger for $PM_{2.5}$ than it is for PM_{10} (Allen et al., 1997).

New techniques designed to minimize or eliminate loss of semivolatile components of PM are under development based on the TEOM technique (Meyer et al., 2000; Patashnick et al., 2001).

1.6.2. Real-time total ambient mass sampler

A real-time total ambient mass sampler (RAMS) for the real-time determination of total fine particulate mass, including semivolatile species, based on diffusion denuder and TEOM monitor technology, has been developed, validated, and field tested (Eatough et al., 1999; Pang et al., 2001; Pang et al., 2002a,b). The RAMS measures total mass of collected particles, including semivolatile species with a TEOM monitor using a "sandwich filter." The sandwich contains a Teflon coated particle collection filter followed by a charcoal impregnated filter (CIF) to collect any semivolatile species lost from the particles during sampling. Because the instrument measures total mass collected by the sandwich filter, all gas phase compounds that can be adsorbed by a CIF must be removed from the sampling stream prior to the TEOM monitor. Laboratory and field validation data indicate that the precision of fine PM mass determination is better than 10%. The RAMS uses a Nafion dryer to remove particle-bound water from the suspended particles and a particle concentrator to reduce the amount of gas phase organics that must be removed by the denuder. An example of data from the RAMS, the TEOM, and the PC-BOSS is shown in Fig. 14.

1.6.3. Continuous ambient mass monitor

Koutrakis and colleagues (Koutrakis et al., 1996; Wang, 1997) have developed the continuous ambient mass monitor (CAMM), a technique for the continuous measurement of ambient PM mass concentration based upon the measurement of pressure drop increase with particle loading across a membrane filter. Recently, Sioutas et al. (1999) examined the increase in pressure drop with increasing particle loading on Nuclepore filters. They tested filters with two pore diameters (2 and 5 μm) and filter face velocities ranging from 4 to 52 cm/s and examined the effects of RH in the range of 10–50%. They found that, for hygroscopic ammonium sulfate particles, the change in pressure drop per unit time and concentration was a strong function of RH, decreasing with increasing relative humidity. These results suggest that particulate concentration measurements like the

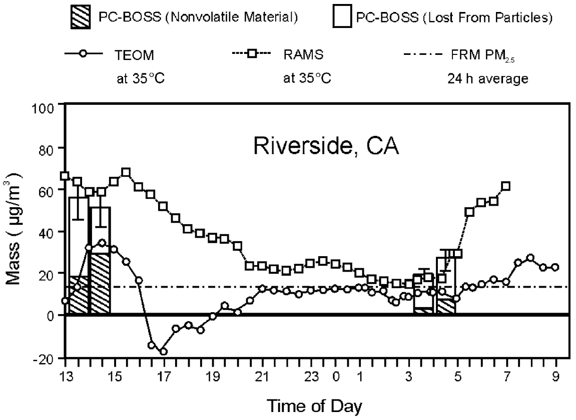

Fig. 14. Comparison of mass measurements with collocated RAMS (real-time data), PC-BOSS (1-h data), FRM $PM_{2.5}$ sampler (average of 24-h data), and a conventional TEOM monitor (real-time data). The semivolatile fine PM is sampled with the RAMS and PC-BOSS, but not with the TEOM monitor or the FRM $PM_{2.5}$ single filter sampler. The PC-BOSS provides information on both the non-volatile component (NV) and the SVOC (Reprinted from Atmospheric Environment, 33, Eatough et al., Integrated and real-time diffusion denuder sampler for $PM_{2.5}$, 2835–2844. Copyright 1996, with permission from Elsevier Science.).

method of Koutrakis et al. (1996) that uses the pressure drop method may be subject to additional uncertainties if used in an environment where the ambient RH cannot be accurately controlled. The current version of the CAMM (Wang, 1997) uses a particle concentrator and a Nafion dryer and frequently moves the filter tape to avoid artifacts due to evaporation of semivolatile components if their atmospheric concentration decreased.

1.6.4. Piezoelectric microbalance

Piezoelectric crystals have mechanical resonances that can be excited by applying an alternating electrical voltage to the crystal. As the resonance frequencies are well defined, such crystals (quartz in particular) have found applications as secondary time and frequency standards in clocks and watches. As for all mechanical resonators, the resonance frequency is a function of mass. Therefore, by monitoring the resonance frequency in comparison with a second crystal, one can continuously measure the mass deposited on the crystal (Sem et al., 1977; Bowers and Chuan, 1989; Ward and Buttry, 1990; Noel and Topart, 1994). Comparison with a second crystal largely compensates for the effect of temperature changes on the resonance frequency.

The piezoelectric principle has been used to measure particle mass by depositing the particles on the crystal surface either by electrostatic precipitation or by impaction (Olin and Sem, 1971). The collection efficiency of either mechanism has to be determined as a function of particle size to achieve quantitative measurements. In addition, the mechanical coupling of large particles to the crystal is uncertain. Both single and multi-stage impactors have been used (Olin and Sem, 1971; Fairchild and Wheat, 1984). Quartz crystals have sensitivities of several hundred hertz per microgram. This sensitivity results in the ability to measure the mass concentration of a typical, 100 µg/m³, aerosol to within a few percent in less than 1 min (Olin and Sem, 1971).

1.6.5. Light scattering

A variety of types of nephelometers, that integrate aerosol light scattering over various solid angles, are available. When used to measure visibility, e.g., to provide pilots with real-time data on visual range, it is desirable to include the light scattering due to particle-bound water. However, when used as an indicator of fine particle mass, it is desirable to exclude particle-bound water. This is frequently done by heating the ambient aerosol to a low reference RH of 40%. However, this heating has the potential of also causing the loss of semivolatile components of the aerosol. The evaporation of ammonium nitrate aerosol in a heated nephelometer has been examined. Bergin et al. (1997) conducted laboratory experiments at low RH (~10%) and as a function of temperature (27–47 °C), mean residence time in the nephelometer, and initial particle size distribution. The evaporation of ammonium nitrate aerosol was also modeled for comparison and was found to accurately describe the decrease in aerosol scattering coefficient as a function of aerosol physical properties and nephelometer operating conditions. Bergin et al. (1997) determined an upper limit estimate of the decrease in the aerosol light scattering coefficient at 450 nm due to evaporation for typical field conditions. The model estimates for their worst-case scenario suggest that the decrease in the aerosol scattering coefficient could be roughly 40%. They estimate that the decrease in aerosol scattering coefficient under most conditions is generally expected to be less than 20%.

1.6.6. Beta-gauge techniques

The use of absorption of beta radiation as a indicator of particle mass has been used effectively to measure the mass of equilibrated PM collected on Teflon filters (Jaklevic et al., 1981; Courtney et al., 1982). The technique has also been used to provide near real-time measurements with time intervals on the order of an hour (Wedding and Weigand, 1993). However, real-time beta-gauge monitors experience the same problems as other continuous or near real-time particular matter mass monitoring techniques. Particle-bound water must be removed to reduce the sensitivity of the indicated mass to relative humidity. However, the simplest technique, mild heating, will remove a portion of the ammonium nitrate and the semivolatile organic compounds as well as the particle-bound water.

An intercomparison study of two beta gauges at three sites indicated that the Wedding beta gauge and the Sierra Anderson SA 1200 PM_{10} samplers were highly correlated ($r > 0.97$) (Tsai and Cheng, 1996). The Wedding beta gauge was not sensitive to RH but was approximately 7% lower. This suggests that the mild heating in the beta gauge causes losses comparable to those due to equilibration although the differences could be due to slight differences in the upper cutpoints. The Kimoto beta gauge, however, which was operated at ambient temperature, was sensitive to RH, yielding significantly higher mass concentrations relative to the Sierra Anderson SA 1200 for RH > 80% than for RH < 80%, even though the correlation with the SA 1200 was reasonable: $r = 0.94$ for RH > 80% and 0.83 for RH < 80%.

1.7. Continuous monitoring of specific components

1.7.1. Carbon

The differentiation of OC and EC based on their thermal properties followed by their detection as carbon dioxide (CO_2) or methane (CH_4) after combustion is commonly applied to filter deposits (e.g., Chow et al., 1993). Turpin et al. (1990a,b) pioneered the continuous thermal/optical carbon analyzer which provides in situ time resolved OC and EC measurements. Another version of the thermal method, the Ambient Carbon Particulate Monitor (ACPM, R&P Series 5400) (Rupprecht et al., 1995), consists of two aerosol collectors: one collector operates in the collection mode while the other one operates in the analysis mode. In the collection mode, particles are drawn through a size-selective inlet and deposited onto an impactor. The temperature of the collector in collection mode can be set either at or above ambient temperature. Once the pre-specified sampling period is achieved (typically one or more hours), the collector is switched into the analysis mode while the second collector is switched from analysis to collection mode. The ACPM provides a continuous measure of OC and EC concentrations. However, its operational definitions of OC and EC and the selected combustion temperatures differ from those of commonly applied laboratory filter analysis protocols (e.g., Chow et al., 1993).

1.7.2. Sulfur/sulfate

Continuous methods for the quantification of aerosol sulfur compounds first remove gaseous sulfur (e.g., SO_2, H_2S) from the sample stream by a diffusion tube denuder followed by the analysis of particulate sulfur (Cobourn et al., 1978; Durham et al., 1978; Huntzicker et al., 1978; Mueller and Collins, 1980; Tanner et al., 1980). Another approach is to measure total sulfur and gaseous sulfur separately by alternately removing particles from the sample stream. Particulate sulfur is obtained as the difference between the total and gaseous sulfur (Kittelson et al., 1978). The total sulfur content is measured by a flame photometric detector (FPD) by introducing the sampling stream into a fuel-rich hydrogen-air flame (e.g., Stevens et al., 1969; Farwell and Rasmussen, 1976) that reduces sulfur compounds and measures the intensity of the chemiluminescence from the electronically excited sulfur molecules (S_2^*).

Because the formation of S_2^* requires two sulfur atoms, the intensity of the chemiluminescence is theoretically proportional to the square of the concentration of molecules that contain a single sulfur atom. In practice, the exponent is between one and two and depends on the sulfur compound being analyzed (Dagnall et al., 1967; Stevens et al., 1971). Calibrations are performed using both particles and gases as standards. The FPD can also be replaced by a chemiluminescent reaction with ozone that minimizes the potential for interference and provides a faster response time (Benner and Stedman, 1989, 1990).

Capabilities added to the basic system include in situ thermal analysis (Cobourn et al., 1978; Huntzicker et al., 1978) and sulfuric acid (H_2SO_4) speciation (Tanner et al., 1980). Sensitivities for sulfur aerosols as low as 0.1 $\mu g/m^3$ with time resolution ranging from 1 to 30 min have been reported. Continuous measurements of particulate sulfur have also been obtained by on-line X-ray fluorescence analysis with a time resolution of 30 min or less (Jaklevic et al., 1980). During a field-intercomparison study of five different sulfur instruments, Camp et al. (1982) reported four out of five FPD systems agreed to within ±5% during a one-week sampling period.

1.7.3. Nitrate

The Automated Particle Nitrate Monitor (APNM) is a new method being developed to provide high-time-resolution measurements of particle nitrate concentration (Hering, 1997; Chow et al., 1998; Hering and Stolzenburg, 1998). It uses an integrated collection and vaporization cell whereby particles are collected by a humidified impaction process and analyzed in place by flash vaporization. The approach is similar to the manual method for measuring the size distribution of sulfate aerosols (Roberts and Friedlander, 1976; Hering and Friedlander, 1982). The difference is that the particle collection and analysis has been combined into a single cell, allowing the system to be automated. Although the automated method that has been recently tested is specific to nitrate, the same technology could be applied for continuous sulfate measurements by using a sulfur detector instead of a nitric oxide detector.

Particles are humidified and collected onto a metal strip by means of impaction. The humidification eliminates particle bounce from the collection surface without the use of grease (Winkler, 1974; Stein et al., 1994). Interference from vapors such as nitric acid is minimized with a denuder upstream of the humidifier. At the end of the 10-min particle sampling period, a valve is switched to stop particle collection and to pass a carrier gas through the cell and into a gas analyzer. For nitrate, the deposited particles are analyzed by flash-vaporization in a nitrogen carrier gas, with quantification of the evolved gases by a chemiluminescent analyzer operated in NO_x mode (Yamamoto and Kosaka, 1994). The flow system is configured such that there are no valves on the aerosol sampling line. Time resolution of the instrument is on the order of 12 min, corresponding to a 10-min collection followed by an analysis step of less than 2 min.

Field calibration and validation procedures include on-line checks of particle collection efficiency, calibration of aqueous standards, and determination of blanks by measurements of filtered ambient air. Particle collection efficiencies have been checked against an optical particle counter that operated between the collection cell and the pump. The analysis step of the monitor has been calibrated by application of aqueous standards (i.e., sodium nitrate and ammonium nitrate) directly onto the metal collection substrate. To ensure the absence of response to ammonium ion, standards of ammonium sulfate have also been applied. Field blanks are determined by placing a Teflon filter at the inlet of the system, collecting for the 10-min sampling period, and then analyzing the strip exactly as done for a normal sample.

During the Northern Front Range Air Quality Study in Colorado (Watson et al., 1998b), the automated nitrate monitor captured 12-min time variability in fine particle nitrate concentrations with a precision of approximately ± 0.5 $\mu g/m^3$ (Chow et al., 1998). A comparison with denuded filter measurements followed by ion chromatographic analysis (Chow and Watson, 1999) showed agreement within ± 0.6 $\mu g/m^3$ for most of the measurements but exhibited a discrepancy of a factor of two for the elevated nitrate periods.

More recent intercomparisons took place during the 1997 Southern California Ozone Study (SCOS97) in Riverside, CA. Comparisons with 14 days of 24-h denuder-filter sampling gave a correlation coefficient of $R^2 = 0.87$ and showed no significant bias (i.e., the regression slope is not significantly different from 1). As currently configured, the system has a detection limit of 0.7 $\mu g/m^3$ and a precision of 0.2 $\mu g/m^3$. Field operations with the system in Riverside showed that it was robust, providing nearly uninterrupted data over the six-week study period (Hering, personal communication).

1.7.4. Continuous ion chromatography

Dasgupta and Slanina have independently developed particle collection systems that grow particles by increasing the RH and collect the particles in an aqueous solution suitable for injection into an ion chromatograph (Khlystov et al., 1995; Simon and Dasgupta, 1995). Automation of these systems yield semi-continuous monitors for those ions that can be determined by IC. A similar system using a particle size magnifier has been reported by Weber et al. (2001).

1.8. Low flow filter samples for multi-day collection of PM

For some purposes, such as demonstrating attainment of an annual standard or as an exposure indicator for epidemiologic studies of chronic health effects, 24-h measurements are not needed. Annual or seasonal averages are adequate. Multi-day sampling techniques can result in lower costs for weighing, chemical analysis, and travel time to change filters. The multi-day sampler serves a second purpose. Most commercially available samplers are optimized for collecting 24-h samples of the PM concentrations found in the US, Europe, or Japan. Many cities in other parts of the world have significantly higher PM concentrations. Under these conditions, the 16.7 l/min flow through 37 or 47 mm diameter filters may lead to overloading of the filter and failure of the sampler to maintain the prescribed flow rate in less than 24 h. A low flow sampler with a 0.4 l/min flow rate and a 47 mm diameter filter has been designed by Aerosol Dynamics, Inc. With this sampler, the sample collection time can be chosen to suit the ambient concentration level. This sampler, with a one-week collection period, has been used to characterize $PM_{2.5}$ in Beijing, PRC (He et al., 2001). With a two-week collection period, it is being used in a chronic epidemiologic study in southern CA, USA (Gauderman et al., 2000).

The sampler, as described by He et al. (2001), has three $PM_{2.5}$ channels. One channel collects PM on a Teflon filter for gravimetric mass measurement and elemental analysis by XRF. A second channel collects PM on a quartz filter for OC and EC analysis. A denuder to remove organic gases and a backup filter to collect semivolatile organic compounds may be added. The third channel uses a carbonate denuder to remove acidic gases (HNO_3 and SO_2), a Teflon filter to collect PM for analysis of ions by ion chromatography, and a nylon filter to collect volatilized nitrate. The Teflon filter can also be weighed prior to extraction. Thus, the multi-day sampler can provide the information needed for source apportionment by Chemical Mass Balance techniques (Watson et al., 1990).

1.9. Conclusions

Much progress has been made over the past five years in understanding the problems in measuring particles from combustion sources and their semivolatile components. Satisfactory measurement techniques are available to measure important ionic species (H^+, $SO_4^=$,

NO_3^-, and NH_4^+), elements (Na and higher atomic number elements), and EC. However, difficulties remain in measuring organic carbon, especially the semivolatile organic compounds. Measurements of mass, either by filter or continuous techniques, suffer from the difficulty of eliminating particle-bound water without removing ammonium nitrate and semivolatile organic compounds. Measurement of mass of PM according to the US FRM is expensive, requiring establishment of a temperature- and humidity-controlled balance room with a microbalance and extensive quality control. Therefore, continuous measurement of mass or mass surrogates and measurement of chemical components of PM is an attractive alternative approach. The possibility of dehumidification prior to continuous measurement of mass or mass surrogates is being investigated and may prove to be a satisfactory approach.

Most combustion particles, and especially those from controlled combustion sources and secondary combustion products formed from SO_2 or NO_x gases, will be in the fine-mode size range. Therefore, the use of size selective sampling to separate combustion products from soil particles and other coarse particles is essential. A 50% cutpoint of 2.5 μm aerodynamic diameter has been used extensively in the US to separate PM_{10} into a fine PM ($PM_{2.5}$) and a thoracic coarse ($PM_{10-2.5}$) fraction. However, a 50% cutpoint at 1 μm aerodynamic diameter might give a better separation, especially if the air stream is dehumidified prior to separation of fine-mode and coarse-mode particles.

A variety of sampling time intervals may be required, from hourly to annually. It may be cost effective to use a combination of continuous monitors and samplers that integrate particles on filters for a week to a month in addition to 24-h sampling.

Many new techniques for measurements of individual species and mass, including semivolatile components, are currently in the development stage. It is hoped that organizations beginning or expanding monitoring programs in the near future will be able to take advantage of these techniques.

Disclaimer

This abstract has undergone technical review by EPA. However, the views expressed are those of the authors and do not represent EPA policy. Mention of trade names or commercial products does not constitute EPA endorsement or recommendation for use.

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