

## APPENDIX B. MEASUREMENTS

### B.1. APPLICATIONS OF DATA FROM AIR-QUALITY MEASUREMENTS

As described in Chapter 5, measuring PM, PM precursors, and copollutants serves a variety of user-community information needs. These communities seek to understand the impact of PM on health and visibility; to determine compliance with existing standards; to establish the sources of compounds that contribute to elevated levels of PM; to determine trends in air-quality; to evaluate the effectiveness of air-quality management strategies (program evaluation referred to in Table B.1); and to provide the scientific understanding required to reliably predict the effectiveness of new management strategies and to forecast air quality using advanced air-quality modeling systems. These information needs are listed in Table B.1.

Three levels of user requirements are indicated in Table B.1: *required* indicates that the measurement is mandated by current air-quality standards (for PM or other copollutants and pollutant precursors); *needed* identifies measurements that supply information to answer current PM-related air-quality questions; and *useful* indicates that the measurement will supply ancillary information required to best address PM-related issues. Table B.1 also indicates the three levels of time resolution (duration of a single measurement) required to meet measurement needs: 24 hours, 1 hour to 6 hours, and less than 1 hour. The appropriate time resolution for the measurement reflects the user's data requirements. For example, a time resolution of 24 hours may be stipulated for compliance monitoring. However, shorter-duration measurements may be required to adequately resolve daily activity for human-exposure monitoring and health-effect research. Likewise, time resolution that is commensurate with meteorological variability would be most useful for source apportionment ( $\leq 1$  hour), while information for model development and testing would be best satisfied by measurement times that capture the characteristic time-scales for chemical and physical evolution of particles and meteorological variability ( $\leq 1$  hour to hours)

(Seigneur et al., 1999). With the exception of airborne measurements for assessment, model development, and testing, and for understanding pollutant transport on hourly and daily time scales, most measurement needs are satisfied by ground-based measurements. For airborne measurements, where the sampling platform moves through the atmosphere at 100 m/s or more, measurement time-response of one second or less is desirable. In addition, advances in remote sensing may allow some aloft data to be collected from surface instruments or from those on satellites.

### B.2. CURRENTLY AVAILABLE TECHNOLOGY AND INSTRUMENT CAPABILITIES

#### B.2.1. Inlets

Because inlets define the range of particle sizes that are sampled, they play a critical role in all phases of aerosol measurements. Chow (1995), Hering (1995), Mark (1998), and Marple and Olson (2001) have summarized a variety of sampling inlets that are used for ambient, workplace, and personal monitoring. Watson and Chow (2001) identify the  $PM_{10}$  and  $PM_{2.5}$  inlets in use for ambient aerosol sampling. All of these devices rely on some form of inertial separation of large (heavy) particles from small (light) particles and the quoted sizes are the diameter at which the collection efficiency falls to 50 percent (usually called the 50 percent cut-point). The effectiveness of the inlets to accurately determine sizes of particles can deteriorate if the inlet becomes dirty.

#### B.2.2 Integrated Denuder and Filter Systems (substrate- and absorbent-based measurements) for Mass and Composition Sampling

Time-integrated filter-based ambient aerosol sampling systems used to obtain data on PM mass and the chemical components of mass require special sampling methods to minimize sampling artifacts and

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Table B.1. Quantifiable properties for particle and particle-related measurements along with the appropriate time resolution for those measurements that are required, needed, or useful to provide information to user communities to address PM air-quality issues. The table also indicates if measurements are needed at other elevations in the atmosphere. Size units are diameter, typically  $\mu\text{m} = 1 \cdot 10^{-6}$  meters.

**Size**

Property	Health Effects	Exposure	Compliance	Visibility Impairment	Source Attribution	Program Evaluation	Scientific Understanding
Size cut; dia. $\leq 10 \mu\text{m}$	Needed hours	Needed hours	Required 24 hr	Useful $\leq 1$ hr	Needed $\leq 1$ hr	Needed 24 hr	Needed $\leq 1$ hr surface/airborne <sup>a</sup>
Size cut; dia. $\leq 2.5 \mu\text{m}$	Needed hours	Needed hours	Required 24 hr	Useful $\leq 1$ hr	Needed $\leq 1$ hr	Needed 24 hr	Needed $\leq 1$ hr surface/airborne <sup>a</sup>
Ultrafine; dia. $\leq 0.1 \mu\text{m}$	Needed hours	Useful $\leq 1$ hr					Useful $\leq 1$ hr surface/airborne <sup>a</sup>

<sup>a</sup>. 1 hr sufficient for surface, much less than 1 hr is needed for measurements aboard aircraft.

**Distribution**

Property	Health Effects	Exposure	Compliance	Visibility Impairment	Source Attribution	Program Evaluation	Scientific Understanding
Distribution 0.1 to 1 $\mu\text{m}$	Needed $\leq 1$ hr	Needed hours		Useful $\leq 1$ hr	Useful $\leq 1$ hr		Needed $\leq 1$ hr surface/airborne
Distribution 0.001 to 0.1 $\mu\text{m}$	Needed $\leq 1$ hr	Needed hours			Needed $\leq 1$ hr		Needed $\leq 1$ hr surface/airborne
Distribution 2.5 to 10 $\mu\text{m}$	Needed $\leq 1$ hr				Useful $\leq 1$ hr		Needed $\leq 1$ hr surface/airborne

**Mass**

Property	Health Effects	Exposure	Compliance	Visibility Impairment	Source Attribution	Program Evaluation	Scientific Understanding
Mass $\leq 10 \mu\text{m}$	Required hours	Required hours	Required 24 hr	Required $\leq 1$ hr	Required $\leq 1$ hr	Required 24 hr	Required $\leq 1$ hr surface/airborne
Mass $\leq 2.5 \mu\text{m}$	Required hours	Required hours	Required 24 hr	Required $\leq 1$ hr	Required $\leq 1$ hr	Required 24 hr	Required $\leq 1$ hr surface/airborne
Mass PM <sub>coarse</sub> <sup>b</sup>							

<sup>b</sup> PM<sub>coarse</sub> = PM<sub>10</sub> - PM<sub>2.5</sub>, and a new standard will be proposed in 2004 defining a PM<sub>coarse</sub> NAAQS, in which case compliance may also apply.

Table B.1. Quantifiable properties for particle and particle-related measurements, continued.

**PM Composition**

Property	Health Effects	Exposure	Compliance	Visibility Impairment	Source Attribution	Program Evaluation	Scientific Understanding
Acidity	Needed hours	Needed hours					Useful $\leq 1$ hr surface/airborne
Sulfate (SO <sub>4</sub> <sup>-</sup> )	Needed hours	Needed hours		Needed $\leq 1$ hr	Needed $\leq 1$ hr	Needed 24 hr	Needed $\leq 1$ hr surface/airborne
Nitrate (NO <sub>3</sub> <sup>-</sup> )	Needed hours	Needed hours		Needed $\leq 1$ hr	Needed $\leq 1$ hr	Needed 24 hr	Needed $\leq 1$ hr surface/airborne
Chloride (Cl <sup>-</sup> )					Needed $\leq 1$ hr		Needed $\leq 1$ hr surface/airborne
Ammonium (NH <sub>4</sub> <sup>+</sup> )				Useful $\leq 1$ hr	Needed $\leq 1$ hr	Needed 24 hr	Needed $\leq 1$ hr surface/airborne
Organic acids	Useful hours	Useful hours			Needed $\leq 1$ hr		Useful $\leq 1$ hr surface/airborne
Organic carbon	Needed hours	Needed hours		Needed $\leq 1$ hr	Needed $\leq 1$ hr	Useful $\leq 1$ hr surface/airborne	Needed $\leq 1$ hr surface/airborne
Elemental carbon	Needed hours	Needed hours		Needed $\leq 1$ hr	Needed $\leq 1$ hr	Useful $\leq 1$ hr surface/airborne	Needed $\leq 1$ hr surface/airborne
Organic (speciated)	Needed hours	Needed hours			Needed $\leq 1$ hr		Needed $\leq 1$ hr surface/airborne
Major soil elements				Useful $\leq 1$ hr	Needed $\leq 1$ hr	Useful 1 hr	Needed 1 hr surface/airborne
Trace elements	Required 24 hr	Required 24 hr			Needed $\leq 1$ hr		Useful $\leq 1$ hr surface/airborne
Biological aerosols	Needed hours	Needed hours					Needed $\leq 1$ hr surface/airborne

**Optical properties**

Property	Health Effects	Exposure	Compliance	Visibility Impairment	Source Attribution	Program Evaluation	Scientific Understanding
Light scattering				Needed $\leq 1$ hr	Needed $\leq 1$ hr		Needed $\leq 1$ hr surface/airborne
Light absorption				Needed $\leq 1$ hr	Needed $\leq 1$ hr		Useful $\leq 1$ hr surface/airborne
Light extinction				Needed, $\leq 1$ hr	Needed $\leq 1$ hr		Needed $\leq 1$ hr surface/airborne
Solar Radiation (Sun-tracking photometers)							
Aerosol Backscatter (LIDAR)					Useful $\leq 1$ hr long-path		Needed $\leq 1$ hr long path

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Table B.1. Quantifiable properties for particle and particle-related measurements, continued.

**Fog (units are mass per unit volume,  $\mu\text{g}/\text{m}^3 = 1 \cdot 10^{-6}$  grams per cubic meter)**

Property	Health Effects	Exposure	Compliance	Visibility Impairment	Source Attribution	Program Evaluation	Scientific Understanding
Water content						Useful, $\leq 1$ hr	Needed, $\leq 1$ hr, event
Composition		Needed, $\leq 1$ hr				Useful, $\leq 1$ hr	Needed, $\leq 1$ hr, event

**Gas phase compounds**

Property	Health Effects	Exposure	Compliance	Visibility Impairment	Source Attribution	Program Evaluation	Scientific Understanding
Ozone (O <sub>3</sub> )	Needed, $\leq 1$ hr	Required, hours	Required, $\leq 1$ hr		Needed $\leq 1$ hr	Needed, $\leq 1$ hr, surface/airborne	Needed, $\leq 1$ hr, surface/airborne
NO, NO <sub>2</sub> (NO <sub>x</sub> )	Needed, $\leq 1$ hr	Required, hours	Needed, $\leq 1$ hr	Useful, $\leq 1$ hr	Needed, $\leq 1$ hr	Needed, 24 hr	Needed, $\leq 1$ hr, surface/airborne
PAN						Needed, $\leq 1$ hr	Needed, $\leq 1$ hr, surface/airborne
Nitric acid (HNO <sub>3</sub> )	Useful, $\leq 1$ hr	Useful, $\leq 1$ hr				Needed, $\leq 1$ hr, long path	Needed, $\leq 1$ hr, surface/airborne
Nitrogen oxides (NO <sub>y</sub> )						Needed, 24 hr	Needed, $\leq 1$ hr, surface/airborne
Sulfur dioxide (SO <sub>2</sub> )	Required, hours	Required, hours	Required, $\leq 1$ hr		Needed, $\leq 1$ hr	Needed, 24 hr, surface	Needed $\leq 1$ hr, surface/airborne
Carbon monoxide (CO)	Needed, hours	Needed, hours	Required, $\leq 1$ hr		Needed, $\leq 1$ hr	Needed, 24 hr	Needed $\leq 1$ hr, surface/airborne
H <sub>2</sub> O <sub>2</sub> and other peroxides		Useful, hours					Useful, $\leq 1$ hr, surface/airborne
VOCs	Useful, hours	Useful, hours			Useful, $\leq 1$ hr	Needed, 24 hr	Needed, $\leq 1$ hr, surface/airborne
Odd-hydrogen radicals (OH, HO <sub>2</sub> , RO <sub>2</sub> )							Useful, $\leq 1$ hr, surface/airborne
Nitrate radical (NO <sub>3</sub> )							Useful, $\leq 1$ hr, surface/airborne

Table B.1. Quantifiable properties for particle and particle-related measurements, continued.

Meteorological variables							
Property	Health Effects	Exposure	Compliance	Visibility Impairment	Source Attribution	Program Evaluation	Scientific Understanding
Wind speed (meter/sec.)	Needed $\leq 1$ hr	Needed $\leq 1$ hr			Needed $\leq 1$ hr	Needed $\leq 1$ hr	Needed $\leq 1$ hr surface/airborne
Wind direction ( $^{\circ}$ from north)	Needed $\leq 1$ hr	Needed $\leq 1$ hr			Needed $\leq 1$ hr	Needed $\leq 1$ hr	Needed $\leq 1$ hr surface/airborne
Temperature (degree)	Needed $\leq 1$ hr	Needed $\leq 1$ hr		Needed $\leq 1$ hr	Needed $\leq 1$ hr	Needed $\leq 1$ hr	Needed $\leq 1$ hr surface/airborne
Relative humidity (%)	Needed $\leq 1$ hr	Needed $\leq 1$ hr		Needed $\leq 1$ hr	Needed $\leq 1$ hr	Needed $\leq 1$ hr	Needed $\leq 1$ hr surface/airborne
Boundary layer height (meters)					Needed $\leq 1$ hr	Needed $\leq 1$ hr	Needed $\leq 1$ hr surface/airborne

other interferences. Chow (1995) specified the requirements of these types of sampling systems, tabulated available sampler components that can meet the specified requirements, and described compliance and research-grade sampling systems. These sampling systems typically include: 1) size-selective inlets (see section B.2.1), 2) sampling surfaces, 3) denuders, 4) filter holders, 5) filters, and 6) flow measurements and controllers. A simplified schematic diagram of the integrated denuder and filter sampling system is given in Figure 5.3.

Some of the elements of these samplers, with their long history of use, have become standard. Commercially available multi-channel speciation samplers include many of these components: 1) RAAS (Reference Ambient Air Sampler, Thermo-Anderson Samples, Inc.), 2) MASS (Mass Aerosol Speciation Sampler, URG), 3) SASS (Spiral Ambient Speciation Sampler, Met One), 4) Partisol Speciation Sampler (R&P), and 5) IMPROVE (Interagency Monitoring of Protected Visual Environments). These instruments employ a denuder and filter-pack approach, to acquire particle and/or precursor-gas concentrations concurrently on a manual or sequential basis (U.S. EPA, 1999). In the United States, the National  $PM_{2.5}$  Speciation Trends Network (STN) uses the denuder and filter-pack method only for collection of  $PM\ NO_3^-$ , without concern for gas-phase precursors,  $NH_4^+$ , or particle phase semivolatile organic material. However, once routine monitoring

capabilities become available for these species, those samplers may be incorporated into the network. The principal sampler components for several systems currently in use are given in Table B.2.

### Denuders

Denuders are placed in the sampling system to remove more than 95 percent of selected gases while transmitting more than 95 percent of particles (Kitto and Colbeck, 1999). Denuders can be used as part of, or immediately behind, size-selective inlets to remove gases that might interfere with the collection of particles on the filter (positive interference). Denuders also can be used to quantify directly the concentrations of gases that are precursors to secondary PM formation (e.g.,  $HNO_3$  and  $NH_3$ , which are precursors of  $NH_4NO_3$ ). In addition, denuders may be placed after the filter to capture semivolatile gases that may evaporate from particles collected on the filters (negative interference). In the latter two cases, the denuders are extracted and the extract analyzed to determine the concentration of the species of interest in the gas phase.

Denuders are fabricated from stainless steel, aluminum, Teflon, etched glass, and cloth, and are coated with substances that retain the gas-phase compounds of interest (e.g.,  $MgO$  or  $Na_2CO_3$  to collect acidic gas-phase species, such as  $HNO_3$ ). To maximize the surface-to-volume ratio, denuder

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Table B.2. Major components of selected integrated particulate samplers as operated in either the EPA National PM<sub>2.5</sub> Chemical Speciation Trends Network or in the IMPROVE Network..

<b>SAMPLER</b>  <b>ELEMENT AND SPECIES</b>	<b>EPA National PM<sub>2.5</sub> Chemical Speciation Trends Network Protocols</b>				<b>IMPROVE Protocol</b>
	<b>RAAS (Reference Ambient Air Sampler, Anderson Samples, Inc.)</b>	<b>MASS (Mass Aerosol Speciation Sampler, 400 &amp; 450, URG)</b>	<b>SASS (Spiral Ambient Speciation Sampler, Met One),</b>	<b>Partisol Speciation Sampler (R&amp;P)</b>	<b>IMPROVE Sampler</b>
<b>Inlet/PM<sub>2.5</sub> Fractionator</b>	PM <sub>10</sub> Size Selective/ PM <sub>2.5</sub> Cyclone	PM <sub>10</sub> Size/ Selective/PM <sub>2.5</sub> WINS	PM <sub>2.5</sub> Sharp-cut cyclone	PM <sub>2.5</sub> Harvard Impactor	PM <sub>2.5</sub> or PM <sub>10</sub> Cyclone
<b>Denuders<sup>a</sup></b>	Glass annular denuder inside an Al tube	Glass annular denuder inside an Al tube	Aluminum honeycomb.	Glass honeycomb	Anodized aluminum
<b>HNO<sub>3</sub><sup>d</sup> (Denuders used to remove HNO<sub>3</sub> and other acidic gases)</b>	MgO Changed after 30 sampling periods.	MgO Changed after 30 sampling periods.	MgO Changed after 30 sampling periods.	Na <sub>2</sub> CO <sub>3</sub> Changed daily.	Na <sub>2</sub> CO <sub>3</sub> Changed once or twice per year.
<b>Filters<sup>b</sup></b>	Four filter channels; Teflon, nylon, quartz, blank	Two filter channels; Teflon/nylon filter pack, quartz	Three filter channels; Teflon, nylon, quartz	Three filter channels; Teflon, quartz, nylon	Four filter channels; Teflon (PM <sub>2.5</sub> and PM <sub>10</sub> ). Nylon, quartz
<b>PM<sub>10</sub> Mass</b>	Not Measured	Not Measured	Not Measured	Not Measured	Teflon: gravimetric
<b>PM<sub>2.5</sub> Mass</b>	Teflon: gravimetric	Teflon: gravimetric	Teflon: gravimetric	Teflon: gravimetric	Teflon: gravimetric
<b>Elements<sup>c</sup></b>	Teflon: XRF (same filter as used for mass)	Teflon: XRF (same filter as used for mass)	Teflon: XRF (same filter as used for mass)	Teflon: XRF (same filter as used for mass)	Teflon: PIXE, XRF, PESA (same filter as used for mass)
<b>Particulate NO<sub>3</sub><sup>-b</sup>, SO<sub>4</sub><sup>=</sup>, NH<sub>4</sub><sup>+b</sup>, other ionic species. (denuder/filter)</b>	Nylon: IC, water extraction	Teflon/nylons: IC, water extraction	Nylon: IC, water extraction	Nylon: IC, water extraction	Nylon: IC, water extraction
<b>Organic<sup>b</sup> and elemental carbon</b>	Quartz: TOT/STN Protocol	Quartz: TOT/STN Protocol	Quartz: TOT/STN Protocol	Quartz: TOT/STN Protocol	Quartz: TOR/IMPROVE Protocol

Note: Ammonia is not collected, removed, or measured in any of these samples.

<sup>a</sup> Used to remove gas phase interferences, acid gases only (e.g., HNO<sub>3</sub>). The denuders are not analyzed routinely in these networks.

<sup>b</sup> Combination of denuder and filter measurements are needed to quantify semivolatile species, but in these samplers it is only for particulate NO<sub>3</sub><sup>-</sup>.

<sup>c</sup> As described in the text, other methods are available, PIXE, INAA, and ICP-MS, but XRF is the most commonly used method and recommended in EPA's National PM<sub>2.5</sub> Chemical Speciation Trends Network

<sup>d</sup> HNO<sub>3</sub>, while not measured currently in either of the networks, could be obtained by the denuder difference method or extraction of Na<sub>2</sub>CO<sub>3</sub>-coated denuders followed by IC analysis of the extract.

designs include tubular, parallel-plate, annular, and honeycomb configurations. The capacity and efficiency of denuders for inorganic acidic gases have been reasonably well documented, but much more effort is needed to determine and document the efficiency and capacity of denuders for collecting gas-phase semivolatile organic material.

### *Filters*

Filtration is the principal method used in integrated sampling systems for collecting atmospheric PM. Selection of filters for collecting PM for gravimetric and chemical analysis is determined by the characteristics that are imposed by the types of chemical analyses to be undertaken (Chow, 1995; Chow and Watson, 1998; Solomon et al., 2001; and U.S. EPA, 2001). Chow (1995) and Chow and Watson (1998) summarize filter substrates and their chemical/physical properties. Chemical analysis (discussed at the end of this section) includes bulk analysis (c.f., Solomon et al., 2001), and single-particle analysis methods (e.g., scanning electron microscopy) (Fletcher et al. 2001).

Stable species, such as  $\text{SO}_4^{2-}$  and trace elements (e.g., Al, Si, Ca, Fe, Mn, Ti, etc), are collected with minimal sampling bias on inert filters (e.g., Teflon) if proper inlets, transport tubes, filter substrates, and flow controls are used in the sampler. Labile species, such as  $\text{NH}_4\text{NO}_3$  and semivolatile organic compounds that exist in both the gas and particle phases, require specialized sampling protocols, typically using denuders and reactive collection substrates (Chow, 1995). For these species, the denuder is used to remove gas-phase material while a reactive backup filter is used to collect the semivolatile particulate-phase species of interest. Most denuder/filter-based systems use either a single absorbent or a chemically treated reactive filter (i.e., either a filter is impregnated with a reactive material or the filter itself is absorbent), or a filter pack. The latter consists of a top inert filter (e.g., Teflon or quartz-fiber) followed by a reactive filter. For example,  $\text{NO}_3^-$  is collected on a nylon filter or a filter impregnated with  $\text{Na}_2\text{CO}_3$ , behind either an MgO coated denuder or a denuder coated with  $\text{Na}_2\text{CO}_3$ , respectively. Organic material is the most problematic to collect using reactive filters, because denuders and reactive filters are not yet well characterized for these compounds.

Currently, the organic fraction of particles is collected using either quartz-fiber filters or filters that are impregnated with charcoal, or coated with finely ground XAD resin or KOH. The denuders used prior to these filters are coated with the same reactive material as the filter, to minimize biases in sampling due to the efficiency of removing the reactive material. While, quartz-filters are widely used for OC and BC analysis (e.g., in STN and IMPROVE networks), they also can have high blank values for OC due to sorption of organic gases. This sorption occurs during sampling as well as during storage and handling, so denuders do not fully solve the problem.

### *Impactors*

Cascade impactors represent a special class of substrate- and absorbent-based techniques for composition sampling. These devices use a series of impactor stages (as described in the inlet section above) to collect a series of size-resolved particle samples (c.f., Marple and Olsen, 2001). The most recent advances have dealt with extending impactor capability to smaller particle sizes (e.g., below  $0.2 \mu\text{m}$ ). Examples of available cascade impactors are the Micro-Orifice Uniform Deposit Impactor (MOUDI), the Berner impactor, the Davis rotating unit for monitoring (DRUM), and the low-pressure impactor. These instruments have been used to obtain size-resolved measurements in ambient chemistry and visibility studies. For example, it is feasible, using the DRUM impactor, to obtain 2-hour concentration data for PM mass and trace elements. In the DRUM sampler, Mylar substrates are mounted on cylinders that rotate below the impaction jet so that particle deposits can be monitored as a function of time and analyzed for mass by beta attenuation, for elements by proton-induced x-ray emission (PIXE), and for particle morphology by scanning electron microscopy/x-ray fluorescence (SEM/XRF). The Low Pressure Impactor (LPI) system allows for the separation and collection of particles down to  $0.05 \mu\text{m}$ .

### *Chemical Analysis Methods for PM Collected on Filters*

During the last half-century, a wide variety of chemical compounds has been identified and quantified using filter-based methods. The chemical

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composition of PM provides clues to its origin and transformations that may have occurred during atmospheric transport. Health studies also are indicating certain chemical components as potential causal factors in observed adverse health effects. In general, the majority of mass is accounted for by just six components ( $\text{SO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , OC, BC, and crustal material [e.g., oxides of Al, Si, Ca, Ti, Mn, Fe, and Zn]). However, in detail, PM is composed of hundreds and even thousands of compounds (e.g., OC is composed of many individual organic compounds). The six major components also are the primary species measured in the STN. Chemical-analysis methods for the STN have been summarized by Solomon et al. (2001). After collection, filters are either analyzed directly or extracted in an appropriate solvent and the extract is analyzed to determine concentrations of the species present. As discussed in the previous sections, special sampling protocols are required to minimize bias and interferences for the collection of semivolatile compounds.

Typically, PM mass is obtained from an inert Teflon filter, which is weighed before and after collection under controlled conditions. The difference in the mass collected on the filter divided by the sampled volume gives the atmospheric concentration. Anions ( $\text{SO}_4^-$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$ ) and cations ( $\text{NH}_4^+$  and water-soluble Na, Mg, K, and Ca) typically are extracted with deionized distilled water (DDW) or another appropriate solvent. Their concentrations in the extract are determined using, for example, ion chromatography (IC; Chow and Watson (1999)).  $\text{NH}_4^+$  also can be determined using an automated colorimeter (AC), while flame and graphite-furnace atomic-absorption spectrometry (AAS) are used to quantify amounts of many trace elements in the collected PM. After back calculation to the amount of species on the filter, the atmospheric concentration is determined by dividing by the sampled volume.

Trace elements are commonly measured directly on the Teflon or other filter substrates using various methods of direct excitation to induce a characteristic atomic or nuclear fluorescence. The main approaches are XRF, PIXE, or instrumental neutron activation analysis (INAA) Watson et al. (1999). Alternatively,

the elements can be extracted from the filter by acid digestion, volatilized, and ionized in an inductively coupled radio-frequency plasma, and measured by inductively coupled plasma mass-spectrometry (ICP-MS) or the extract directly analyzed by flame AAS or flameless graphite-furnace AAS. In-vitro and in-vivo studies have focused on the effects of air-toxic elements such as the soluble fractions of transition metals and/or hazardous air pollutants. Thus, soluble metal fractions can be obtained by extracting the filters in DDW followed by graphite-furnace AAS, instead of flame AAS, to accommodate the low sample loadings. Other methods for analysis of metals are available.

The OC, EC, carbonate, and total carbon (TC) components in PM collected on the filters are analyzed by thermal combustion, thermal manganese oxidation, and organic extraction/thermal methods. The IMPROVE thermal/optical reflectance protocol (TOR, Chow et al., 1999, 2001) and the NIOSH (Method 5040) protocol that is based on thermal/optical transmission (TOT, after Birch and Cary, 1996) are used in the IMPROVE and EPA STN networks, respectively. Intercomparisons (Countess, 1990; Schmid et al., 2001; Fung et al., 2002; Sharma et al., 2002) of different carbon-analysis methods reported good agreement ( $\pm 10$  percent) on TC, but resulted in factor of two or higher differences in OC and EC concentrations. With the two thermal-optical methods, Chow et al. (2001) and Norris et al. (2002) reported differences of a factor-of-two in OC when comparing TOR and TOT methods using the IMPROVE and NIOSH protocols, respectively, on the same filters owing to the different temperature programs. EPA's speciation program uses the TOT method with a slightly modified version of the NIOSH temperature protocol, similar to that described by Norris et al. (2002). Primary standards for OC and BC are needed to minimize these discrepancies. However, work is underway at the National Institute of Standards and Technology (NIST) to resuspend bulk soil (Klouda and Parish, 2000) and bulk PM to establish filter-based carbon standards. As well, work is underway at NIST and EPA to understand the OC and BC STN and IMPROVE protocols in more detail and to optimize the methods to minimize potential artifacts (Conny et al., 2002).

Individual organic compounds also can be measured by extracting quartz-fiber and Teflon filters using a variety of organic solvents followed by GC-MS. This type of analysis can provide a great deal of information regarding the sources and formation processes of carbonaceous particles (Schauer et al., 1996). Although speciation is desirable, it is not easy to perform because there is no single analytical method that can be used to analyze all classes of organics. Currently, analysis is conducted to obtain non-polar compounds, and to date typically only 10-20 percent of the total OC mass has been identified as individual compounds. However, more advanced methods are beginning to look at polar organic materials using GC-MS and LC-MS methods. As with OC and BC, considerable effort is needed to develop calibration and reference standards and a standard set of organic markers (e.g., alkenes, alkenes, alcohols, acids, PAHs) that can explain the major portion of total organic material in air. Work is underway at EPA in conjunction with NIST to develop a series of reference and calibration standards and to evaluate differences among laboratories that perform organic species analyses for a wide variety of important marker compounds.

Overall, measurements of OC, BC, and OC species are challenging and prone to errors due to PM volatility, interferences from gaseous organic species, limitations with analytical methods, and lack of accepted primary and transfer standards. However, significant advances are expected in the near future permitting more widespread measurements of OC, BC, and organic species.

While not included in the analyses for the STN, filters collected from these samplers or others can be analyzed by single-particle techniques to obtain the chemical compositions of single particles (Fletcher et al., 2001). These analyses are extremely useful for source-apportionment studies. While this is a time-consuming analysis, recent advances using computer-controlled SEM/XRF are allowing these methods to be more practical (Mamane et al., 2001). In SEM/XRF, atoms in the collected PM are excited and the x-rays from the fluorescence are detected. The method is semi-quantitative for composition, but it provides morphological information of the collected particles, which gives clues to their source and fate in air.

### B.2.3 Continuous and Semi-continuous Real-time Measurements

#### *Mass and Mass Equivalent*

Continuous or semi-continuous methods obtain PM mass concentrations by measuring changes associated with 1) the inertia imparted to a dynamic element by collected particles; 2) electron attenuation through a surface by particles collected on the surface, and 3) pressure drop across small pores in a filter due to collected particles. Continuous and semi-continuous methods for mass are reviewed by Watson et al. (1998). Table B.3a summarizes the methods discussed here.

#### *Inertial Methods*

The inertial methods in use currently include the TEOM (tapered element oscillating microbalance) RAMS (real-time ambient mass sampler), and piezoelectric crystals. The TEOM measures directly the inertial mass of particles collected on a filter, 0.5 cm in diameter, mounted on top of a tapered hollow glass element that oscillates when an electric field is applied. The inlet temperature is maintained at 30 to 50° C to minimize thermal expansion of the tapered element and to control relative humidity. However, this heating can result in the loss of semivolatile species, such as water,  $\text{NH}_4\text{NO}_3$ , and SVOCs. These losses can be in the range of 10 percent to 30 percent or more in the reported PM measurements (i.e., dry mass or volatile reduced-mass) as compared to filter-based gravimetric measurements. Among recent developments is a “differential TEOM system,” which is aimed at acquiring accurate PM mass at ambient temperature. The technique places a diffusion drier behind the size-selective inlet to remove particle-bound water. This is followed by a parallel pair of electrostatic precipitators (ESP) that alternately switch on and off. Frequency data are collected for both TEOM sensors on a continuous basis. The technique allows the correction for volatilization and absorption (Patashnick et al., 2001).

The RAMS combines TEOM principles with diffusion denuder technology (Eatough et al., 2001; Obeidi and Eatough, 2000) to measure  $\text{PM}_{2.5}$ , including  $\text{NH}_4\text{NO}_3$  and semivolatile organic material.

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The RAMS uses five denuders in tandem: 1) a triethanolamine-coated (TEA) annular denuder to remove  $\text{NO}_2$  and  $\text{O}_3$ ; 2) a Nafion diffusion dryer to remove particle-bound water, followed by a particle concentrator to reduce the amount of gas-phase organics that must be removed by diffusion denuders; 3) a BOSS (Brigham Young University Organic Sampling System) diffusion denuder to remove gas-phase organic compounds; 4) an additional TEA denuder; and 5) an additional Nafion dryer. The Teflon-coated filter is backed up with a charcoal-impregnated filter (CIF) (to retain semivolatile species lost from those collected on the filter) and mounted at the tip of the tapered oscillating element of a TEOM. Field comparison with PC-BOSS (Particle Concentrator-BOSS) showed that  $\text{PM}_{2.5}$  mass, including semivolatile fine particulate  $\text{NO}_3^-$  and organic species, can be continuously and accurately monitored with RAMS (Eatough et al., 2001).

Piezoelectric microbalances determine PM mass concentrations by measuring the changes in natural resonant frequency of the crystal caused by the deposition of particles (either by electrostatic precipitation or inertial impaction) on a piezoelectric quartz crystal disk. The changing frequency of the sampling crystal is electronically compared to a clean reference crystal, generating a signal that is proportional to the collected mass. Work needs to be done to establish the equivalence between piezoelectric microbalances and filter-based mass measurements.

### *Pressure-Drop Method*

The CAMM (continuous ambient mass monitoring) system measures the pressure drop across a porous membrane (Fluoropore) filter (Koutrakis et al., 1996; Sioutas et al., 1999). The pressure drop is linearly correlated to the particle mass deposited on the filter under properly chosen conditions (Koutrakis et al., 1996; Wang, 1997; Sioutas et al., 1999). The Andersen CAMM is equipped with a Nafion dryer to remove particle-bound water. This is followed by a concentrator prior to sampling on the membrane filter (Babich et al., 2000).

### *Electron-Attenuation Method*

The BAM (beta attenuation monitor) measures the attenuation of beta rays from a radioactive source after they pass through a filter where particles have been deposited. BAM technology also has been used to measure aerosol liquid water content (Spear et al., 1997). Watson et al. (1998) showed that measured differences with other methods appear mostly during wintertime and when semivolatile species are the major component. Differences are minimized during summertime, however. Chow and Watson (1997; Chow et al., 1998a) and Dutcher et al. (1999) compared some collocated  $\text{PM}_{10}$  filter-based and continuous BAM measurements. Equivalent measurements can be achieved if the instrument is adequately calibrated and maintained.

### *Size Distribution and Mobility*

A wide range of techniques and protocols has been used for particle-size measurements. Since the range of particle sizes of interest can vary over more than four orders of magnitude, from  $<0.003 \mu\text{m}$  to  $>10 \mu\text{m}$ , different techniques are used to measure different size distributions. The techniques to measure size distribution fall into three broad categories: 1) Aerodynamic techniques, measured by inertial methods such as impactors and cyclones, depend on particle shape, density and size; 2) Electrical mobility techniques, obtained by electrostatic mobility analyzers, depend on particle shape and size, and are obtained by the rate of migration of charged particles in an electrostatic field; and 3) Optical techniques, obtained by light-scattering detectors, depend on particle refractive index, shape, and size. Table B.3b summarizes the methods discussed here.

Recent developments in instruments for obtaining continuous or semi-continuous measurements of particle-size sampling show promise. Chief among these is the scanning mobility particle sizer (SMPS), which measures the size distribution of particles that range from  $0.003$  to  $0.05 \mu\text{m}$  or  $0.01$  to  $0.5 \mu\text{m}$ , depending on its configuration. The SMPS provides adequate time response ( $<5$  minutes) for ambient sampling and resolves particle sizes into a user-selected number of fractions, or bins. Collocating

Table B.3. Summary of real-time particle monitoring techniques.

a. Mass <sup>a</sup> (c.f., McMurry, 2000).

Observables	Methodology	Specifications	Availability	Comments
<b>PM<sub>2.5</sub> or PM<sub>10</sub> mass by Tapered element Oscillating Microbalance (TEOM)</b>	Particles are continuously collected on a filter mounted on the tip of a hollow glass element that oscillates in an applied electric field. The resonant frequency of the element decreases as mass accumulates on the filter, directly measuring inertial mass. Temperatures are maintained at a constant value, typically 30 °C or 50 °C, to minimize thermal expansion of the tapered element.	Particle mass. Detection limit ~ 5 µg/m <sup>3</sup> for a 5-minute average.	Commercial	The typical signal averaging period is 10 minutes. Volatile species can evaporate due to the heated airflow. This results in low mass concentrations compared to gravimetric methods. A differential TEOM system that acquires PM mass at ambient temperatures is commercially available. A new method, the Filter Dynamics Measurement System, also is commercially available and appears to provide an even better estimate of PM mass by accounting for both volatilization and absorption.
<b>PM<sub>2.5</sub> or PM<sub>10</sub> mass by Real-Time Total Ambient Mass Sampler (RAMS)</b>	Measures mass concentration (including volatilized species) using a combination of TEOM principles with diffusion denuder technology. The sampling system consists of two TEA-coated annular denuders, a Nafion dryer, a BOSS carbon denuder, a third TEA-coated denuder, and a final Nafion dryer.	Particle mass. Detection limit ~ 5 µg/m <sup>3</sup> for a 1-hour average.	Research	
<b>PM<sub>2.5</sub> or PM<sub>10</sub> mass by Continuous Ambient Mass Monitor System (CAMMS)</b>	Measures the pressure drop across a porous (Fluoropore) membrane filter. For properly chosen conditions, the pressure drop is linearly correlated to the particle mass deposited on the filter.	Particle mass. Detection limit ~ 2 µg/m <sup>3</sup> for a 1-hour average.	Commercial	
<b>PM<sub>2.5</sub> or PM<sub>10</sub> mass by Beta Attenuation Monitor (BAM)</b>	Beta rays (electrons with energies in the 0.01 to 0.1 MeV range) are attenuated according to an approximate exponential (Beer's Law) function of particulate mass, when they pass through deposits on a filter tape. Filter tape samplers measure the attenuation through unexposed and exposed segments of tape. The blank-corrected attenuation readings are converted to mass concentrations.	Particle mass. Detection limit ~ 2 µg/m <sup>3</sup> for a 1-hour average.	Commercial	Averaging times can be as short as 30 minutes. Encounters interference under high relative humidity.
<b>PM<sub>2.5</sub> or PM<sub>10</sub> mass by Piezoelectric Microbalance</b>	Particles are deposited by inertial impaction or electrostatic precipitation onto the surface of a piezoelectric quartz crystal disk. The natural resonant frequency of the crystal decreases as particle mass accumulates. The clean reference crystal, used for comparison, allows for temperature compensation.	Particle mass. Detection limit ~ 10 µg/m <sup>3</sup> for a 1-minute average.	Commercial	

<sup>a</sup> Continuous mass methods have not been approved as Federal Equivalent Methods (FEM), and therefore, have not been used in compliance monitoring.

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Table B.3. Summary of real-time particle monitoring techniques, continued.  
 b. Number density and size distribution (c.f., McMurry, 2000).

Observables	Methodology	Specifications	Availability	Comments
<b>Condensation Particle Counter (CPC)</b>	Total particle number determined by exposure to high super-saturation of a working fluid such as alcohol. Droplets are subsequently nucleated and detected by light scattering.	Total particle number	Commercial.	Particle size cut off at 3-20 nm depending on model. Multiple models can be operated in parallel to give coarse size resolution in the Aitken mode.
<b>Particle number concentration (0.003 to 0.5 <math>\mu\text{m}</math>) by Scanning Mobility Particle Sizer (SMPS) that consists of Differential Mobility Analyzer and (usually) a CPC.</b>	Particles are charged and selected based on their electrical mobility. Particle number measured with a CPC, but possibly with an aerosol electrometer.	Particle number by size in user selected number of size fractions.	Commercial.	Extremely accurate technique in constant aerosol conditions. More expensive commercial unit reports equivalent electric mobility size.
<b>Particle number concentration (0.3 to 10 <math>\mu\text{m}</math>) by Aerodynamic Particle Sizer.</b>	Parallel laser beams measure the velocity lag of particles suspended in accelerating airflow.	Number of particles in different size ranges.	Commercial.	Reports aerodynamic diameter. Suffers inaccuracies at high concentrations.
<b>Fine (0.1 to 2.5 <math>\mu\text{m}</math>) and coarse (2.5 to 10 <math>\mu\text{m}</math>) particle number concentration by Optical Particle Counter/Size Spectrometer.</b>	Light scattered by individual particles traversing a light beam is detected at various angles; these signals are interpreted in terms of particle size via calibrations.	Number of particles in the 0.1 to 50 $\mu\text{m}$ size range.	Commercial.	Reports optical diameter. Manufacturer specifies number of size ranges and size fractions for each instrument. Sensitive to refractive index (i.e., composition and shape)
<b>Electrical Low Pressure Impactor (ELPI).</b>	Particles are charged and separated by their inertia onto impactor stages. The electrical charge that accumulates on each impactor stage is measured. Particle sizes are obtained from 0.03 to 10 $\mu\text{m}$ in 13 size classes.	0.03 to 10 $\mu\text{m}$ in 13 size classes.	Commercial.	Measures aerodynamic size with relatively coarse size resolution. Suffers inaccuracies at low particle concentrations.

Table B.3. Summary of real-time particle monitoring techniques, continued.  
c. Chemical composition (Watson et al., 1998).

Observables	Methodology	Specifications	Availability	Comments
<b>OC, EC, and TC by Ambient Particulate Carbon Monitor (APCM)</b>	Measurement of particulate carbon by automatic thermal evolution of CO <sub>2</sub> at 340 °C (adjustable) for OC and 750 °C for TC. The carbon collected on a ceramic impactor plate oxidizes at elevated temperatures after sample collection is complete. A CO <sub>2</sub> monitor measures the amount of carbon released as result of sample oxidation.	Detection limit, ~ 0.3 μg/m <sup>3</sup> for a 30-minute average.	Commercial	
<b>OC and EC by In-Situ Thermal/Optical Carbon Analyzer</b>	This sampler provides on-line thermal/optical analysis of exposed quartz-fiber filters; OC and EC are acquired by thermal evolution in He and He/O <sub>2</sub> atmospheres, respectively. Light transmission through the filter is used to correct for charring (pyrolysis) of OC during analysis.	Detection limit, ~ 0.2 μg/m <sup>3</sup> for a 1-hour average.	Commercial	The analysis principles follow thermal/optical analysis. Prototype was tested at the St. Louis Supersites project.
<b>Total carbon (TC) by Total Carbon Analyzer</b>	TC is measured using flash volatilization of particles collected by impaction onto a filament followed by non-dispersive infrared (NDIR) detection of CO <sub>2</sub> .	Detection limit, 1 μg/m <sup>3</sup> for a 10-minute average.	Commercial	Prototype was tested during summer 2000 at the Houston Supersites project.
<b>Total carbon (TC) by Particles in Liquid</b>	TC is measured by collection of particles into purified water and analyzed in aqueous systems.	Detection limit, ~ 0.5 μg/m <sup>3</sup> for 10-second to 5-minute averages.	Research	This system shows potential for short-time-resolution carbon measurements, but is restricted to the analysis of soluble organic components.
<b>Particulate NO<sub>3</sub><sup>-</sup> by Automated Particle NO<sub>3</sub><sup>-</sup> Monitor</b>	Particles are humidified prior to collection by impaction followed by flash vaporization and detection of the evolved gases in a chemiluminescence NO <sub>x</sub> analyzer.	Detection limit, ~ 0.5 μg/m <sup>3</sup> for a 12-minute average.	Commercial	
<b>Particulate NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>=</sup>, NH<sub>4</sub><sup>+</sup>, and gases (HCl, HNO<sub>2</sub>, HNO<sub>3</sub>, SO<sub>2</sub>, NH<sub>3</sub>) by Continuous Gas and Particle Speciation Monitor</b>	Samples acquired in collection vessels or continuously, followed by on-line ion chromatographic analysis with conductivity detector. This system uses wet denuders to collect gases into a liquid buffer solution for gas measurement and a chamber to grow particles for cyclone collection in a liquid effluent for ion measurements.	Detection limit, ~ 0.5 μg/m <sup>3</sup> .	Commercial	Several IC-based units, that analyze liquid obtained from denuders, provide concentrations of a variety of acidic and basic gases and aerosol components.
<b>Particulate SO<sub>4</sub><sup>=</sup> by Automated Particulate SO<sub>4</sub><sup>=</sup> Monitor</b>	Particles are humidified prior to collection by impaction followed by flash vaporization and detection of the evolved gases in an ultraviolet absorption of SO <sub>2</sub> .	Detection limit, 0.5 μg/m <sup>3</sup> for a 12-minute average.	Commercial	

Table B.3. Summary of real-time particle monitoring techniques, continued.

c. Chemical composition (Watson et al., 1998), continued.

Observables	Methodology	Specifications	Availability	Comments
<b>Particulate SO<sub>4</sub><sup>=</sup> by Continuous SO<sub>2</sub> Analyzer</b>	Thermally convert SO <sub>4</sub> <sup>=</sup> to SO <sub>2</sub> at high temperature (1,000 °C) using a high-efficiency (>95%) stainless steel converter followed by high-sensitivity pulsed fluorescence analysis of SO <sub>2</sub> .	Detection limit, ~ 0.5 µg/m <sup>3</sup> for a 1-hour average.	Research	Uses a diffusion denuder upstream of the converter to remove gaseous sulfur compounds. Options to add NH <sub>3</sub> -coated denuder tube to remove H <sub>2</sub> SO <sub>4</sub> . Prototype was tested at the St. Louis Supersites project.
<b>Particulate sulfur by Flame Photometric Detection (FPD)</b>	Sulfur species are combusted in a hydrogen flame, creating excited sulfur dimers (S <sub>2</sub> <sup>*</sup> ). Fluorescence emission near 400 nm is detected by a photomultiplier. The photomultiplier current is related to the concentration of sulfur in all species.	Detection limit, 0.1 µg/m <sup>3</sup> for a 1-hour average.	Research	Four out of five FPD systems agreed to within ± 5% in a 1-week ambient sampling intercomparison.
<b>PM<sub>2.5</sub> and PM<sub>10</sub> elements by Streaker</b>	Particles are continuously collected on two impaction stages and a Nuclepore polycarbonate-membrane after-filter followed by particle-induced x-ray emission (PIXE) analysis for multiple elements.		Commercial	
<b>PM<sub>2.5</sub> elements by Semi-continuous Elements in Aerosol System (SEAS)/ High Frequency Aerosol Slurry Sampler (HFASS)</b>	Particles containing Al, Ca, Fe, Cu, Cr, Mn, Zn, Cd, As, Sb, Pb, Ni, V, and Se are collected in an aqueous slurry after condensing with water vapor.	Detection limit, potentially 0.1 ng/m <sup>3</sup> (see text) depending on element, for 30- to 60-minute averages.	Research	System was used at the Baltimore Supersite, St. Louis Supersite, and Pittsburgh Supersites project.

an SMPS with optical particle counters and/or aerodynamic particle sizers allows the acquisition of particle-size distributions over a complete range from 0.003 to >10 µm (c.f. Woo et al., 2001). Among other recently developed techniques, the electrical low-pressure impactor (ELPI) produces particle-size distributions with very fast time response (<5 seconds) over a wide size range (0.007 to 10 µm), but with relatively crude particle-size resolution. Techniques for determining the size distributions of ultrafine particles using condensation of a vapor and light scattering have been used (Saros et al., 1996), but may be more suitable for specific process studies than for routine monitoring.

#### *Bulk Chemical Composition Methods*

Many advances in PM species-specific continuous and semi-continuous measurement methods have occurred recently (c.f., Weber et al., 2003). The

following section reviews some of the current methods and further summarizes them in Table B.3c.

#### *Black Carbon (BC) and Organic Carbon (OC)*

The carbonaceous component of atmospheric particles consists of BC, which is often described as elemental carbon (EC) or soot<sup>1</sup>, and OC, which is composed of hundreds and even thousands of individual organic compounds. Both of these terms are operationally defined (Chow et al., 2001). No real-time technique is available that can adequately speciate OC. Hence, measurements usually are restricted to the major carbon fractions and are labeled accordingly, OC and BC. Typically, OC and BC (or EC) measurements involve collecting particles on a substrate (e.g., a filter or impaction plate) for a period of time sufficient to achieve the desired sensitivity. This is typically several minutes to an hour depending on the concentration of

carbon-containing compounds in the collected particles. The substrate or plate is then heated in a controlled atmosphere to first volatilize the OC and then further heated to burn off the EC. The OC and EC evolve to CO<sub>2</sub> gas, which can be measured directly by a non-disperse infrared detector (NDIR), or converted to CH<sub>4</sub> and measured by flame ionization detection (FID). Several methods use absorption or transmittance to correct for pyrolysis of OC that would otherwise be reported as EC.

The R&P 5400 Ambient Carbon Particulate Monitor (Rupprecht & Patashnick, Albany, NY) collects particles by impaction on a ceramic plate and measures OC and EC by determination of the CO<sub>2</sub> that is evolved upon heating to 350 °C (adjustable) and 750 °C (Rupprecht et al., 1995). Temperature programmable research-grade instruments for real-time OC and BC/EC measurements have been developed that use transmittance (rather than reflectance) of a 638 nm laser to adjust for OC pyrolysis (c.f., Birch and Cary, 1996). Stolzenburg and Hering (2000) acquire TC through flash vaporization of particles collected by impaction onto a filament followed by NDIR detection of CO<sub>2</sub>. Total water-soluble OC also is measured by collecting particles into purified water (Khlystov et al., 1995; Weber et al., 2001) and analyzed in aqueous systems (e.g., Sievers Instruments Inc, Boulder CO, OI Corp. Houston, TX). Although these techniques are under development, they have the potential for time resolution on the order of minutes.

The PAS2000 real-time PAH monitor (EcoChem Analytics, League City, TX) measures particle-bound PAH based on the ionization of particles and their detection with an electrometer. The photoionization method for particle-bound PAH is reproducible, but at present it can only be related to absolute concentrations of particle-bound PAH via collocated filter samples (Watson and Chow, 2002a; 2002b). A method for real-time determination of BC content of single particles using laser-induced incandescence is also under development and shows promise.

### *Ionic Component of Aerosol Particles*

Ion chromatography (IC) permits speciation and quantitative measurement for a range of ions, including cations (e.g. NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>), inorganic anions (e.g., SO<sub>4</sub><sup>=</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>), and organic acids (e.g., formate, acetate, and oxalate) (Chow and Watson, 1999). Efforts have been made to collect ambient particles directly into purified water for on-line IC analysis. In all cases, diffusion denuders need to be placed upstream of the instrument to remove potentially interfering gases such as SO<sub>2</sub>, NH<sub>3</sub>, and HNO<sub>3</sub>.

Recent research has involved the measurement of NO<sub>3</sub><sup>-</sup> by using a diffusion denuder to remove the gaseous nitrogen-containing compounds, heating the sample, and converting the evolved gaseous NO<sub>3</sub><sup>-</sup> to NO, which is measured by chemiluminescence. Similar techniques are being developed for the measurement of NH<sub>4</sub><sup>+</sup>. These techniques have high sampling rates (1 Hz) but generally result in lower sensitivities. Continued developmental work is required for reliable real-time inorganic NO<sub>3</sub><sup>-</sup> measurements.

Variations on real-time SO<sub>4</sub><sup>=</sup> detectors, based on the use of a flame-photometric detector (FPD), were developed originally for measuring gaseous sulfur compounds. It was found that SO<sub>4</sub><sup>=</sup> could be measured directly with this detector if diffusion denuders were used to remove SO<sub>2</sub> prior to detection. Work is under way (George Allen, personal communication) to refine continuous SO<sub>4</sub><sup>=</sup> measurements. This approach is based on thermally converting SO<sub>4</sub><sup>=</sup> to SO<sub>2</sub> at high temperature (1,000° C) using a stainless steel converter oven with high efficiency (>95 percent) followed by high-sensitivity pulsed-fluorescence SO<sub>2</sub> analysis. A diffusion denuder is used upstream of the converter to remove gas-phase sulfur compounds. If needed, an NH<sub>3</sub>-coated permeation tube can be added to convert H<sub>2</sub>SO<sub>4</sub> to (NH<sub>3</sub>)<sub>2</sub>SO<sub>4</sub> to prevent any reduced response to acidic SO<sub>4</sub><sup>=</sup>.

<sup>1</sup> In concordance with the practice in earlier chapters the term BC shall be used here as a general term describing the sooty carbon component of PM, unless distinction by measurement technique (e.g., optical vs. thermal evolution) necessitates specific reference to BC or EC, respectively.

A commercially available continuous  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  analyzer (Rupprecht & Patashnick, Albany, NY) involves the flash vaporization of particles collected by impaction onto a filament, followed by chemiluminescence detection of nitrogen oxides for  $\text{NO}_3^-$  by ultraviolet absorption of  $\text{SO}_2$  for  $\text{SO}_4^{2-}$ , (Stolzenburg and Hering, 2000) or by NDIR for OC.

### *Particulate Metals*

Many of the techniques that have been developed to identify the metals contained in PM collected on filters are being adapted for continuous time-resolved measurement. Detection methods include XRF and PIXE. In each case, the metals are identified by the X-ray emissions of the elements that are excited in the sample (Cooper, J., Cooper Environmental Services, Portland, OR, personal communication, 2002).

In addition, collection and flash vaporization - followed by detection using atomic-emission spectrometry, emission spectrometry, and mass spectrometry - are being developed to measure metals in aerosols. Also, the same detectors are used to distinguish the soluble metals contained in aerosols sampled into a solvent stream. The application of single-particle analysis using mass spectrometry for detection has great potential to give semi-quantitative, size-resolved real-time measurement of PM metals. On-line elemental analysis, developed by the University of Maryland and Harvard University (semi-continuous elemental analysis system SEAS), provides for semi-continuous analysis of as many as 6 trace metals simultaneously. The PM is collected by water condensation into an aqueous slurry and then analyzed by graphite furnace AAS (Kidwell et al., 2001; Ondov and Kidwell, 2000a, 2000b). The averaging time is 30 to 60 minutes for Al, Ca, Fe, Cu, Cr, Mn, Zn, Cd, As, Sb, Pb, Ni, V, and Se measured with detection limits of  $\sim 1$  to  $5 \text{ ng/m}^3$ . An improved version uses the high frequency aerosol slurry sampler (HFASS) with a dynamic aerosol concentrator. The HFASS grows particles by steam condensation to facilitate separation of the particles from the air stream.  $\text{PM}_{2.5}$  samples are acquired at a high flow rate (200 L/min) and delivered to either a graphite AAS for on-line analysis or to an auto-sequencing sample collector for off-line analysis. This new system provides higher sensitivity, with

5-minute average sample duration and allows for the determination of elements at lower ( $0.1 \text{ ng/m}^3$ ) detection limits.

### **B.2.4. Single-Particle Measurements**

Single-particle mass spectrometers (SPMS) allow real-time detection of the chemical composition of individual particles. These recently developed systems detect the basic chemical and physical properties of individual particles and, hence, promise to provide the most information concerning the sources of the particles and the history of atmospheric processes that determine their composition. Of particular value is their ability to provide information on the mixing of different particle components. The salient features these instruments are listed in Table B.4 (Middlebrook et al., 2003).

These instruments decompose individual particles, ionizing their components and providing mass spectra that give elemental identification and some molecular structure information. Most importantly, these in-situ instruments can largely avoid the artifact problems associated with the collection of semivolatile species by filter/denuder methods, such as  $\text{NH}_4\text{NO}_3$ . Some specific analytical achievements made with these techniques include the detection of internal mixing of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  in remote continental accumulation mode particles (Murphy and Thomson, 1997), the measurement of the conversion of NaCl to  $\text{NaNO}_3$  as sea-salt particles traversed the Los Angeles region (Gard et al., 1997), and the measurement of substantial amounts of organic material in upper-tropospheric particles (Murphy et al., 1998).

To date, SPMS methods are qualitative; however, some level of quantification has been obtained using chemical composition obtained simultaneously using a MOUDI and SPMS. This is the most significant limitation to the current generation of laser ionization instruments. Since most instruments use optical and aerodynamic sizing, there also is a deficiency in measurements at size ranges  $< 0.4 \mu\text{m}$ , although this limit is being extended. However, instruments have been designed to measure the composition of single particles down to 10-20 nm (RSMS; Rhoads et al., 2003).

Finally, another type of mass-spectrometer instrument is becoming available, which evaporates particles and uses a more conventional electron-impact mass spectrometer for analysis (AMS, Jimenez et al., 2003; Tobias and Ziemann, 1999; Jayne et al., 2000). Its capabilities have not been fully evaluated, but it is likely that it will enable quantification of more molecular species than the laser-ionization instruments. These instruments can respond to a single chemical species in single particles but usually must average over many particles if more than one species is being analyzed. They may fill a middle ground between complete analyses of single particles and fully quantitative analyses of bulk samples.

### B.2.5. Optical Properties of Aerosols and Long-Path Optical Measurements

Current methods allow for the real-time determination of the optical properties of aerosols at both point locations and along a path. Together these methods allow for total extinction to be measured directly and as individual components (PM and gas absorption and scattering). These measurements are extremely useful for understanding regional haze, and along with chemical measurements obtained using

either integrated or continuous methods, allow visibility reduction to be apportioned back to its sources. Table B.5 summarizes the measurements of the optical properties of aerosols.

#### *In-situ Measurements of Light Scattering and Light Absorption*

In-situ properties of primary interest are the aerosol light-scattering and absorption coefficients. The particle light-scattering coefficient ( $b_{sp}$ ) is measured directly with an integrating nephelometer. A number of vendors produce field-ready versions of this instrument suitable for monitoring applications. The most commonly used technique for monitoring the particle light-absorption coefficient ( $b_{ap}$ ) measures the attenuation of light transmitted through a deposit of particles on a filter, such as the traditional paper-tape measurements of coefficient of haze. The commonly used aethalometer and the particle soot absorption photometer (PSAP) applies optical attenuation to estimate BC.

The methods described above are mostly adequate for routine measurements of the integral optical properties of aerosols related to visibility reduction. In most cases, air must be drawn from a sample inlet to the instrument, which means that care must be

Table B.4. Summary of real-time single particle measurement techniques. (Middlebrook et al., 2003).

Name	Methodology	Aerodynamic size ( $\mu\text{m}$ )	Comments
<b>PALMS (particle analysis by laser mass spectrometry)</b>	Laser detection and ionization at $\lambda=193$ nm. Detection by single polarity time-of-flight mass spectrometer.	0.35 - 2.5	Semi-quantitative. Real time detection. Laser-based instruments are broadly consistent and show similar trends as a function of size for organic/sulfate and mineral particles.
<b>ATOFMS (Aerosol time-of-flight mass spectrometry)</b>	Laser detection and ionization at $\lambda=266$ nm. Detection by dual polarity time-of-flight mass spectrometer.	> 0.2	Semi-quantitative. Real time detection. Laser-based instruments are broadly consistent and show similar trends as a function of size for organic/sulfate and mineral particles.
<b>RSMS (Rapid single-particle mass spectrometer)</b>	Laser detection and ionization at $\lambda=193$ nm. Detection by single polarity time-of-flight mass spectrometer.	0.015 - 1.3	Semi-quantitative. Real time detection. Laser-based instruments are broadly consistent and show similar trends as a function of size for organic/sulfate and mineral particles.
<b>AMS (Aerosol mass spectrometer)</b>	Collection on surface followed by vaporization at $T \sim 550^\circ$ C. Gases ionized by electron impact, with Detection by quadrupole mass spectrometer.	0.05 - 2.5	AMS provides size-resolved measurements of volatile aerosol components. Real time detection and analysis. Quantitative measurements are possible. Does not yield single-particle spectra.

taken to avoid particle losses. Changes in relative humidity can affect the measurements, requiring measurement and, in general, control of sample relative humidity. Particles larger than a few  $\mu\text{m}$  in diameter are difficult to characterize quantitatively, due to inlet effects and optical truncation. More work is needed to characterize measurement artifacts of the filter-based methods for light absorption, as well as development of methods to determine the RH-dependence of aerosol light absorption.

In that regard, new methods are emerging that can determine scattering, absorption and/or total particulate extinction. Methods such as cavity ringdown spectrometers and direct absorption cells, by virtue of their principle of operation, do not have the negative biases noted for the integrating nephelometer in Table B.5a. In addition, the photoacoustic absorption cell, which is a real-time method for determining the absorption coefficient, has shown promise in laboratory and surface field measurements and is being adapted for airborne studies.

#### *Long-Path Measurement Techniques: Remote Sensing and Visibility*

Sun-tracking photometers measure vertical optical depth by observing the transmission loss between the sun and the instrument. Measurements can be made only in daytime, and a cloud-free line-of-sight is essential if particles are to be measured. The effects of all species in the column are inseparably combined, and the molecular contribution must be subtracted to isolate the attenuation by particles.

Spectral sun-photometer measurements can be inverted to obtain information about the average size-distribution of the particles in the column. Interpretation of the size distributions should be limited to general rather than detailed features, because the results are typically quite sensitive to measurement errors and data-retrieval algorithms. Shadow-band radiometers measure both direct and diffuse radiation and provide similar information as a sun photometer, but with less accuracy. However, estimates of the single-scattering albedo of the particles in the column can be made from the diffuse-

direct measurements. Automated spectral sun photometers and shadow-band radiometers are available commercially, and are standard instruments in some radiation monitoring networks. Radiative-transfer and climate issues usually motivate use of these instruments, but they also can contribute to pollution research, especially in combination with other instruments.

Telephotometers or teleradiometers have been used to measure the contrast reduction of a distant reference target due to the intervening haze. The results are closely applicable to human perception, but depend on lighting conditions. Scene cameras are even more attuned to visual perception and are less quantitative than telephotometers in terms of quantifying aerosol optical properties. Transmissometers measure one-way transmission loss, and hence the average extinction coefficient, along a path. The contribution of scattering and absorption of light by gas-phase molecules in the light path is also embedded in the signal, and must be subtracted to isolate the particulate portion. Transmissometers designed for long-term operational use are commercially available, e.g., as a standard instrument in the IMPROVE network. Transmissometers often have been used at airports, where the design is optimized for very low visibility (fog and dense haze). Transmissometers can operate continually, but measurement periods of minutes or longer are necessary to average the signal variations caused by atmospheric turbulence.

Long-path measurements are becoming available that can provide spatial resolution. Lidar (light detection and ranging) uses a laser to transmit a pulse of light into the atmosphere. The small portion that is scattered back from the air is detected as a function of time, or equivalently, of distance from the device. The information provided by current instruments is semi-qualitative, indicating the approximate distribution of aerosols in the atmosphere. This information is extremely valuable for locating aerosols and determining the thickness of the layers. Lidar can operate from the surface or from aircraft. Automated, eye-safe lidars are commercially available along with new emerging research prototypes.

Table B.5.a. In-situ measurements. Measurements of aerosol optical properties, c.f., Seigneur et al., 1998.

Method	Specifications	Comments
<b>Integrating Nephelometer</b>	Continuous. Measures optical scattering of sampled aerosols.	Commercially available. Size and refractive index of many aerosol particles change with relative humidity (RH), leading to a pronounced RH-dependence. Open-air nephelometers operate at ambient RH, heated nephelometers operate at a low RH, and humidity-controlled nephelometers allow direct measurement of dependence on RH. Nephelometers have significant negative biases for particles with diameters larger than 1 $\mu\text{m}$ .
<b>Aethalometer</b>	Continuous. Converts optical attenuation to BC. Collects on portion of moving tape. Unexposed part of the tape is used for blank	Commercially available. Difference in light attenuation between two parallel segments of tape is related to BC by comparison with thermal evolution methods. BC estimated by this method is operationally defined by the carbon method used for comparison. Method has considerable uncertainty.
<b>Absorption Photometer (PSAP)</b>	Collects particles on filter and convert optical attenuation through filter to BC.	Commercially available. Bond et al. (1999) demonstrated that filter interferences and light scattering by the deposited particles introduce considerable uncertainty. Nevertheless, the simplicity and sensitivity of filter-based methods make them the method of choice for present monitoring applications.

Table B.5.b. Long path measurements. Measurements of aerosol optical properties.

Method	Specifications	Comments
<b>Sun-tracking Photometers</b>	Continuous. Measures the vertical optical depth by observing the transmission loss between the sun and the instrument.	Commercially available. Standard instruments in radiation monitoring networks (e.g., AERONET). Measurements made only in daytime. Cloud-free line-of-sight is required to determine particle scattering. The molecular contribution must be subtracted to isolate the portion from particles. Spectral photometer measurements obtain information about average size distribution of particles in the column.
<b>Shadow-band Radiometer</b>	Continuous. Measures direct and diffuse radiation.	Commercially available. Provides similar information as a sun photometer, but with less accuracy.
<b>Transmissometers</b>	Continuous. Measures the one-way transmission loss, and hence the average extinction coefficient, along a path.	Accuracy is approximately 1 percent in transmission loss. The molecular scatter and absorption must be subtracted to isolate the particulate portion.
<b>Teleradiometers</b>	Continuous. Measures radiances of distant, preferably dark topographical features and the horizon sky, from which the apparent target-sky contrast is calculated.	Commercially available. Measure the contrast reduction of a distant reference target by the intervening haze. Results are closely applicable to human perception, but linkage to light extinction varies with lighting conditions
<b>Lidar</b>	Continuous. Detects as a function of time (distance) backscatter from pulsed laser. Multi-spectral lidar can provide profiles of the size distribution.	Commercially available. Can operate from the surface or from aircraft. Vertical profile of aerosol backscatter coefficients can be derived from calibration. High spectral resolution lidar (HSRL) separates the return from aerosol and molecules to obtain calibrated profiles.
<b>DOAS (Differential Optical Absorption Spectrometer)</b>	Continuous. Detects attenuation of a multi-spectral light source. Can infer information about scattering, absorption and size distribution. (see transmissometers, above)	Can detect light scattering and absorption by particles over a long path between light source and detector or between light source/detector and retro-reflector. Corrections must be made for molecular scattering and absorption.

With assumptions, or with the help of independent information and ancillary measurements, the optical extinction-coefficient profile can be estimated from the calibrated lidar backscatter profile. In addition, recent research has shown the value of data from various lidar systems for inferring profiles of the physical properties of particles, such as  $PM_{2.5}$  and even the size distribution. The influence of relative humidity on the distribution, optical properties of aerosols and their behavior with height in the atmosphere can be studied using simultaneous lidar measurements of water vapor and aerosol backscatter or extinction. In addition, lidar is capable of determining the depolarization ratio of backscattered light, a source of information relatively untapped in aerosol studies. The depolarization ratio indicates the morphology of aerosols by specifying the degree to which particles are non-spherical. Finally, coupling lidar measurements with other measurements (e.g., a spectral sun photometer) can greatly enhance the information available. Additional development and evaluation of such methods should yield valuable dividends for future aerosol studies.

### *Satellite Measurements*

Several techniques exist for detecting aerosols from space using passive remote-sensing methods (c.f., Kaufman et al., 1997 and King et al., 1999). Each method has its own advantages and disadvantages. Satellite techniques are at present most suited to define aerosol-distribution patterns, and may be useful in evaluating total aerosol optical depth for comparison with model computations. They can usually provide the only information available in remote areas and can offer global coverage.

Visible and near-infrared techniques also have been tested for detecting dust aerosols (e.g., Ackerman, 1997). The TOMS uses the ultraviolet spectrum and has the ability to distinguish between absorbing and non-absorbing aerosols (Hsu et al., 1996; Herman et al., 1997; Torres et al., 1998). A 20-year record is available globally, over land and ocean. A major advantage of this technique is the availability of aerosol coverage since the surface UV reflectivity is low and nearly constant over land and water. However, the TOMS aerosol product is not sensitive to aerosols below 1 km and the spatial resolution of the instrument is on the order of 40 by 40 km. Multi-

angle measurements also can be used to detect aerosols (e.g., Kahn et al., 1997) while polarization techniques can be used to retrieve PM properties.

### **B.2.6. Gas-Phase Aerosol Precursors, Ozone, Ozone Precursors and Oxidants**

The techniques available to measure the ambient atmospheric concentrations of gas-phase PM precursors, ozone, ozone-precursors (including the odd-hydrogen free radicals) and oxidation products of these compounds and their salient features are presented in Tables B.6a through B.6i. The tables are divided as follows: a) the sulfur compounds,  $SO_2$  and  $H_2SO_4$ ; b)  $NH_3$ ; c)  $O_3$ ; d) CO; e) speciated VOC; f) NO,  $NO_2$  and total reactive nitrogen ( $NO_y$ ); g) other nitrogen oxides (PAN,  $HNO_3$ , HONO,  $NO_3$ , and total gas-phase reactive nitrogen); h) peroxides ( $H_2O_2$  and ROOH); and i) odd hydrogen species. Parrish and Fehsenfeld (2000) recently reviewed most of these techniques and discussed their capabilities and limitations.

The VOCs are of particular interest in connection with measurement uncertainties. VOC measurements are difficult due to the extreme complexity of the organic-compound mixtures that can be present in the atmosphere. Over 850 different VOCs have been detected in the vapor over gasoline, and over 300 different VOCs from vehicle exhaust have been identified. Natural hydrocarbons emitted by vegetation, which are estimated to account for approximately 50 percent of the VOCs emitted into the atmosphere in North America, are highly reactive olefins. Air samples obviously can contain a very great number of different VOCs of natural and anthropogenic origin, and the oxidation of each of these species creates additional VOCs that are reactive.

The difficulties associated with VOC measurement increase with the complexity of the compound, depending on whether its carbon bonds are saturated and if it is oxygenated. Apel et al., (1999) identified large measurement uncertainties for many of these VOCs. Serious problems have been observed for higher molecular-weight ( $\geq C_8$ ) compounds which have a high probability of participating in particle formation. Clearly, one of the most critical needs of

the ambient VOC measurement community is a rigorous field intercomparison of measurement techniques. Such an intercomparison will define measurement capabilities more clearly and identify prevalent problems that must be addressed.

### B.2.7. Meteorological Measurements

Surface meteorological measurements are well established and allow for the determination of wind speed (WS), wind direction (WD), temperature (T), relative humidity (RH), barometric pressure (BP), and solar radiation. Many of these parameters are measured nationwide at numerous sites with needed accuracy, under most conditions. Surface methods are not reviewed here but summaries can be found in Seigneur et al. (1998).

Measurements aloft of some of these parameters can be obtained in near-real time up to 10 km, with vertical resolutions of less than 50 m. NOAA has a national network of radar profilers that measure WS and WD aloft. A series of tropospheric profilers in the central United States, make measurements from

about 100 m or so up to 10 km, while along the east and west coasts a series of boundary-layer profilers make measurements from about 75 m or so up to about 5 km. Many of these profiler stations are augmented with radio acoustic sounding systems (RASS), which allow simultaneous temperature profiles to be measured.

RASS allows for determination of boundary-layer mixing height if measurements are obtained properly. Sodar also allows measurements of WS and WD aloft. Its measurements are limited to about 500 m; but it has better resolution within that range. Lidar uses backscatter of gases or aerosols and allows for determination of boundary-layer mixing height. It also allows observation of PM and ozone in the vertical direction, either from the surface looking up or from aircraft looking downward. While these determinations are qualitative, they provide considerable information about layering in the atmosphere (Solomon et al, 2000b). These and others relevant methods are described in Table B.7 and additional information can be found in Seigneur et al. (1998).

Table B.6. Summary of real-time gas-phase precursor measurements. **a. Sulfur compounds: sulfur dioxide (SO<sub>2</sub>) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)<sup>a</sup>.**

Observable	Methodology	Specifications	Availability	Comments
SO <sub>2</sub>	Pulsed-fluorescence: A gas sample is excited with radiation at 190- 230 nm and detects fluorescence at 220-400 nm	Continuous DL = 0.1 ppbv MT = 10 sec.	Commercially available	Currently employed in monitoring networks. The inlet usually has method to remove hydrocarbon interferences. Commercial instruments are adequate for most ground-based measurements.
	Differential optical absorption spectroscopy (DOAS)	Continuous DL = 0.5 ppbv MT = 1 min. PL = 1 km	Commercially available	Uses light and wavelength-dependent absorption features to determine the path-integrated concentration of many molecules including SO <sub>2</sub> . Increasing the path length can reduce the detection limit.
H <sub>2</sub> SO <sub>4</sub>	Chemical ionization mass spectrometric (CIMS)	Continuous DL = 10 <sup>5</sup> cm <sup>-3</sup> MT = 10 sec.	Research grade instrument	Basis of the OH CIMS technique.

Note: DL is detection limit; MT is measurement (or integration) time required to achieve the stated detection limit.

<sup>a</sup> Sulfur dioxide (SO<sub>2</sub>) is a major precursor to secondary particle formation. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) produced from the oxidation of SO<sub>2</sub> is a very effective nucleating center for fine particles. Because of this role, the measurements of SO<sub>2</sub> are useful additions to most particle measurement sites in order to help determine fine particle sources.

Table B.6. Summary of real-time gas-phase precursor measurements, continued. **b. Ammonia (NH<sub>3</sub>)**<sup>a</sup>.

Methodology	Specifications	Availability	Comments
<b>Coated filter and denuders, extracted, and analyzed.</b>	Individual samples DL = 10 pptv MT = 2 hr.	Prescription for coating described in literature.	Methods are currently used in networks. Collecting surface coated with citric or oxalic acid. Analysis for NH <sub>4</sub> <sup>+</sup> by ion chromatography after extraction. For comparison of techniques see Wiebe et al. (1990), Appel et al (1988). Incorporated in many integrated sampling systems. Methods require laborious post-exposure processing.
<b>Photofragmentation/two-photon laser-induced fluorescence. (LIF)</b>	DL = 5 pptv MT = 5	Research grade instrument	Ammonia is photolysed by a UV laser and the resulting NH radical detected by LIF Schendel et al. (1990)
<b>Chemical ionization mass spectrometry (CIMS)</b>	Continuous DL = 0.1 ppbv MT = 10 sec.	Research grade instrument	Tested in ground-based comparison (Leibrock and Huey, 2000, Fehsenfeld et al., 2003)

Note: DL is detection limit; MT is measurement (or integration) time required to achieve the stated detection limit.

<sup>a</sup> Ammonia plays a critical role in the formation of particles. Because of this role, the measurements of ammonia are often incorporated in particle measurement systems. The development of new sampling techniques also must be accompanied by improved inlet design to reduce ammonia uptake on sampling lines.

Table B.6. Summary of real-time gas-phase precursor measurements, continued. **c. Ozone (O<sub>3</sub>)**<sup>a</sup>.

Methodology	Specifications	Availability	Comments
<b>UV absorption at 254 nm</b>	Continuous DL = 1 ppbv MT = 10 sec.	Available commercially	Widely used standard method. Absolute; but VOC interferences can be important at very low ozone concentrations. Calibration procedures should be used only to identify field instruments in need of cleaning and/or repair, never to alter the instrument measurement results. Currently employed in monitoring networks.
<b>Chemiluminescence using NO</b>	Continuous DL= 0.01 ppbv MT = 1 sec.		Not absolute but faster response than UV absorption (c.f., text) making technique especially suitable for aircraft measurements. Reaction vessel must be maintained at sub-ambient (20 torr) pressure. NO is toxic.
<b>Chemiluminescence using ethylene</b>	Continuous DL ≤ 1 ppbv MT = 10 sec.	Available commercially	Not absolute. Much less sensitive than NO chemiluminescence method above.
<b>Differential optical absorption spectrometer (DOAS)</b>	Continuous DL = 5 ppbv MT = 1 min. PL = 1 km	Available commercially	Longer path length, longer integration time can be used to improve detection limit.
<b>Lidar</b>	Continuous DL = 5 ppbv MT = 1 sec. Resolution = 0.1 km	Available commercially	Eye-safe technology currently available. Allows determination of ozone over a range of altitudes. Can be scanned from vertical to horizontal. Techniques have been improved sufficiently so that ozone profiling is becoming an increasingly attractive measurement tool. Typical accuracy of ozone lidar is 10 ppbv, but can be considerably better or worse depending on the particular instrument, spatial and temporal averaging, and distance from the lidar.

Note: DL is detection limit; MT is measurement (or integration) time required to achieve the stated detection limit.

<sup>a</sup> In-situ measurement of ozone can be made accurately and routinely with chemiluminescence and commercial UV absorption instruments. Wide-range ozone measurement technology exists to supply special measurement needs (e.g., airborne and long path). Recent developments of note are multi-wavelength lidars using the DIAL method (differential absorption of light), which can measure profiles of ozone (also, H<sub>2</sub>O, and occasionally SO<sub>2</sub>) from the ground or from aircraft (c.f., Alvarez et al., 1998).

Table B.6. Summary of real-time gas-phase precursor measurements, continued.

**d. Carbon monoxide (CO)<sup>a</sup>.**

Methodology	Specifications	Availability	Comments
<b>Non-dispersive infrared absorption (NDIA)</b>	Continuous DL = 2 ppbv MT = 1 hr.	Available commercially	Widely used in monitoring networks. CO absorbs radiation from a wideband IR source. Selectivity obtained by use of a sample cell. The commercial instrument has proven to be satisfactory for most ground-based measurements but the basic instrument must be modified to improve zero and calibration methods. If this is not done the drift in the zero baseline of the instrument greatly increases the uncertainty in the measurements.
<b>Vacuum UV resonance fluorescence (VUV)</b>	Continuous DL = 1 ppbv MT = 1 sec.	Research instrument	Fast response, suitable for aircraft use.
<b>Differential absorption CO measurement (DACOM)</b>		Research instrument	Instrument relies on the differential absorption of two laser-generated infrared wavelengths by CO within the multi-pass cell of a laser spectrometer. Fast response, suitable for aircraft use.

Note: DL is detection limit; MT is measurement (or integration) time required to achieve the stated detection limit.

<sup>a</sup>There are presently a variety of instruments that are capable of measuring CO. The choice of instrument depends on the accuracy, precision and frequency demanded of the measurements.

Table B.6. Summary of real-time gas-phase precursor measurements, continued. **e. Speciated volatile organic compounds (VOCs)<sup>1</sup>.**

Methodology	Specifications	Availability	Comments
<b>Gas chromatograph with flame ionization detection (GC – FID)</b>	Sample/analyze DL = 0.1 ppbvC for one cm <sup>3</sup> sample MT, see comment C <sub>2</sub> – C <sub>10</sub>	Commercially available.	Gas Chromatography (GC) with flame ionization detection (FID). FID detects carbon in VOC and is therefore not compound specific. Identification set by compound passage through GC column. Samples either real time measurements in the field or collected in canisters with subsequent lab analysis. Detection limit depends on sample size. Sampling time set by rate of filling of canister or sample loop. In practice, the number of samples that can be taken is limited by the analysis time in the gas chromatograph. In complex mixture of VOCs interferences become increasing likely.
<b>Gas chromatograph with mass spectrometric detection (GC – MS)</b>	Sample/analyze DL = 100 pptv MT, see comment.	Commercially available.	Gas Chromatography (GC) with mass spectrometer detection (MS). MS is therefore compound specific. Samples either collected in canisters or with subsequent lab analysis or real time measurements at the site. Sampling time set by rate of filling of canister or sample loop. In practice, the number of samples that can be taken is limited by the analysis time in the gas chromatograph.
<b>Proton Transfer mass spectrometry (PTR-MS)</b>	Continuous, DL = 100 pptv MT = 10 sec.	Research grade	Detects compounds with proton affinity greater than H <sub>2</sub> O. Sensitivity and specificity are limited for many compounds by the multitude of organic species and fragment ions with similar masses. (Hansel and Wisthaler, 2000)
<b>Differential optical absorption spectrometer (DOAS)</b>	Continuous, DL, see comments, MT = 1 min. PL = 1 km	Commercially available.	Detection limit depends on compound. Ranges from 1 ppbv for benzene to 0.1 ppbv for phenol. Has utility for measurements of aromatic hydrocarbons such as benzene and toluene and polycyclic aromatic compounds.
<b>Chemical ionization mass Spectrometry (CIMS)</b>	Continuous, DL = 100 pptv MT = 1 sec.	Research instrument	Specific ion chemistry allows fast-response sensitive detection of specific VOCs suitable for use on aircraft. Isoprene has been measured and undergone intercomparison studies (Leibrock and Huey 2000)

Note: DL is detection limit; MT is measurement (or integration) time required to achieve the stated detection limit.

<sup>1</sup>The VOCs constitute a very large class of compounds generally defined as volatile at STP. VOC measurements are difficult due to the extreme complexity of the hydrocarbon mixtures that can be present in the atmosphere.

Table B.6. Summary of real-time gas-phase precursor measurements, continued. **f. Nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>), and total reactive nitrogen (NO<sub>y</sub>).**

Observable	Methodology	Specification	Availability	Comments
<b>Nitric Oxide (NO)</b>	Chemiluminescence with ozone:	Continuous DL = 1 pptv MT = 1 sec.	Several commercial suppliers	Widely used standard method. Currently employed in monitoring networks. Commercial instruments adequate for most surface measurements. Research grade instruments have pptv detection limits and very fast response.
	Two photon laser-induced fluorescence (LIF)	Continuous DL = 1 pptv MT = 1 sec.	Research instrument	
<b>Nitrogen Dioxide (NO<sub>2</sub>)</b>	Photolysis of NO <sub>2</sub> to NO by UV followed by chemiluminescence detection of NO	Continuous DL = 10 pptv MT = 1 sec.	Commercial version available	Retrofitting existing NO measurements to detect NO <sub>2</sub> may allow NO <sub>2</sub> to be monitored in networks.
	Tunable diode laser absorption (TDLAS)	Continuous DL = 0.1 ppbv MT = 10 sec.	Research instrument	Absorption of infrared laser radiation in a low pressure, multi-pass cell
	Differential optical absorption spectrometer (DOAS)	Continuous DL ≤ 0.1 ppbv RT = 1 min. PL = 1 km	Commercial version available	Longer path length, longer integration time can be used to improve detection limit.
<b>Total reactive Nitrogen (NO<sub>y</sub>)</b>	Conversion of NO <sub>y</sub> to NO followed by Chemiluminescence	Continuous DL = 1 pptv MT = 1 sec	Commercial versions of the MoO reduction instrument available.	Measures all reducible species, although the conversion of fine particulate NO <sub>3</sub> <sup>-</sup> is problematic. Instruments based on molybdenum oxide (MoO) or gold catalyzed reduction.

Note: DL is detection limit; MT is measurement (or integration) time required to achieve the stated detection limit.

<sup>a</sup>The oxides of nitrogen (NO and NO<sub>2</sub>) are precursors of particles and ozone, and the total oxidized nitrogen family (NO<sub>y</sub>) in an air parcel represents the total emissions of these precursors that remain in the atmosphere.

## APPENDIX B

Table B.6. Summary of real-time gas-phase precursor measurements, continued. **g. Other nitrogen oxides (PAN, Nitric acid, nitrous acid, nitrogen trioxide and total gas-phase reactive nitrogen)** <sup>a</sup>.

Observable	Methodology	Specifications	Availability	Comments
<b>Peroxyacetyl nitrate (PAN)</b>	Gas chromatograph with electron capture detection (GC-ECD)	Continuous DL = 10 pptv MT = 10 sec sample each 3 minutes.	Instrumentation readily available	Gas chromatography (GC) with electron capture detection (ECD). Calibration is difficult. Not measured in networks.
<b>Nitric Acid (HNO<sub>3</sub>)</b>	Tunable diode laser absorption spectrometer (TDLAS)	Continuous DL = 0.1 ppb MT = 15 min.	Research grade instrument	Absorption of infrared laser radiation in a low pressure, multi-pass cell. (Fehsenfeld, et al., 1998).
	Filter collection, extraction, analysis	Individual filters DL = 10 pptv MT = 2 hr.	Nylon filters available commercially	Widely used standard method. Either nylon or base-impregnated filters used for collection. Laboratory analysis for NO <sub>3</sub> <sup>-</sup> by ion chromatography. Problems with sampling artifacts described in literature.
	Chemical ionization mass spectrometry: (CIMS)	DL = 10 pptv MT = 1 Hz.	Research grade instrument	Recently developed technique. Sensitive, fast response interference-free. Used in aircraft studies Huey et al. (1998).
<b>Nitrous acid (HONO)</b>	Differential optical absorption spectrometer (DOAS)	Continuous DL = 0.5 ppbv MT = 1 min. PL = 1 km	Commercial version available	Longer path length, longer integration time can be used to improve detection limit.
<b>Nitrogen trioxide (NO<sub>3</sub>)</b>	DOAS	Continuous DL = 25 pptv MT = 1 min. PL = 1 km	Commercial version available	Uses light and wavelength-dependent absorption features to determine the path-integrated concentration of NO <sub>3</sub> . Longer path length, longer integration time can be used to improve detection limit.
	Cavity ring-down spectrometer (CaRDS)	Continuous DL = 0.5 pptv MT = 5 sec.	Research grade instrument	Sensitive light-absorption method based on the time constant for the exponential decay of light intensity in an optical cavity.
<b>Dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>)</b>	(CaRDS)	Continuous DL = 0.5 pptv MT = 5 sec.	Research grade instrument	Thermal dissociation of N <sub>2</sub> O <sub>5</sub> to release NO <sub>3</sub> followed by measurement of the decay of light intensity in an optical cavity that is produced by the light absorption of NO <sub>3</sub> .

Note: DL is detection limit, MT is measurement time, and PL is path length.

<sup>a</sup>The atmospheric chemistry involving these species is currently of research interest. PAN and nitric acid sequester NO and NO<sub>2</sub>. Nitrous acid and NO<sub>3</sub> are important factors in nighttime chemistry. Reliable methods to calibrate these systems are problematic, owing to the low levels of calibration standards required, the ability to generate these standards in the field, and their stability.

Table B.6. Summary of real-time gas-phase precursor measurements, continued. **h. Peroxides (H<sub>2</sub>O<sub>2</sub> and ROOH).**<sup>a</sup>

Observable	Methodology	Specifications	Comments
<b>Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)</b>	Tunable diode laser absorption (TDLAS).	Continuous DL = 0.2 ppbv MT = 3 min.	
	Enzymatic derivatization with fluorometric detection:	Continuous DL = 0.05 ppbv MT = 1 min.	Collects gas phase H <sub>2</sub> O <sub>2</sub> into solution, followed by derivatization for sensitive detection.
	Fenton derivatization with fluorometric detection is similar to method above	Continuous DL = 1 ppbv MT = 1 min.	
<b>Multiple peroxides</b>	High-pressure liquid chromatography with fluorometric detection.	Continuous DL = 1 ppbv MT = 1 min	Similar to methods above, except that the peroxides are separated by HPLC.

Note: DL is detection limit; MT is measurement (or integration) time required to achieve the stated detection limit.

<sup>a</sup> The peroxides play an important role the heterogeneous conversion of sulfur oxides to SO<sub>4</sub><sup>=</sup>. Variation of these gas-phase techniques may be incorporated into particle composition measurements since the peroxides have been suggested as contributing to the adverse health effects of fine-particles. Peroxide measurements are not made in current networks and no commercially available instruments exist. Significant developments have been made in the measurement of peroxides. However, intercomparisons indicate that important problems remain especially with regard to differentiating between organic and inorganic peroxides. Through-the-inlet calibrations with standard additions of H<sub>2</sub>O<sub>2</sub> and, other organic peroxides are essential to determine differentiation afforded by various techniques.

Table B.6. Summary of real-time gas-phase precursor measurements, continued. **i. Odd hydrogen species.**<sup>a</sup>

Observable	Methodology	Specifications	Comments
<b>Hydroxyl radical (OH)</b>	Chemical ionization mass spectrometry (CIMS)	Continuous DL = 2•10 <sup>4</sup> cm <sup>-3</sup> MT = 0.5 min	Intercomparisons have indicated that long path absorption (LPA), laser induced fluorescence (LIF-FAGE), and chemical ionization mass spectroscopy (CIMS) appear to be capable of measuring OH at levels observed in the troposphere.
	Differential optical absorption spectrometer (DOAS)	Continuous DL = 10 <sup>6</sup> cm <sup>-3</sup> MT = 1 min	See comment for CIMS.
	Laser induced fluorescence (LIF)	Continuous DL = 10 <sup>6</sup> cm <sup>-3</sup> MT = 1 min	See comment for CIMS.
<b>Hydro Peroxy Radical (HO<sub>2</sub>)</b>	Chemical conversion to OH by reaction with NO; OH detected by LIF.	Continuous DL = 10 <sup>7</sup> cm <sup>-3</sup> MT = 1 min	
<b>Peroxy radicals (RO<sub>2</sub>)</b>	Radical conversion to NO <sub>2</sub> with amplification	Continuous DL = 10 ppbv MT = 1 min	

Note: DL is detection limit; MT is measurement (or integration) time required to achieve the stated detection limit.

<sup>a</sup> Odd hydrogen measurements are not made in current networks and no commercially available instruments exist. These measurements are important for development and testing of diagnostic and predictive chemical models. Significant headway has been made in the development of methods to measure OH and HO<sub>2</sub>. A measurement technique for OH and HO<sub>2</sub> using laser induced fluorescence detection has been developed and provided the first measurements of OH and HO<sub>2</sub> that are produced during the night by NO<sub>3</sub> and O<sub>3</sub> chemistry. In addition, an instrument has been developed to measure the OH loss rate due to reactions with other atmospheric chemicals. This new instrument, the Total OH Loss-rate Measurement (TOHLM), has been successfully deployed (Kovacs and Brune, 2001). Mauldin et al., (1999) developed a fast response instrument that measures OH and H<sub>2</sub>SO<sub>4</sub> that has been used in ground-based and aircraft studies. Calibration of measurements remains a significant problem.

Table B.7 Instruments used to measure meteorological parameters over a long-path and/or above the surface.

<b>Instrument</b>	<b>What is measured and how it is measured</b>
<b>Sodar (Acoustic Remote Sensing)</b>	Transmitter broadcasts power at audio frequencies (a few thousand Hertz). Detects reflection from atmospheric turbulence. Continuous, height-resolved (typically, 1-30 meter resolution) measurement from surface to about 500 meters above the surface of the temperature distribution in the atmosphere. Can determine boundary layer height, turbulent mixing properties of the boundary layer, sensible heat flux and surface friction. With Doppler sodar wind speed and direction also can be determined.
<b>Profilers (Radar with radio acoustic sounding system, RASS)</b>	Radar, typically operating 915 Megahertz, senses refractive index variations, primarily humidity, in clear air with vertical resolution of approximately 60 meters. System measures wind speed and direction continuously from near the surface ( $\geq 100$ meters) to several kilometers. RASS generates audio power that allows radar reflectance measurement of temperature profiles. Profilers are commercially available.
<b>Lidar</b>	Reflection of pulsed light beam allows space resolved (typically, 1 meter resolution) detection of particle distribution in the atmosphere in the atmosphere (see Section 4.4.5). Information can be used to infer boundary-layer height and turbulence. This provides valuable information concerning atmospheric layering.
<b>Doppler lidar</b>	Doppler shifted reflection of pulsed light beam, allows detection of particle distribution in the atmosphere. Measures the radial components of the wind, usually in a scanning mode. Can measure the details of boundary-layer mixing processes including boundary-layer height, turbulence, and winds.
<b>Optical crosswind sensors</b>	Observes a distant light source through two optical receivers. Correlates the time delay in the scintillation patterns and determines the wind component normal to the beam. Optical crosswind sensors measure the wind component normal to the path (path-lengths between 100 m and several kilometers between a transmitter and receiver). The instrument uses naturally occurring inhomogeneities in optical refractive index as a tracer for the wind. Provides a path-averaged wind with no mechanically limited threshold for low wind speeds. Major use has been to measure drainage flows channeled in narrow valleys.
<b>In-situ (tethered balloon and kite borne) measurements</b>	Tethered balloons and kites provide platforms for in-situ sensors with the advantage that the measurement devices are reusable. Commercial instruments are used to measure wind, temperature, relative humidity, pressure, and radiation. Sonic anemometers and fast-response hygrometers can also be used to measure the turbulent transfer of heat, moisture, and momentum through the atmospheric surface layer. The primary concern in the application of surface meteorological instruments in networks is adequacy of their location. The interference of tethers with aircraft operation is a clear concern and limitation.
<b>Inert tracers</b>	Inert tracer releases are used to evaluate conceptual and numerical models of atmospheric dispersion. Sulfur hexafluoride ( $\text{SF}_6$ ) is an example of a frequently used short-range tracer. A number of perfluorocarbon tracers are also available for this application.

### B.3. MEASUREMENT UNCERTAINTY AND VALIDATION

Numerous studies have been conducted to test the equivalency of methods for PM mass and its physical and chemical properties. The results from these studies are contained in several recent reports and reviews (c.f., Chow, 1995; Hering, et al., 1988; Lawson and Hering, 1990; Ito, et al., 1998; Seigneur et al., 1998; McMurry, 2000; Turpin et al., 2000; Solomon et al.; 2000a; Solomon et al. 2000b, Chameides and McMurry, 2001, Solomon et al., 2001; Watson and Chow, 2001; Solomon, et al., 2003;

Middlebrook et al., 2003). Descriptions of other studies that compare and evaluate instruments can be found on the web (See <http://www.epa.gov/ttn/amtic/supersites.html>). This web site also provides links to the web pages of several other PM projects). Given the proliferation of methods being developed that measure the chemical components and the physical properties of PM, and the important role these measurements are playing in understanding effects of PM on health and within the regulatory arena, it is imperative that benchmark techniques, reference methods, and calibration standards be further developed to better evaluate the accuracy or bias of the methods used to measure fine particles.

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