

## ***New Instruments and Data Inversion Methods***

# **Development, Operation and Applications of an Aerosol Generation, Calibration and Research Facility**

**Olga Hogrefe, Frank Drewnick, G. Garland Lala, James J. Schwab, and Kenneth L. Demerjian**

*Atmospheric Sciences Research Center, University at Albany, State University of New York, Albany, New York*

---

An aerosol generation, calibration, and research facility has been developed with the major purpose of evaluating aerosol instrumentation, including quality assurance testing, intercomparison, performance evaluation, and calibration of aerosol sizing, bulk, and speciated mass-measuring instruments. The aerosol facility also provides excellent opportunities for basic aerosol research.

Polydisperse test aerosols are generated most often through spray atomization of solutions. Monodisperse test aerosols can be produced by mobility classification of polydisperse aerosols, by a vibrating orifice aerosol generator, by an electrospray aerosol generator, or by nebulization of polystyrene latex (PSL) particle suspensions. Generated inorganic, organic, and mixed aerosol particles range in size from 0.005 to greater than 1 micrometer. Physical characterization of the test aerosols is done using scanning mobility particle sizers, condensation particle counters, and an aerodynamic particle sizer.

The facility includes a 450 l cylindrical glass slow-flow chamber that is used mainly for the dilution, equilibration, and controlled

humidification of generated primary aerosol particles larger than 50 nm as well as for the generation of secondary aerosols through the choice of appropriate precursor reactants. Test aerosols can also be subjected to controlled concentrations of pollutant gases (O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub>, and VOCs). Smaller particles can also be generated and sampled either from a fast-flow chamber or a static chamber.

The well-characterized aerosol environment produced in the slow-flow chamber is used to evaluate the performance of various instruments designed to measure aerosol mass, composition, and size over a range of ambient conditions. Instruments evaluated to date include an R&P standard TEOM mass monitor; a SES TEOM mass monitor; a Differential TEOM mass monitor with an electrostatic precipitator (ESP); R&P Ambient Particulate Sulfate, Nitrate, and Carbon monitors; a Particle-Into-Liquid Sampler with IC (PILS-IC); an Aerodyne Aerosol Mass Spectrometer (AMS); TSI scanning mobility particle sizers (SMPSs); and condensation particle counters (CPCs). Several examples of applications of the aerosol facility involving the TEOM mass monitors and the AMS are also discussed in this article.

---

Received 23 October 2003; accepted 5 March 2003.

This work was supported in part by the New York State Energy Research and Development Authority (NYSERDA), contract # 4918ERT-ERES99, the U.S. Environmental Protection Agency (EPA) cooperative agreement # R828060010 and New York State Department of Environmental Conservation (NYS DEC), contract # C004210. Although the research described in this article has been funded in part by the U.S. Environmental Protection Agency, it has not been subjected to the Agency's required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred. The authors would like to thank Jeffrey Ambros from Rupperecht and Patashnick Company, Inc., and summer undergraduate students Jeff Ausfeld and Cara Weismann.

Frank Drewnick's current address: Institute of Atmospheric Physics, University of Mainz, D-55128 Mainz, Germany.

Address correspondence to Olga Hogrefe, Atmospheric Sciences Research Center, University at Albany, State University of New York, 251 Fuller Road, Albany, NY 12203. E-mail: olga@asrc.cestm.albany.edu

---

## **INTRODUCTION**

Aerosol particles participate in many atmospheric processes and are strongly associated with heterogeneous chemistry, cloud formation, and climate forcing (Charlson et al. 1992; Seinfeld and Pandis 1998). Atmospheric aerosols also affect air quality and, consequently, human health (Finlayson-Pitts and Pitts 1986; Pope et al. 2002; Samet et al. 2000). Information about ambient aerosol concentration, composition, and size distribution is essential in order to estimate their impact on environmental health and welfare. Measuring and characterizing ambient aerosols is the only way to obtain this information.

Calibration of aerosol-measuring instrumentation is one of the conditions ensuring high-quality data. Still, for a variety of reasons calibration of aerosol instruments has proven to be a

difficult task. Calibration establishes the relationship between the instrument response and a specific aerosol property (size, number, mass concentration, or chemical composition) (Cheng and Chen 2001). Most instruments are tested by the manufacturer, but since there are few, if any, suitable reference standard materials for aerosols, these tests may or may not constitute a calibration in terms of accepted quality assurance standards for air quality monitors. To further complicate the picture, actual aerosol measurements may take place under ambient conditions different from those under which the instrument was tested or calibrated. Furthermore, the properties of the actual aerosol may differ significantly from those of the calibration standards—e.g., ambient aerosol particles are not necessarily spherical, they are often internally or externally mixed, and they can be chemically reactive—and these properties may be highly variable over time. These and many other factors can affect the accuracy of the measurement system. To assure the quality of measurement data, instrument users must either recalibrate or verify calibrations done by the manufacturer, or compare instrument measurements to a standard or a well-established reference. An aerosol calibration facility equipped with particle generation, conditioning, and measurement systems can be used to perform full-scale calibrations and evaluations of aerosol instruments. Cheng and Chen (2001) list requirements for a reliable aerosol generation facility, these including (1) stable aerosol concentrations maintained over extended periods of time, (2) constant size of generated aerosol, and (3) isokinetic or static air sampling. McMurry (2000) discusses laboratory techniques that are commonly used to calibrate atmospheric aerosol instrumentation. These techniques may include monodisperse polystyrene latex (PSL) particles, generation of monodisperse aerosol by a vibrating orifice generator, and electrostatic classification by the differential mobility analyzer (DMA). The latter can be used either to produce monodisperse aerosol of known size and composition or for selecting “monodisperse slices” of atmospheric aerosol.

Although many aerosol research and analysis laboratories exist, and several review papers have been written discussing the generation of calibration aerosols (McMurry 2000; Cheng and Chen 2001) and listing requirements for such aerosols (Cheng and Chen 2001), discussing components of test facilities (Cheng and Chen 2001), and summarizing laboratory analysis methods (Chow 1995), to our knowledge there are no articles detailing the specific design, operation, and performance characteristics of an aerosol calibration and research laboratory. In addition, this article provides some examples of recent applications of the facility and an indication of its general utility.

## DESCRIPTION OF THE AEROSOL FACILITY AND ITS OPERATION

The aerosol generation, calibration, and research facility consists of two laboratories, the PM Laboratory (PMLab), which generates and characterizes test aerosols in the 0.04–20  $\mu\text{m}$  diameter range, and the small particle laboratory (SPLab), with similar capabilities for test aerosols in the 0.005–0.5  $\mu\text{m}$  di-

ameter range. The PMLab includes aerosol generation equipment; a dilution system; a slow-flow aerosol chamber, where aerosols undergo humidification, reaction (if desired), and equilibration; aerosol measurement and characterization instrumentation; and data acquisition, storage, and processing equipment. The SPLab is equipped with an aerosol generator and a simpler dilution system along with a fast-flow chamber. Both laboratories are equipped with ducts to let outside air into the chamber if needed. In addition, the facility is equipped with a temperature- and humidity-controlled microweighing chamber.

### Aerosol Generation

A schematic of the generation system for polydisperse aerosols is shown in Figure 1. One of the aerosol-generation instruments commonly utilized in the PMLab is a constant output atomizer (COA; TSI Model 3076) operating in the recirculation mode. Droplets are produced by atomizing a liquid (solution or suspension) using a high-velocity air jet (air at pressure  $2.4 \times 10^5$  Pa expands through an orifice 0.34 mm in diameter). A flat-plate impactor is installed at the generator outlet to remove droplets larger than 3  $\mu\text{m}$ . The impactor can be modified or removed if there is a need to generate larger particles. The generated aerosol is then mixed with a dry airflow, which leads to its dilution and partial evaporation of the solvent. The aerosol, after predilution and partial drying, passes through an aerosol neutralizer (TSI Model 3054) and then enters a dilution system.

For the generation of monodisperse aerosol or polydisperse aerosol with a narrow size distribution, the polydisperse aerosol flow is directed into an electrostatic classifier (EC; TSI Model 3080) with a long differential mobility analyzer (LDMA; TSI Model 3081) prior to entering the dilution system. Polydisperse aerosol particles pass through a charger and then are separated in the DMA according to their electrical mobility. The DMA voltage and the aerosol flow are adjusted so that particles of a preselected size range leave the DMA. The width of the aerosol size distribution is adjusted by selecting an appropriate ratio of DMA sheath flow to sample flow, which should be equal to 10 for the narrowest size distribution. Decreasing this ratio leads to a widening of the aerosol size distribution. The mean size of the dry aerosol distribution generated by this method will depend on the relative humidity in the EC. To minimize this size variation, the sheath flow must be dried within the Classifier. This is achieved by installing a dryer in the bypass flow loop of the EC, consisting of a lab gas drying unit filled with indicating Drierite<sup>®</sup>.

The generation system can maintain stable concentrations of polydisperse aerosol over extended periods of time (up to 24 h). After equilibration of the system, typical standard deviations from the mean mass concentration measured by a SES TEOM mass monitor (described below) in the middle of the slow-flow chamber are 5–10% for mass concentrations in the range of 20–30  $\mu\text{g}/\text{m}^3$ . Aerosol mass concentrations of this range can be obtained in the slow-flow chamber, for example, when using a 0.5 g/l aqueous solution of a nonvolatile salt, the aerosol flow

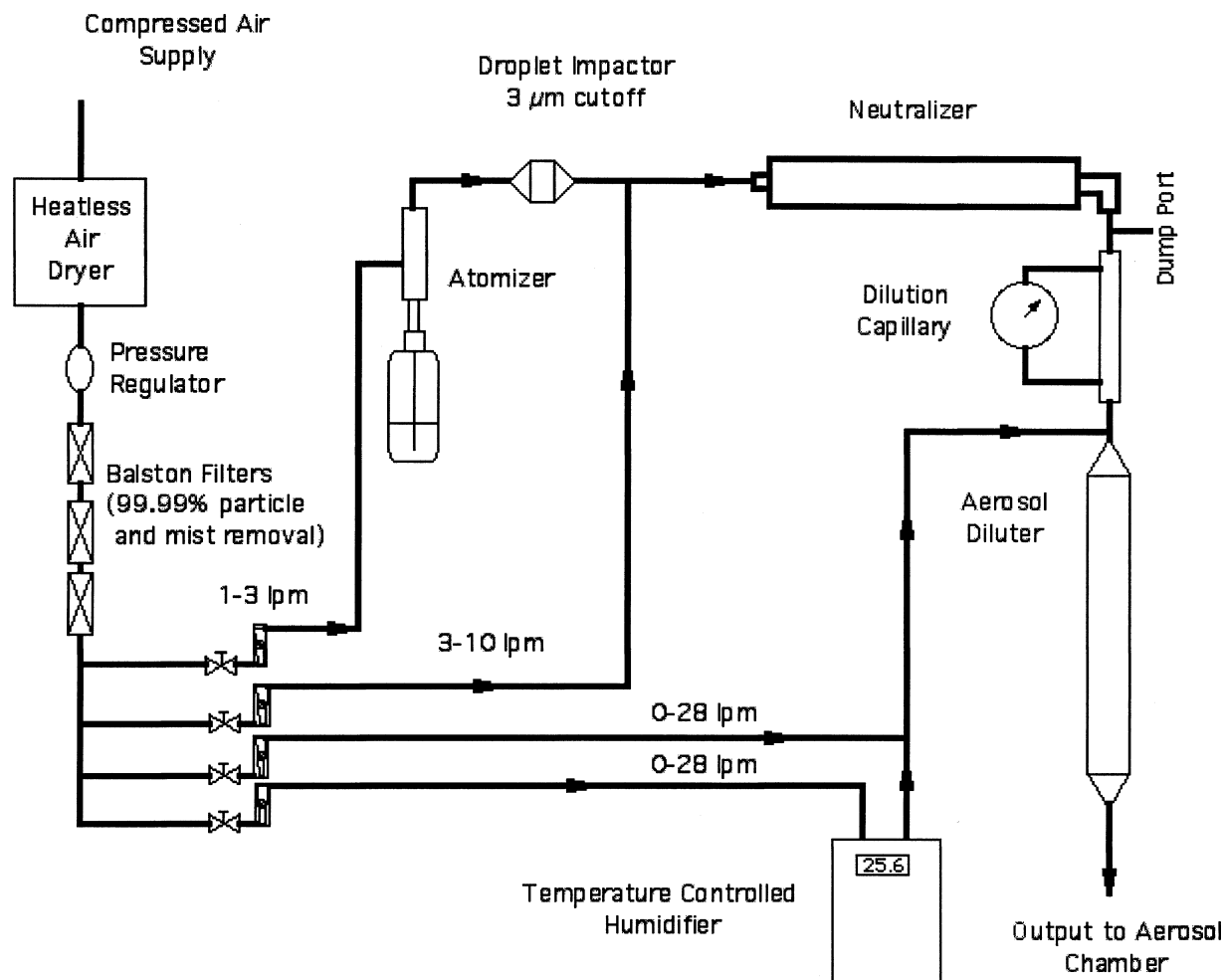


Figure 1. The PMLab aerosol generation and dilution system.

through a dilution capillary (described below) of 1.5 l/min, and the total chamber flow of ca. 25 l/min. Higher mass concentrations of aerosol are usually characterized by smaller deviations from the mean measured mass concentration (i.e., aerosol is more stable). Ways to obtain higher aerosol concentrations in the chamber are listed below; one of them is to increase the concentration of the solution. However, clogging of components of the generation instruments or of the dilution capillary is more likely to occur if high concentration solutions are used in the COA. The clogging can cause steady trends or abrupt changes in measured aerosol mass concentration. This problem becomes pronounced only for solutions with concentrations higher than 2 g/l. Frequent cleaning and maintenance procedures eliminate the problem; however, the time of unattended operation of the generation system under these high concentration conditions is limited to 2–5 h.

The generation of larger monodisperse aerosol particles is accomplished through the use of a vibrating orifice aerosol generator (VOAG; TSI Model 3450). This device produces particles by breaking a pressurized liquid jet with an orifice vibrating at a preset frequency. The generated particles pass through

the neutralizer and enter the dilution system. Although particles generated by the VOAG are highly monodisperse, this device is capable of producing stable, reproducible aerosol concentrations for only a few hours.

Solutions for the generation of aerosols (using the COA or the VOAG) are prepared by dissolving a predetermined amount of a soluble inorganic salt or an organic compound in water or another suitable solvent. Organic solvents are used to prepare solutions of water-insoluble organic compounds. To reduce the impurities in generated aerosols, distilled/deionized water (DD water; resistivity > 15 MΩ cm) is used for preparation of water-based solutions.

In the SPLab, aerosols are generated using (1) a propane torch, (2) a hot tungsten wire, (3) the COA (followed by the EC with the LDMA or a Nano-DMA (TSI Model 3085) if monodisperse aerosol is needed), or (4) an electrospray aerosol generator (EAG; TSI Model 3480). The latter generates monodisperse aerosol by using an electric field to pull a charged solution out of a capillary and form droplets.

Nanosize polydisperse carbon-containing aerosol can be produced by burning a commercial propane torch (Bernzomatic).

The flame is directed into a portable, static aerosol chamber (described later) for a few seconds, filling it with particles. This method does not have much flexibility in terms of controlling particle size and concentration; however, it is capable of quickly generating a large concentration of extremely small particles. Small particles can be also generated by resistively heating a tungsten wire ( $\sim 3.5A$ , producing a red glow) from a 12 V automotive light bulb within a dry airflow stream.

### Aerosol Dilution and Humidification System

The COA typically produces particles with mass concentrations on the order of  $mg/m^3$ , but for most instrument testing and evaluation concentrations in the  $5\text{--}100\ \mu g/m^3$  range, typical of ambient PM<sub>2.5</sub> concentrations, are required and reflect the typical dynamic range over which the instruments were designed to operate. Therefore, a dilution system is a necessary feature of the aerosol facility.

The aerosol dilution system is shown in Figure 1. After neutralization, the aerosol flow passes through a glass capillary dilution system, where the particle flow is split between a bore capillary and a dump port. The “dump flow” is regulated by a rotameter (Dwyer), which regulates the fraction of the total aerosol flow that mixes with the much larger dilution flow before entering the slow-flow chamber. If higher aerosol mass concentrations are needed, the capillary can be removed easily. In this case, only aerosol number and mass concentrations increase, while aerosol size distribution does not change significantly.

Particle-free filtered air from an oil-free compressor is used for aerosol generation and dilution. First, air passes through a Heatless Dryer (Puregas CDA112) and three in-line Ballston capsule filters. The airflow is then split in four subflows, each of which is regulated by a rotameter (Dwyer). Two subflows are used in the COA, one to produce a high-velocity jet necessary to atomize the liquid stream, and the other to dilute and partially dry the aerosol flow at the atomizer outlet. The third subflow is the

main dry dilution flow and is directed through a mixing/dilution tube and into the slow-flow aerosol chamber.

The last subflow is bubbled through a temperature-controlled reservoir of DD water. The temperature of the circulating bath, which stabilizes the water reservoir, is typically maintained at  $26^\circ C$ . The saturated air exiting the reservoir flows through a PTFE filter ( $2\ \mu m$  average pore size) and through a plastic container used to collect excess water and to prevent liquid from entering the system. Dry and saturated airflows are then combined and directed through an aerosol diluter/mixer (71 cm long brass tube with 5 cm ID) and into the slow-flow aerosol chamber. Typical chamber dilution airflow ranges from 15–50 l/min. Humidity of the airflow (and, consequently, the relative humidity in the flow chamber) is controlled by changing the ratio of dry-to-humid airflows. The present design can maintain stable relative humidity levels (at ambient laboratory temperatures of approximately  $20\text{--}23^\circ C$ ) ranging from below 5% to approximately 90%. Two Vaisala temperature/relative humidity probes (HMD 70Y) are used to monitor conditions in the chamber. One probe is mounted at the aerosol entrance side of the chamber, and the other one is mounted in the middle of the chamber (see Figure 2).

The SPLab aerosol dilution system is much simpler and consists of a compressed dry air supply, a HEPA filter, and two rotameters, connected in parallel to increase the range of dilution flow.

### Aerosol Chambers and Aerosol Sampling

Before sampling, the generated aerosol is conditioned/ equilibrated in one of the aerosol chambers. The choice of the chamber is determined by the desired characteristics of the generated aerosols and the nature of the desired tests. The slow-flow chamber is used for most tests involving mass and mass concentration aerosol instruments. In particular, these experiments include studies of aerosol evolution and reaction, the effects of ambient

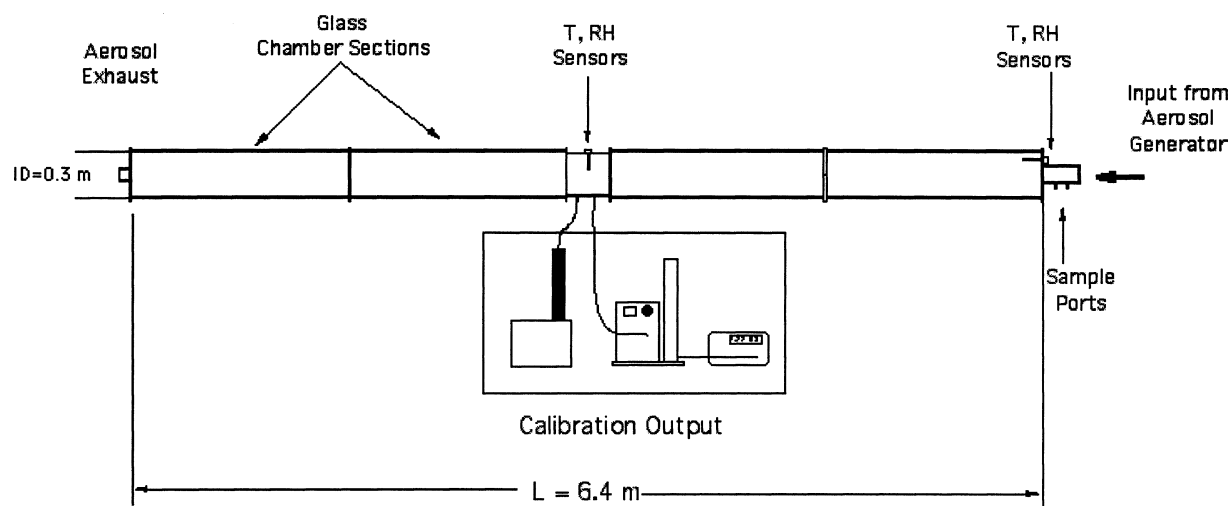


Figure 2. The PMLab aerosol slow-flow chamber.

humidity on aerosol properties, and most other types of experiments that do not require aerosol particles smaller than  $0.05\ \mu\text{m}$ . The fast-flow chamber and/or the portable, static chamber are used for experiments with aerosol particles in  $0.005\text{--}0.2\ \mu\text{m}$  diameter range. These particles are mainly used for calibration and evaluation of the performance of aerosol counting and sizing instrumentation.

The aerosol slow-flow chamber is a 6.4 m long horizontal glass tube 30 cm in diameter and with an approximate volume of 450 l (Figure 2). Aerosol and controlled humidity dilution airflows are premixed in the dilution tube shown in Figure 1, and then the resulting flow is introduced into the chamber at a flow rate of 15–50 l/min (corresponding Re range from 70–230). The magnitude of the aerosol flow is normally set to be at least twice the total flow demand of the sampling instruments. Various reactive gases (e.g.,  $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ , VOCs) can be added to the dilution air or at the aerosol inlet. Sampling usually occurs from the center of the chamber, while sampling at the chamber entrance and exit is done for aerosol evolution studies only. Mean aerosol transit time from the chamber inlet to the chamber center is largely determined by the total chamber flow and ranges between 5–15 min. The time constant for equilibration of aerosol mass concentration in the chamber also depends on the flow and is about 3–10 min for the typical flow range used. Usually experiments are performed after a 1 h equilibration period to allow the generation and measurement systems to stabilize.

The central chamber sampling manifold is a 30 cm length of stainless steel tube connected to the glass sections of the chamber with flanges. The inner diameter of the manifold is approximately 29 cm. There are four 0.95 cm ID sampling ports and two 5 cm stainless tubes with 7 cm flanges welded into the center section. One of the 5 cm tubes is used to house a temperature/humidity probe, and inside the other is a 25 mm ID glass manifold with sample ports for gas analyzers. The gas analyzer sampling lines are 0.78 cm ID PFA Teflon tubing sealed with o-ring fittings, passed through the 0.95 cm diameter manifold ports. The glass manifold extends about 5 cm into the slow-flow chamber.

Sampling from the slow-flow chamber may be considered sampling from still air since the average chamber velocity ranges from 0.2–0.7 m/min, and typical sampling flows range from 1 to 10 l/min. Conductive rubber tubing (Simolex Rubber Corporation) is used for aerosol sampling lines, to prevent losses due to electrostatic effects. Some losses of aerosol particles due to diffusion, settling, and impaction inside sampling lines are unavoidable, but every effort is made to minimize or to account for these losses. Sample line lengths are kept to a minimum, and bends in the lines are at the largest possible curvature to minimize impaction losses. Every effort is made to assure parity in the sample line configurations for instrument intercomparison studies.

The aerosol fast-flow chamber is a 10.2 cm diameter, 1.6 mm thick steel electrical conduit with 0.64 cm ID sampling ports placed approximately every meter along its adjustable length

(typically either 2.6 m or 16.5 m). The flow rates range from 5–50 l/min, resulting in aerosol transit times of tens of seconds to minutes. Diffusional losses in the fast-flow chamber are minimal (e.g., for 50 l/min flow and 2.6 m chamber length, losses of 20 nm particles are estimated to be approximately 2%) making it ideal for smaller particle experiments.

The portable, static aerosol chamber is a grounded 250 l steel barrel with multiple sampling ports. It is typically used for temporal storage and mixing of dry salt particles obtained via electrostatic classification and needed for size calibration of the scanning mobility size analyzers (SMPS; TSI Model 3936), performance evaluations of condensation particle counters (CPCs), etc. The portable chamber can be moved between the two laboratories, allowing access to the generation system of the PMLab and the particle sizing and characterization instrumentation in the SPLab. While sampling from the chamber, the particle concentration is constantly decreasing; however, this is not an obstacle for the experiments mentioned above. Chamber  $1/e$  time constants range from 15–60 min (e.g., for monodisperse 40 nm sodium chloride particles with initial concentration of  $9,000\ \text{particles}/\text{cm}^3$ , the time constant was measured to be 55 min) and do not impede the typical performance tests mentioned above.

## DATA ACQUISITION AND STORAGE

All analyzer and chamber data are collected with internal loggers, data acquisition, or dedicated computers. Generator and dilution flows, solution concentrations, etc., are recorded in laboratory logbooks. Collected data are periodically backed up on CDs and onto a central server. The postprocessing of raw data is typically performed on off-line PCs and stored on the central server soon after the completion of the experiment.

The flow chamber temperature and humidity data, as well as the room temperature and humidity data, is recorded as 5 min averages with a PC using a National Instruments A/D board and the LabWindows software package.

Data from gas analyzers, which produce analog signals, are collected continuously via a data logger (ESC Model 8816), processed, and stored as 1 min averages (the averaging time is user-selectable).

Aerosol sizing and counting instruments are connected to a dedicated PC via serial connections. Particle-sizing data from the SMPSs and concentration data from the CPCs are collected and plotted in real time using aerosol instrumentation manager software (TSI Version 5.2). Data then are exported as delimited text files and further analyzed. For some experiments, the CPC data are collected and stored using an IgorPro-based ASRC-developed software.

## CHARACTERISTICS OF GENERATED TEST AEROSOLS

The aerosol facility is equipped to produce a large variety of polydisperse and monodisperse aerosols of controlled composition, particle size, and concentration.

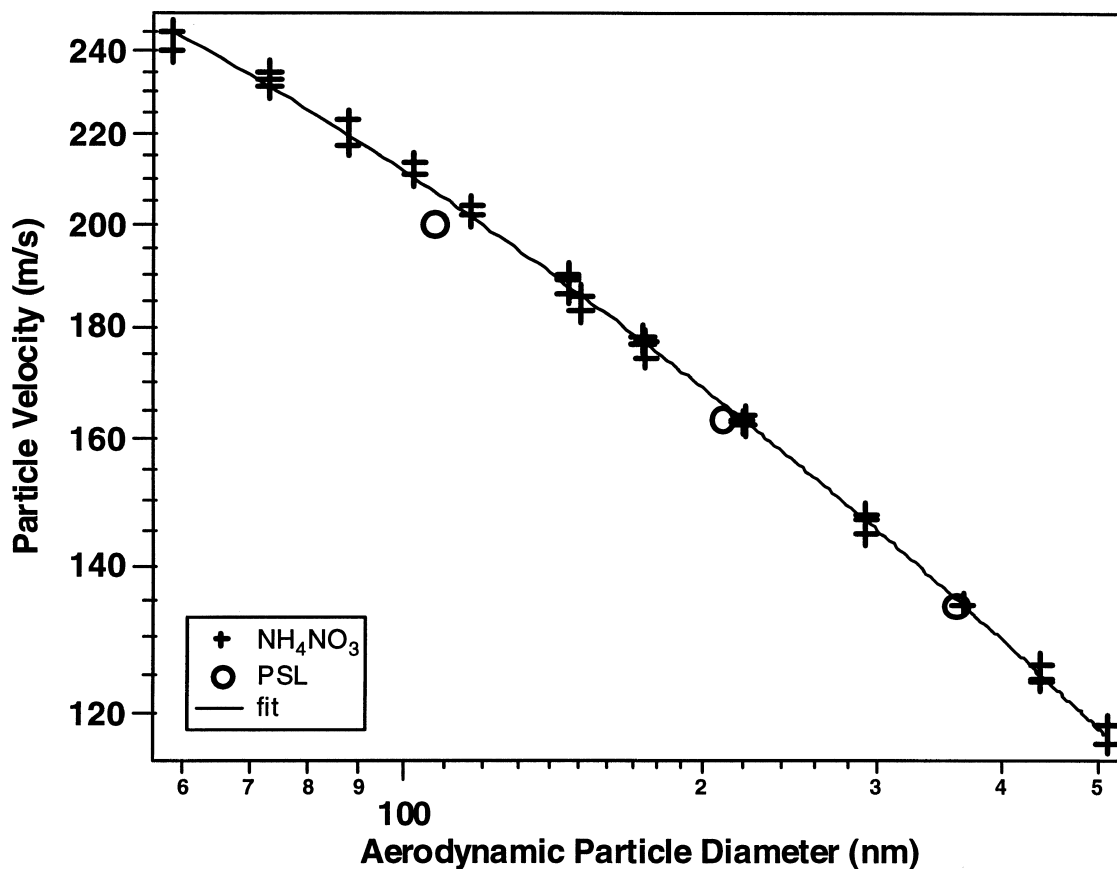
Among the pure inorganic salt aerosols generated in the facility are NaCl, NaNO<sub>3</sub>, KNO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>HSO<sub>4</sub>, and CuSO<sub>4</sub>. Organic aerosols include (but are not limited to) carbowax, polyvinyl alcohol, DOP, and organic acids (oxalic, glutaric, succinic, pinic, and pinonic). Mixed (inorganic/inorganic and inorganic/organic) aerosols have also been generated to evaluate instrumentation using particles simulating those observed in the atmosphere.

Commercially available NIST-traceable polystyrene latex particles (PSL) of known size (Duke Scientific) are used for quality assurance of the generated test aerosol. Individual particles are generated from a PSL suspension and are delivered directly to the instrument to be tested. In order to avoid formation of latex particle aggregates, the suspension is diluted and sometimes sonicated. SMPS size measurements of the PSL particles and of lab-generated sodium chloride particles (of the same nominal diameters as the PSL particles) were performed. Excellent agreement between these measurements was demonstrated. Similar results were observed in the size calibration of an Aerodyne Aerosol Mass Spectrometer (AMS). Figure 3 illustrates the use of lab-generated ammonium nitrate particles and PSL particles for one of the AMS calibrations (this facility application is discussed later in this article).

Physical characteristics of aerosols generated from solutions are summarized in Table 1. The table lists properties of aerosols as measured in the flow chambers and the instruments used to generate the aerosols. Spray atomization of solutions results in the production of polydisperse aerosols, which can be either directly used as test aerosol or further classified according to their electrical mobility to produce a monodisperse aerosol.

The size of aerosols generated from solution depends on the solution concentration (COA, EAG, VOAG) and on various operational parameters of the generation instruments, e.g., the liquid flow rate and the orifice size (VOAG), or the high voltage (EAG). The median diameter of the polydisperse aerosol generated by atomizing a solution also depends on the nature of the solute. The mass and number concentrations of aerosols generated from solutions (or suspensions) is determined by the solution/suspension concentration (COA, VOAG), and additional operating parameters of generation instruments, e.g., the vibration frequency (VOAG). The number/mass concentrations of the aerosol in the flow chambers can be adjusted by varying the dilution flow in the aerosol generator, the aerosol flow entering the dilution system, and the dilution flow.

When using the COA to produce a polydisperse aerosol, an increase of the solution concentration leads not only to an



**Figure 3.** Aerosol Mass Spectrometer time-of-flight calibration curve: comparison of particle velocity and aerodynamic particle diameter for NH<sub>4</sub>NO<sub>3</sub> and PSL particles.

**Table 1**  
Physical characteristics of aerosols generated from solutions

| Aerosol            | Size,<br>$\mu\text{m}$ | Mass<br>concentration,<br>$\mu\text{g}/\text{m}^3$ | Relative<br>humidity, % | Generation instrument(s)   |
|--------------------|------------------------|--|-------------------------|--|
| Polydisperse       | 0.01–0.5               | 5–1000   | 10–90                   | Constant output atomizer   |
| Monodisperse small | 0.005–0.4              | 5–30   | 10–90                   | Electrospray aerosol generator,<br>constant output atomizer +<br>electrostatic classifier<br>(with LDMA or Nano-DMA) |
| Monodisperse large | 0.5–20                 | 5–100  | <50                     | Vibrating orifice aerosol generator  |

increase of the aerosol concentration but to an increase of the median diameter of generated aerosol as well. Size distributions for ammonium sulfate aerosol for different concentrations of the solution are shown in Figure 4. Information on the size distribution of aerosols generated by the COA is essential for producing desired concentrations of monodisperse test aerosol by electrostatic classification of the polydisperse aerosol. The concentration of solutions used to generate aerosols by spray atomization range from 0.01 to 5 g/l. Salt concentrations shown in Figure 4 are typical for generation of the particles in the SPLab. Solution concentrations used in the PMLab typically start from 0.5 g/l. Figure 5 illustrates stable generation of a polydisperse  $\text{NaNO}_3$  aerosol from a 2 g/l salt solution. The figure shows time series of the median mass diameter and the mass concentration of a polydisperse as measured by the SMPS. Standard deviation of the mass concentration is 5% relative to the average of  $26 \mu\text{g}/\text{m}^3$ ; standard deviation of the mass mean diameter is 3% relative to the average of 177 nm.

Figure 4 also shows size distributions of small particles generated from spray atomization of pure distilled water. These aerosols will be referred to as residual aerosols. While the total number concentration of residual aerosols is approximately the same for HPLC-grade distilled water purchased from Baker and day-old ASRC-produced DD water, the particle size is much smaller for the aerosols generated from freshly produced ASRC DD water. The amount of residual aerosols can be decreased by three orders of magnitude by using fresh ASRC-produced DD water. This may become crucial for experiments with very small polydisperse particles (10–30 nm).

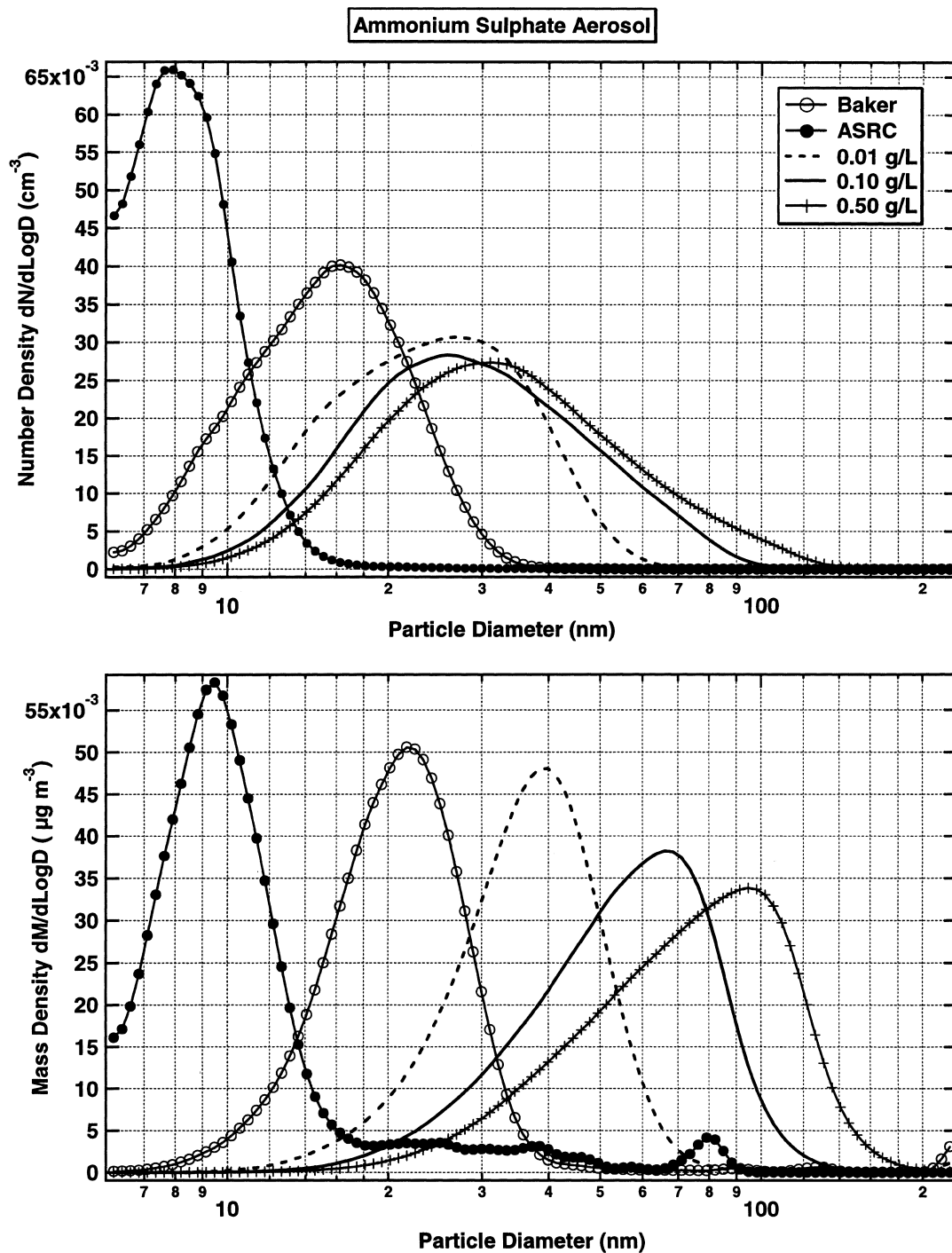
Smaller monodisperse aerosols are produced from polydisperse aerosols via electrostatic classification. Examples of size distributions of (1) “monodisperse” (obtained by keeping the DMA voltage at a preset value), (2) “dual monodisperse” (obtained by switching the DMA voltage between two preset values), and (3) “top-hat” (obtained by scanning through a preset voltage range) aerosol size distributions are shown in Figure 6. Aerosol size distributions similar to a top-hat type can also be obtained by keeping the DMA voltage constant and changing the ratio of the sample and the sheath flows to reduce DMA resolution.

As discussed earlier, nanosized carbon and metal particles are generated in the SPLab. Polydisperse carbon-containing particles have diameters 7–50 nm. The initial number concentration of the particles in the portable, static chamber depends on the length of torch burning. Initial number concentrations of about  $1 \times 10^5$  particles/ $\text{cm}^3$  (mass concentration in the range of  $1 \mu\text{g}/\text{m}^3$ ) are commonly used in small particle experiments conducted in the SPLab. Diameters of tungsten particles range from 5 to 15 nm. Typical number concentrations are on the order of  $10^6$  particles/ $\text{cm}^3$  as measured with a CPC. Both size and number concentration of the particles depend on the airflow in the fast-flow chamber and (to a lesser extent) on the magnitude of the electric current.

## AEROSOL CHARACTERIZATION AND MEASUREMENT INSTRUMENTATION

Aerosol detection and measurement instrumentation used in the aerosol facility can be divided into three groups: (1) mass or mass concentration (including chemical speciation), (2) aerosol sizing, and (3) aerosol number (see Figure 7). The reference method for total aerosol mass is a Partisol-FRM air sampler (R&P Model 2000-FRM). Continuous total aerosol mass concentration is monitored by a tapered element oscillating microbalance (TEOM) mass monitor (R&P Model 1400). The PMLab has three TEOM mass monitors, the standard TEOM mass monitor operated with its filter held at  $50^\circ\text{C}$  and two modified systems—a TEOM mass monitor with a Sample Equilibration System (SES) with its filter held at  $30^\circ\text{C}$  and equipped with a Nafion dryer; and a Differential TEOM mass monitor with an electrostatic precipitator (ESP), Nafion dryer, and filter held at  $30^\circ\text{C}$ . In all TEOM instruments, flow continuously passes through an oscillating Pallflex filter, and changes in the filter mass due to collected aerosol are calculated from the changes in oscillation frequency of the tapered element. Design and operation principles of a standard TEOM mass monitor are described in Patashnick and Rupprecht (1991), and modified systems are described in Meyer et al. (2000) and Patashnick et al. (2001).

A variety of instruments for the measurement of chemical-speciated mass aerosol concentration have been tested in the

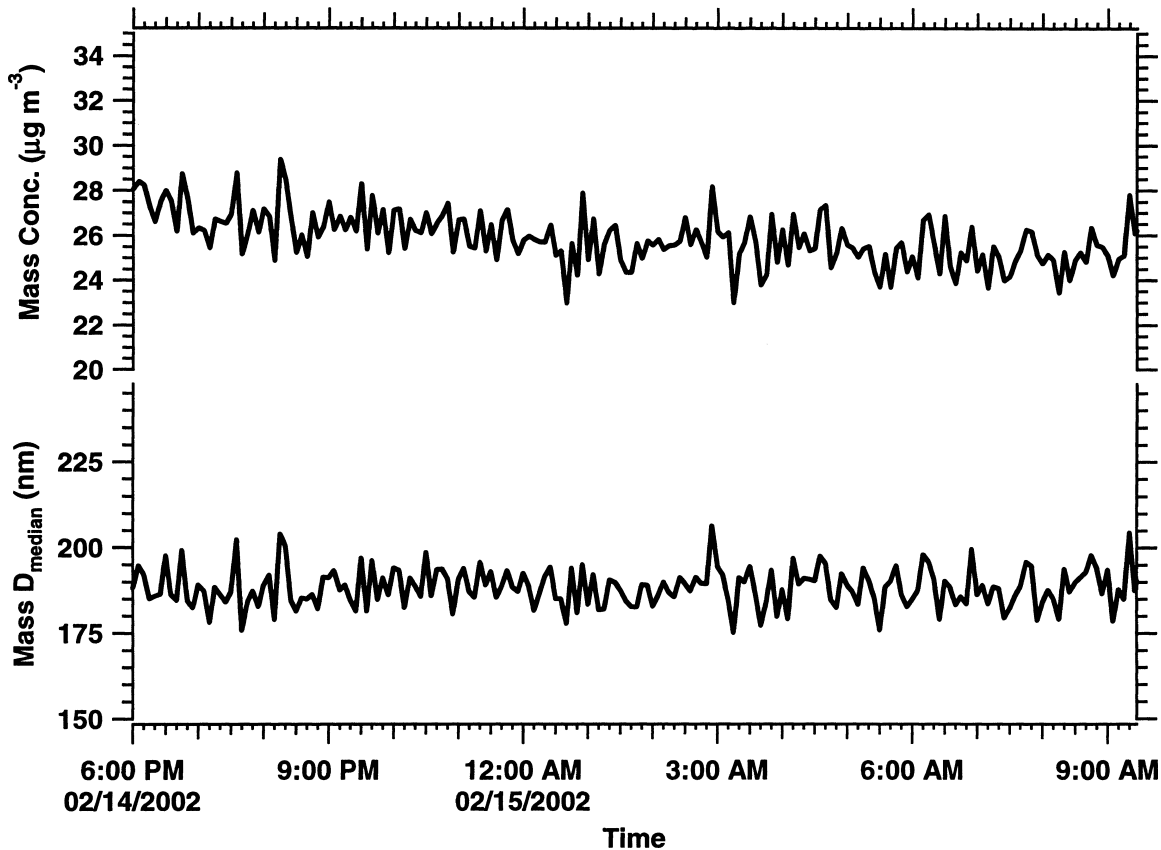


**Figure 4.** Size distributions of polydisperse  $(\text{NH}_4)_2\text{SO}_4$  aerosol, generated by the COA, and residual aerosol, generated with different supplies of nominally clean water.

aerosol facility. These include Ambient Particulate Carbon, Nitrate and Sulfate Monitors (R&P Models 5400, 8400N, and 8400S, respectively), an Aerosol Mass Spectrometer (AMS) built by Aerodyne Research Inc., and a Particle-Into-Liquid Sampler with Ion Chromatographs (PILS-IC) developed at

Georgia Institute of Technology. Comprehensive descriptions of these instruments are given elsewhere (Rupprecht et al. 1995; Jayne et al. 2000; Stolzenburg and Hering 2000; Weber et al. 2001). The AMS measures mass concentrations and size distributions of volatile and semivolatile aerosol chemical species.





**Figure 5.** Stable generation of polydisperse aerosol using the COA. Time series of the mass concentrations and mass median diameters of polydisperse aerosol generated from a 2 g/l solution of  $\text{NaNO}_3$ . Measurements were performed in the middle of the slow-flow chamber.

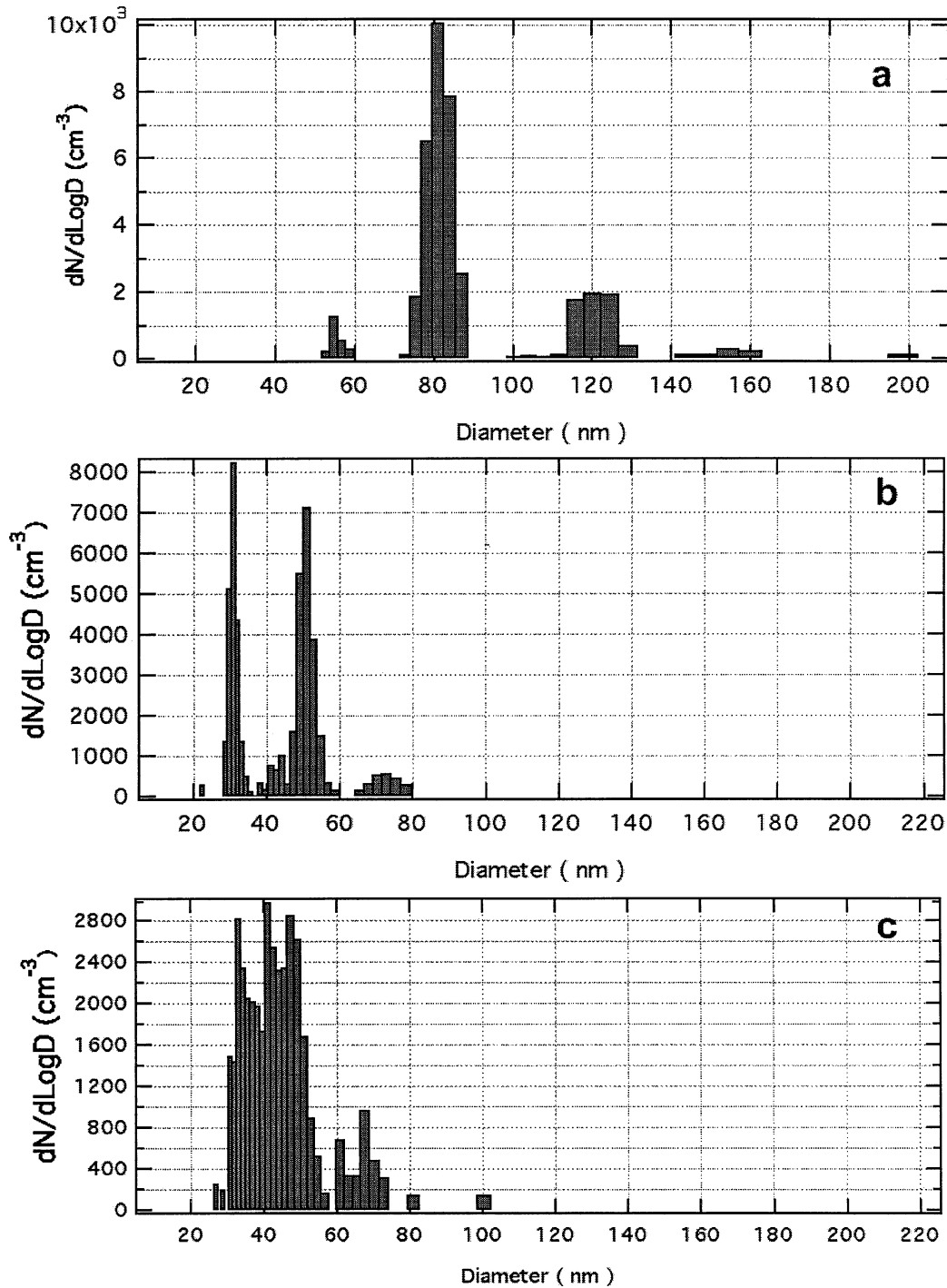
The PILS-IC measures mass concentrations of water-soluble inorganic ions and organic acids. The R&P 5400 carbon monitor uses a direct thermal- $\text{CO}_2$  technique to measure mass concentration of total carbon and organic carbon contained in particulate matter. The R&P 8400N monitor utilizes a flash vaporization technique followed by quantification of evolved nitrogen oxides to measure mass concentration of aerosol nitrate. The 8400S monitor uses the same flash vaporization technique followed by quantification of sulfur dioxide to measure aerosol sulfate.

Aerosol-counting instruments used for physical characterization of the generated particles include CPCs (TSI Models 3010, 3022, 3025) and expansion instruments (a GE CN Detector, a Pollak CNC (BGI Instruments), and a Gardner small particle detector, type CN (Gardner Associates). Particle-sizing instruments include the AMS, an aerodynamic particle sizer (APS; TSI Model 3322), an optical particle counter (PMS; ASASP-X), and a scanning mobility particle sizer (SMPS; TSI Model 3936) with a Long DMA or a Nano-DMA. The SMPS system includes a CPC used for particle counting, and may be used as a backup for mass concentration measurements for nonvolatile aerosol.

Reference instruments and/or calibration standards are needed for calibration, calibration verification, and performance

evaluation of aerosol instrumentation. Such standards are listed in the literature, e.g., Chen and John (2001), Cheng and Chen (2001). While most sources agree on the primary standards for aerosol size measurements (monodisperse spherical particles of known size) and for mass concentration measurements (gravimetric measurement of filter samples); no such agreement can be found regarding a standard for number concentration. Cheng and Chen (2001) suggest the use of an electrical classifier with an electrometer as a detector for a calibration standard. Chen and John (2001) call the aforementioned combination a *primary calibration standard*, along with a Pollak counter and a photographic counter, while an Aitken particle counter is suggested as the reference standard. More discussion on the comparisons of these standards can be found in Hogan (1979). Even more troubling is the following quote from NIST (2002): “Currently, there are no aerosol concentration standards for the CPCs, nor are there certified reference materials available for aerosol concentration standardization. The measurement process currently has no links or traceability to a standards granting organization.”

Although the aerosol facility has a Pollak CNC, the facility’s reference instrument for number concentration is a thoroughly



**Figure 6.** Special aerosol distributions produced by the electrostatic classifier: (a) monodisperse, (b) dual monodisperse, and (c) top-hat.

calibrated CPC 3025, which agrees within 20% or better with several other number concentration instruments (other CPCs or the SMPS/Nano-SMPS). According to Buzorius (2001), data from the CPC 3025 were very similar to Faraday electrometer total charge counter for particles larger than 5 nm.

Reference instruments routinely used in the PMLab for performance evaluation of the aerosol mass concentration instruments are the SES TEOM mass monitor or the Differential TEOM mass monitor. The choice of a specific reference TEOM mass monitor (SES or Differential) is largely determined by the

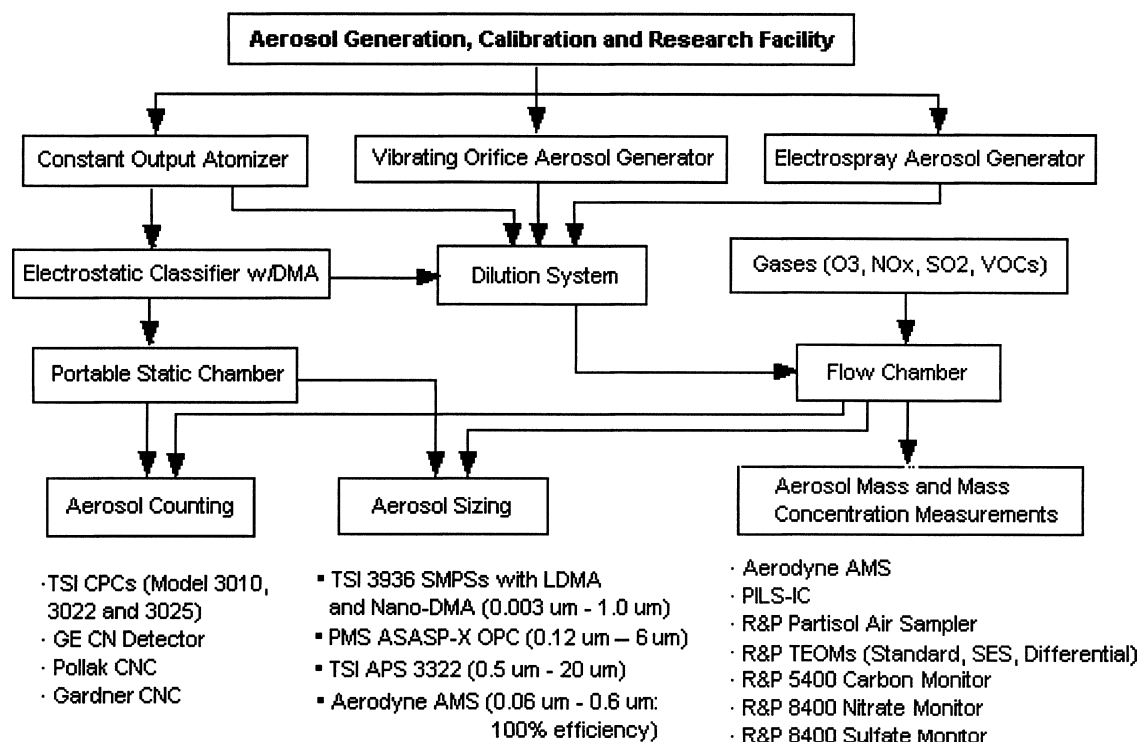


Figure 7. Schematic of the aerosol generation, calibration and research facility.

composition of the test aerosol. Nonvolatile inorganic aerosol can be quantitatively measured by the SES TEOM mass monitor, while semivolatile inorganic and organic aerosols cannot. For semivolatile aerosols, the Differential TEOM mass monitor appears to be a promising and more reliable reference instrument (Schwab et al. 2004). Figure 8 shows time series of the mass concentrations of polydisperse sodium nitrate aerosol measured by several mass-measuring instruments. For this type of experiment using nonvolatile aerosols, the SES TEOM mass monitor is used as a reference instrument.

Since mass is a reliable absolute standard, filter samples from the chamber are periodically collected using the Partisol-FRM. Handling and weighing of the filter samples is done in a temperature- and humidity-controlled microweighing chamber according to EPA guidelines. A brief description of the procedure can be found in Schwab et al. (2004). The Sartorius MC5 microbalance used for weighing the filters was calibrated with Class "1" weights, is traceable to NIST, and conforms to NIST accuracy standards.

Comparisons between the filter samples weighed by the microbalance and simultaneous measurements using the TEOM mass monitor are used to confirm the accuracy of the TEOM monitor for continuous mass measurement. Typically the difference between mass concentrations measured by the Partisol and the TEOM mass monitors (for nonvolatile or only slightly volatile compounds) is no more than 5–15% (ref. to Partisol). Therefore, using the TEOM mass monitors in conjunction with specific aerosol generation processes for evaluation of chem-

ical speciation aerosol instrumentation is itself traceable to a NIST-certified microbalance. Laboratory QC/QA procedures include regular maintenance of the TEOM mass monitors and the Partisol-FRM sampler, as well as maintenance and calibration of the chemical speciation aerosol instrumentation and aerosol sizing and counting instrumentation.

## AEROSOL FACILITY APPLICATIONS

Most of the instruments mentioned above have been deployed in field programs. Many of the facility applications listed in this section were a part of the Quality Assurance program for the PM<sub>2.5</sub> Technology Assessment and Characterization Study–New York (PMTACS–NY). Whenever possible, performance of the field instruments is evaluated in the laboratory prior to deployment in the field using a variety of synthetic aerosols and operating conditions. This is especially useful and instructive for recently commercialized instrumentation (8400N, 8400S) and research-grade instruments (AMS, PILS-IC). Intercomparison of several aerosol mass- and number-concentration-measuring instruments is usually a part of such evaluations. Figure 8 shows the results of one of these comparisons for the 8400N Ambient Particulate Nitrate Monitor. The facility has been also used to calibrate and verify manufacturer's calibration curves for aerosol-sizing instruments. More extensive tests using synthetic aerosols with known properties are essential for the interpretation of some field measurements (e.g., AMS, PILS-IC) and for providing explanations

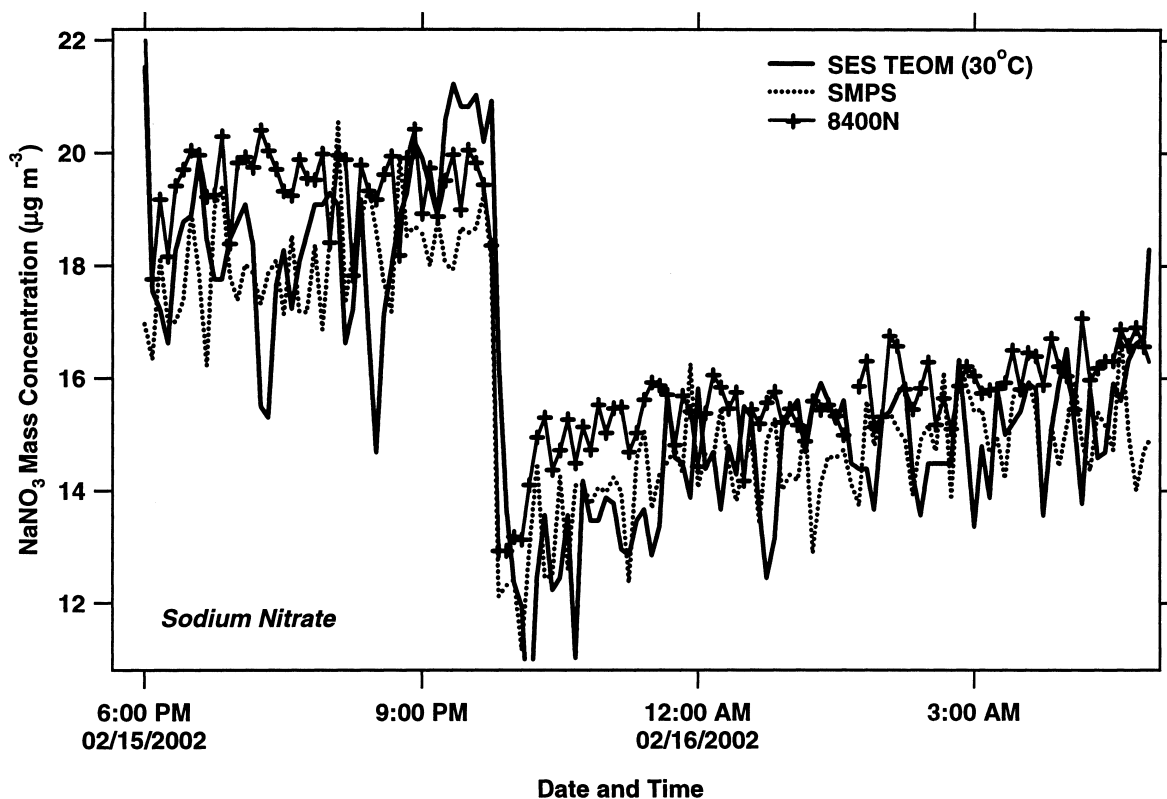


Figure 8. 8400N-SES TEOM mass monitor—SMPS comparison for polydisperse  $\text{NaNO}_3$  aerosol.

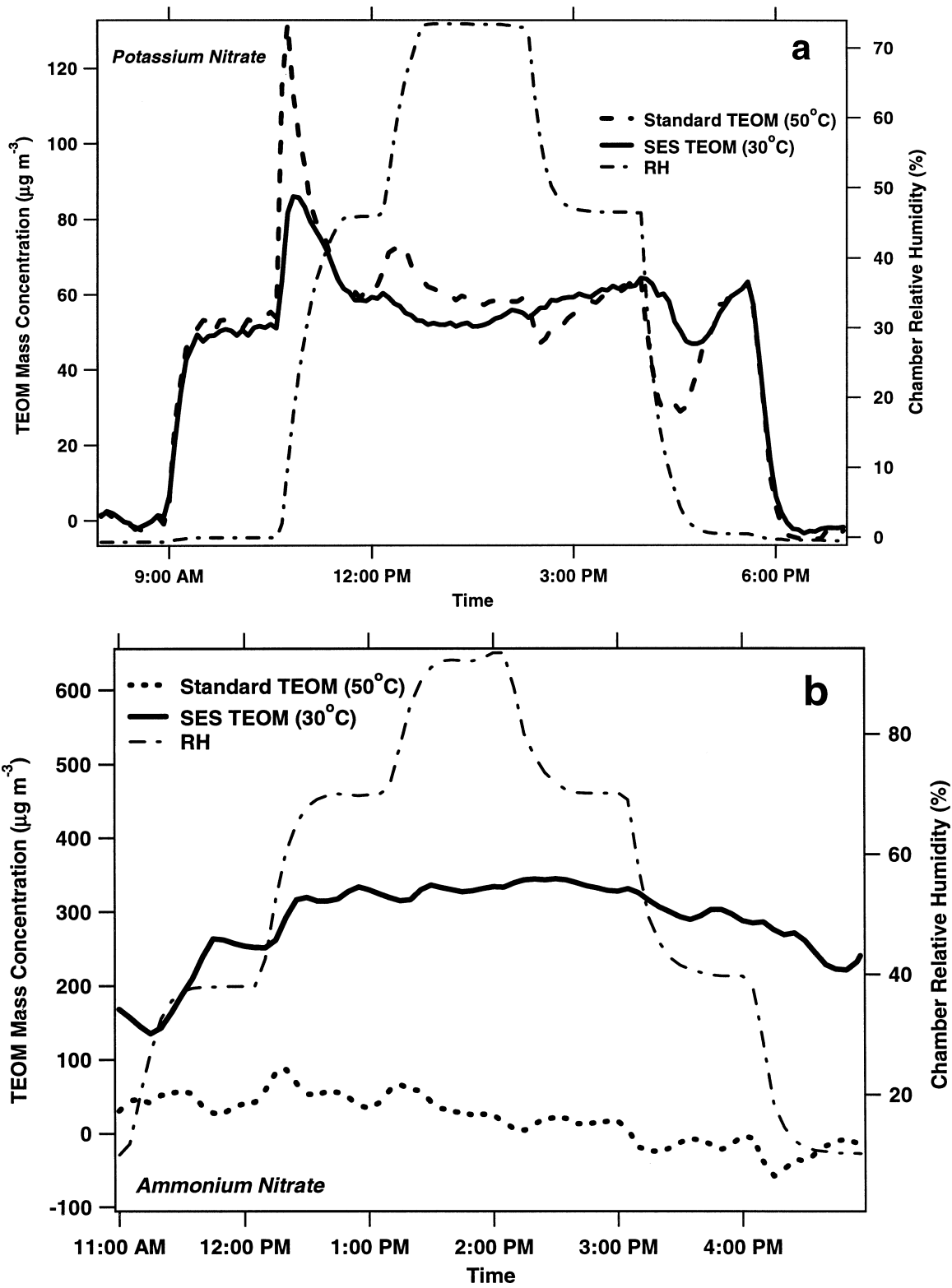
of discrepancies between field measurements from different instruments.

Applications of the aerosol facility include (1) size calibration of aerosol instruments, e.g., the AMS and the SMPS (note the calibration plot shown in Figure 3); (2) performance evaluation of the SMPS, Nano-SMPS, and several models of CPC; (3) performance evaluation of the 8400S and 8400N monitors and studies of the effect of varying ambient conditions, operational parameters, and design modifications on the performance of those monitors; (4) extensive testing of the efficacy of the TEOM mass monitor with the SES (Schwab et al. 2004); (5) testing of several aerosol mass-measuring technology upgrades, such as a Filter Dynamics Measurement System (FDMS) for a TEOM monitor and a Differential TEOM mass monitor; (6) time-of-flight calibration of the AMS; (7) determination of fragmentation patterns for  $\text{CaNO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $(\text{NH}_4)\text{HSO}_4$ ,  $\text{NaNO}_3$ , and a mixture of  $\text{NH}_4\text{NO}_3/(\text{NH}_4)_2\text{SO}_4$  particles in the AMS, as well as studies of the effect of the AMS heater temperature on the fragmentation patterns of various aerosols; and (8) investigation of the AMS sulfate correction factor. Some of these examples are discussed in more detail below.

#### Comparison of a SES-Equipped TEOM Mass Monitor with a Standard TEOM Mass Monitor—Ramped Humidity Tests

Performance of a TEOM mass monitor with the SES (a Nafion dryer is placed upstream a main inlet line, a filter is maintained at

$30^\circ\text{C}$ ) was extensively tested in the PMLab. As a part of the testing, the TEOM was compared to a standard TEOM mass monitor (a filter is maintained at  $50^\circ\text{C}$ ). The polydisperse aerosol was generated using the COA and equilibrated in the chamber before being sampled. Figures 9a and 9b illustrate the responses of both TEOM mass monitors to humidity changes in the slow-flow chamber. Figure 9a shows time series of the mass concentration of ammonium sulfate aerosol measured by both TEOM mass monitors. The relative humidity in the chamber was step-changed as follows: 0%~45%~75%~45%~0%. The apparent mass concentration measured by the standard TEOM mass monitor exhibited large swings corresponding to humidity changes, while the SES TEOM mass monitor showed much weaker response to those changes. An additional feature to be noted in this figure is that the mass concentrations measured during stable relative humidity periods agree very well for both instruments. This is to be expected for ammonium sulfate, which is a nonvolatile aerosol. Figure 9b shows time series of the mass concentration of ammonium nitrate aerosol, which is, in contrast to ammonium sulfate, a semivolatile aerosol. Ammonium nitrate is poorly retained on the standard TEOM filter, as a result of increased volatilization at  $50^\circ\text{C}$ , while the SES TEOM mass monitor measures much higher concentrations of ammonium nitrate. Responses of the SES TEOM mass monitor to the ramped humidity changes ( $\sim 10\% \sim 40\% \sim 70\% \sim 95\% \sim 70\% \sim 40\% \sim 10\%$ ) are less pronounced and in some cases eliminated.



**Figure 9.** Comparison of the standard  $50^{\circ}\text{C}$  TEOM mass monitor– $30^{\circ}\text{C}$  SES TEOM mass monitor response ramped humidity changes in the flow chamber: (a) polydisperse  $\text{KNO}_3$  aerosol, and (b) polydisperse  $\text{NH}_4\text{NO}_3$  aerosol.

These experiments allowed us to conclude that the SES TEOM mass monitor is much less sensitive to ambient humidity changes and that it is more suitable for measuring semivolatile aerosols than the standard TEOM mass monitor (although evaporative losses do occur at 30°C as well). A complete description of the SES TEOM mass monitor tests, experimental conditions used in these tests, a list of compounds used in the experiments, as well as detailed discussion of the results can be found in (Schwab et al. 2004).

### **Self-Referencing Differential TEOM Mass Monitor—Measurements of Semivolatile Aerosols and Volatile/Nonvolatile Mixed Aerosols**

Performance evaluation of a TEOM mass monitor with the electrostatic precipitator (ESP) was done in the PMLab. The ESP is located downstream of a Nafion dryer and is used to remove particles from the sample flow. Switching the ESP voltage on and off allows the instrument to self-reference the mass concentration measurements. As a result, the effects of many mass-measuring artifacts can be mitigated. The polydisperse aerosols for these tests were generated using the COA and equilibrated in the chamber before the sampling. As a part of the testing, Differential TEOM mass monitor measurements were compared to those from a SES TEOM mass monitor (filters on both instruments were maintained at 30°C).

Figures 10a and b show results of the comparisons for ammonium nitrate and for a mixed ammonium sulfate/oxalic acid aerosol. The Differential TEOM mass monitor measured higher mass concentrations of ammonium nitrate compared to the SES TEOM mass monitor. The opposite was observed in the case of mixed ammonium sulfate (nonvolatile) and oxalic acid (volatile) aerosol. The Differential TEOM mass monitor therefore is capable of accounting for volatilization of previously collected PM and for organic gas adsorption on the filter. The ability of the Differential TEOM mass monitor with the ESP to accurately measure mass concentrations of volatile aerosol makes its presence invaluable for measurement of volatile species. Detailed description and discussion of the Differential TEOM tests, which also included the studies of the particle efficiency removal by the ESP and effect of gaseous SO<sub>2</sub> and NO<sub>x</sub> on the ESP performance, is given in Schwab et al. (2004).

### **Time-of-Flight Calibration of the AMS**

The Aerosol Mass Spectrometer (AMS) is capable of measuring chemically resolved size distributions by setting the quadrupole mass spectrometer on a specific mass and measuring the time-resolved ion signal at this mass (Drewnick et al. 2004b). For this purpose the aerosol beam is chopped by a mechanical chopper and the flight time of the particles through the particle-sizing chamber of the AMS is determined by the time-resolved mass spectrometer measurement. Transformation of the measured flight times of the particles into aerodynamic particle diameter is done using a time-of-flight calibration.

The time-of-flight calibration of the AMS was performed in the PMLab, using monodisperse ammonium nitrate and polystyrene latex (PSL) spheres of known diameter. Ammonium nitrate particles were generated by atomizing an ammonium nitrate solution and selecting a certain particle size from the dried polydisperse aerosol with a previously calibrated DMA. An aerosol of PSL particles of certified diameters (Duke Scientific,  $D_p = 100, 200, \text{ and } 350 \text{ nm}$ ) was generated from a PSL suspension.

The monodisperse aerosols were sampled into the AMS where the flight time was determined for every particle size. The flight time was converted into particle velocity using the length of the flight path (39 cm), and the geometric particle diameter  $D_{\text{mob}}$  was converted into the aerodynamic diameter  $D_{\text{aero}}$  using

$$D_{\text{aero}} = D_{\text{mob}} \cdot \rho \cdot \chi^{-1},$$

where  $\rho$  is the particle density and  $\chi$  is the dynamic shape factor of the particles. For ammonium nitrate  $\rho$  is 1.72 g/cm<sup>3</sup> and  $\chi$  is 1.18, and for PSL particles  $\rho$  is 1.054 g/cm<sup>3</sup> and  $\chi$  is 1.00 (sphere). Note, that this “vacuum” aerodynamic diameter as defined here differs from the classical aerodynamic diameter. It is measured under free molecular flow expansion conditions as they occur in the inlet of the AMS, while the classical aerodynamic diameter is measured under continuum flow expansion conditions (Jimenez et al. 2003).

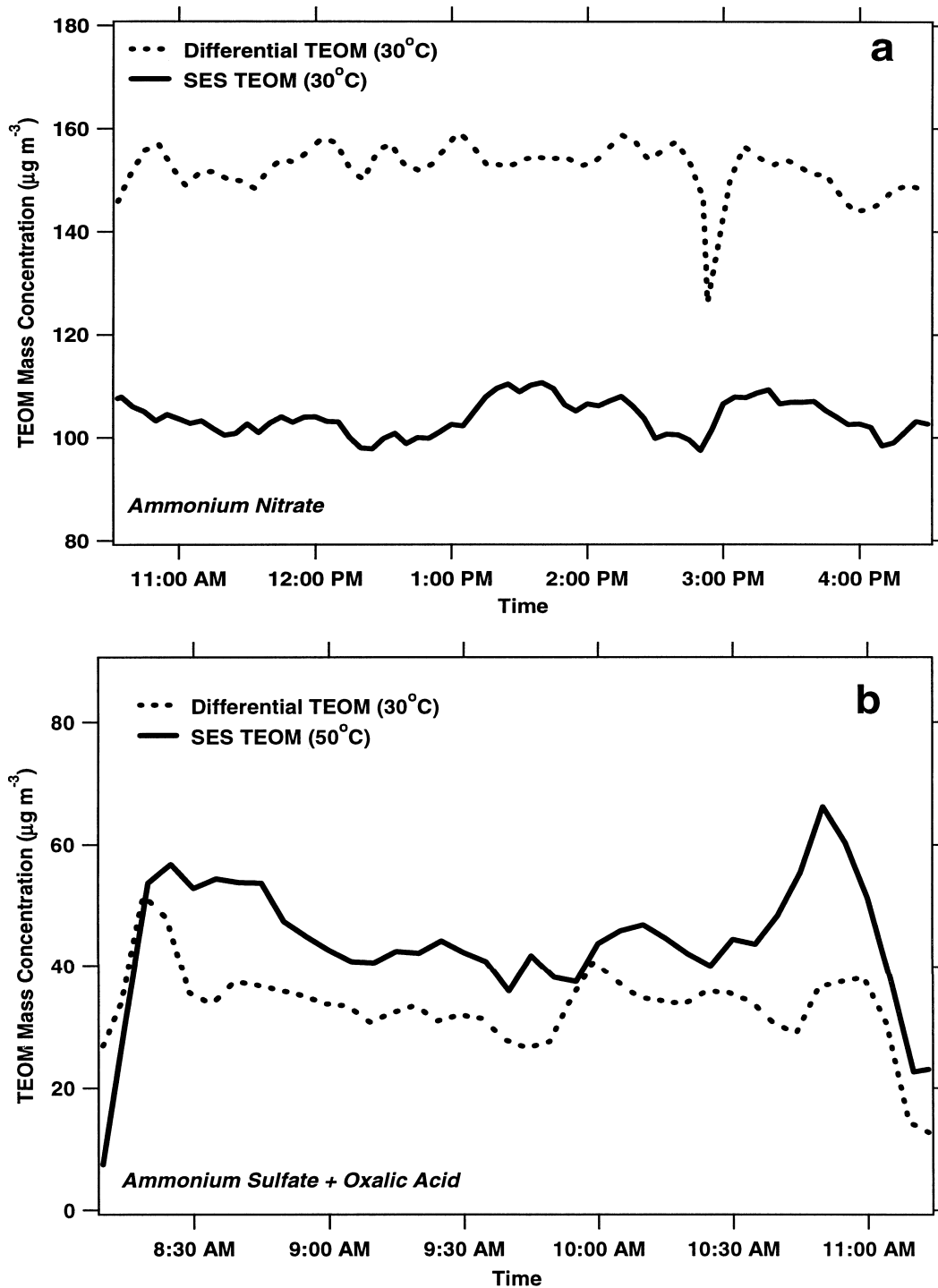
As shown in Figure 3, the measured particle velocities  $V_p$  were plotted versus aerodynamic particle diameter  $D_{\text{aero}}$  and fitted with the expression given in Jayne et al. (2000):

$$V_p = \frac{V_g}{1 + (D_{\text{aero}}/D^*)^b},$$

where  $V_g$  is the gas velocity at the exit of the aerodynamic lens, and  $D^*$  and  $b$  are fit parameters. Using this equation and the fitted coefficients, measured particle velocities were converted into aerodynamic particle diameters.

### **Determination of Sulfate and Nitrate Fragmentation Patterns**

The AMS determines ammonium, nitrate, sulfate, and total nonrefractory organics mass concentrations from the bulk aerosol mass spectrum (Drewnick et al. 2004a). While the inorganic species only have a very limited number of fragments in the mass spectrum, fragments of the “organics” are spread almost all over the mass spectrum. The mass concentrations of the inorganic species were calculated from the mass spectrometric signals of their most prominent fragments to avoid serious interferences by “organic” fragments at the less-intense inorganic signals. To correct these mass concentrations for the omitted fragments the fragmentation patterns of the particular inorganic species as they appear in the evaporation and ionization process of the AMS have to be known. These fragmentation patterns were also used to correct the rest of the mass spectrum (that



**Figure 10.** Differential TEOM mass monitor–SES TEOM mass monitor comparison. Filters on both TEOM monitors are maintained at 30°C; the Differential TEOM monitor is also equipped with the SES upstream the ESP: (a) polydisperse  $\text{NH}_4\text{NO}_3$  aerosol and (b) polydisperse  $\text{NH}_4\text{NO}_3$  + oxalic acid aerosol.

is, those associated with the organics mass concentration) for contributions from the minor inorganic fragments.

The nitrate and sulfate fragmentation patterns were determined by laboratory experiments in the PMLab using dried am-

monium nitrate and ammonium sulfate particles. The particles were generated by atomizing liquid solutions of the salts, using argon (99.998%) as carrier gas to avoid confounding mass contributions from the various components of air to the mass spectra

of the select particle species. The aerosol first passes an aerosol neutralizer (TSI Model 3054) and a DMA (TSI Model 3080 with EC TSI Model 3081). The sheath flow of the DMA is dried with a diffusion dryer and filled with CaSO<sub>4</sub>. The monodisperse aerosol flow then passes an aerosol dryer (TSI Model 3062, filled with silica gel) before it is transported to the inlet of the AMS.

The AMS is operated in the mass spec mode (Drewnick et al. 2004a), where the complete mass spectrum (1 to 300 amu) is measured for the bulk aerosol. First the whole setup is purged with argon for 30 min to remove the air from the system. The DMA mainly is used as a switch to turn the aerosol flow on and off without changing any gas flows. The aerosol is turned off by setting the DMA to 0 nm to determine the gas background with the AMS. With the DMA set to 200 nm the particle (plus gas) mass spectrum is measured.

The fragmentation pattern of nitrate was determined by averaging the particle mass spectrum of ammonium nitrate particles for 15 min with the background spectrum measured before and after each particle measurement for 15 min each. Using the same sampling scheme, the sulfate fragmentation pattern was measured using ammonium sulfate particles. Then the difference of the “particle spectrum” and the “background spectrum” was computed to extract the pure particle contribution to the spectra without any gas-phase interference. The fragmentation patterns reported here were taken from seven measurements of ammonium nitrate particles (Table 2) and five measurements of ammonium sulfate particles (Table 3).

In Tables 2 and 3 the masses and the fragments associated with these masses are listed together with the relative intensity of each line (relative to the most prominent mass) and the fraction of the contribution of the signal to the total fragmentation pattern. Because some of the minor isotopes produce very small signals, and consequently low signal-to-noise ratios, the relative intensities of these minor isotopic fragments were calculated from the signal measured at the main isotope. The measured signal intensities for these minor isotopes were consistent with the calculated values, but with lower uncertainty limits. The uncertainties of the fragment fractions given in Tables 2 and 3 correspond to one standard deviation. The measurements described here were taken with a temperature of the AMS heater of 500°C,

**Table 2**

Fragmentation pattern of particulate nitrate, measured at ammonium nitrate particles with the AMS

| Mass | Fragment                      | Rel. intensity | Fraction (%) |
|------|-------------------------------|----------------|--------------|
| 30   | NO <sup>+</sup>               | 100.00         | 56.49 ± 4.64 |
| 31   | NO <sup>+</sup>               | 0.41           | 0.23 ± 0.02  |
| 32   | NO <sup>+</sup>               | 0.20           | 0.11 ± 0.01  |
| 46   | NO <sub>2</sub> <sup>+</sup>  | 74.93          | 42.32 ± 8.04 |
| 47   | NO <sub>2</sub> <sup>+</sup>  | 0.34           | 0.19 ± 0.04  |
| 48   | NO <sub>2</sub> <sup>+</sup>  | 0.30           | 0.17 ± 0.03  |
| 63   | HNO <sub>3</sub> <sup>+</sup> | 0.86           | 0.49 ± 0.11  |

**Table 3**

Fragmentation pattern of particulate sulfate, measured at ammonium sulfate particles with the AMS

| Mass | Fragment   | Rel. intensity | Fraction (%) |
|------|--|----------------|--------------|
| 16   | O <sup>+</sup>   | 0.70           | 0.18 ± 0.01  |
| 17   | OH <sup>+</sup>  | 16.80          | 4.25 ± 0.34  |
| 18   | H <sub>2</sub> O <sup>+</sup>                                | 78.16          | 19.75 ± 1.58 |
| 24   | SO <sup>2+</sup>   | 0.62           | 0.16 ± 0.02  |
| 32   | S <sup>+</sup>   | 14.06          | 3.55 ± 0.09  |
| 33   | S <sup>+</sup>   | 0.11           | 0.03 ± 0.001 |
| 34   | S <sup>+</sup>   | 0.62           | 0.16 ± 0.004 |
| 48   | SO <sup>+</sup>  | 67.09          | 16.95 ± 0.41 |
| 49   | SO <sup>+</sup>  | 0.56           | 0.14 ± 0.003 |
| 50   | SO <sup>+</sup>  | 3.11           | 0.79 ± 0.02  |
| 64   | SO <sub>2</sub> <sup>+</sup>                                 | 100.00         | 25.26 ± 1.50 |
| 65   | SO <sub>2</sub> <sup>+</sup> , HSO <sub>2</sub> <sup>+</sup> | 5.69           | 1.44 ± 0.17  |
| 66   | SO <sub>2</sub> <sup>+</sup> , HSO <sub>2</sub> <sup>+</sup> | 4.92           | 1.24 ± 0.02  |
| 80   | SO <sub>3</sub> <sup>+</sup>                                 | 56.70          | 14.33 ± 2.15 |
| 81   | SO <sub>3</sub> <sup>+</sup> , HSO <sub>3</sub> <sup>+</sup> | 26.23          | 6.63 ± 0.53  |
| 82   | SO <sub>3</sub> <sup>+</sup> , HSO <sub>3</sub> <sup>+</sup> | 1.32           | 0.33 ± 0.03  |
| 83   | HSO <sub>3</sub> <sup>+</sup>                                | 1.32           | 0.33 ± 0.03  |
| 98   | H <sub>2</sub> SO <sub>4</sub> <sup>+</sup>                  | 16.70          | 4.22 ± 0.51  |
| 99   | H <sub>2</sub> SO <sub>4</sub> <sup>+</sup>                  | 0.16           | 0.04 ± 0.005 |
| 100  | H <sub>2</sub> SO <sub>4</sub> <sup>+</sup>                  | 0.88           | 0.22 ± 0.03  |

approximately the heater temperature used in field campaigns. It is expected that the fragmentation patterns change with changing heater temperature. Experiments where the fragmentation patterns were determined for different heater temperatures were carried out recently and will be reported elsewhere (Drewnick and Demerjian 2004c).

### Investigation of the AMS Sulfate Correction Factor

Ambient particulate mass concentrations were determined with the AMS operating in the mass spec mode where it measures the complete mass spectrum (1–300 amu) of the bulk aerosol (Drewnick et al. 2004a). Absolute mass concentrations were calculated from the ion signals of the mass lines that are associated with the species of interest using the calibrated ionization efficiency, which is determined with lab-generated ammonium nitrate particles of known size. With this calibration and the measured inlet flow rate, the calculation of ambient nitrate concentrations from ammonium nitrate particles is straightforward (Jimenez et al. 2003):

$$C_{\text{NO}_3} = \sum_f \frac{J_f \cdot M_{\text{NO}_3}}{\text{IE} \cdot G \cdot Q},$$

where  $J_f$  is the multiplier signal at fragment  $f$ ,  $M_{\text{NO}_3}$  is the molecular weight of nitrate, IE is the calibrated ionization and quadrupole transmission efficiency,  $G$  is the multiplier gain and  $Q$  is the inlet flow rate.



Since approximately 99% of the nitrate ion signal is found in the two most prominent fragments ( $m/z = 30$  and  $46$  amu; see section on fragmentation patterns) and only these two masses were used in the ionization efficiency calibration of the AMS, using just these two fragments yields the nitrate mass concentration with sufficient accuracy. However, for ammonium sulfate particles this calculation is slightly more complicated and needs several corrections:

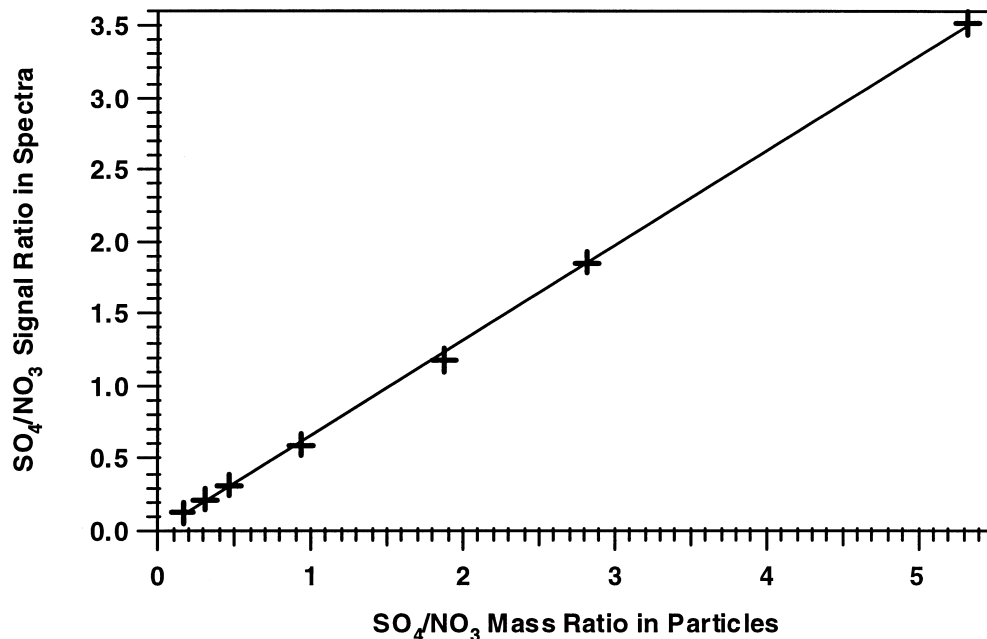
- To avoid interferences with organic fragments, only the three most prominent fragments of sulfate ( $m/z = 48, 64,$  and  $80$  amu) were used to calculate the sulfate mass concentrations. According to the fragmentation pattern measurements, these fragments only contain about  $56.54 \pm 2.65\%$  of the total sulfate ion signal. The omitted fragments were accounted for by multiplying the mass concentration of the sum of these three fragments with a correction factor of  $1.77 \pm 0.08$ .
- Due to their nonsphericity, ammonium sulfate particles are subject to lift forces in the aerodynamic lens, which results in an enhanced divergence of the aerosol beam. This effect leads to an incomplete collection of these particles in the heater and ionizer assembly of the AMS. In addition, ammonium sulfate has a different ionization efficiency than ammonium nitrate, which is the compound used for field calibrations. To account for these two effects another correction factor is needed for sulfate mass concentrations. During the PMTACS-NY 2001 campaign, this correction factor was determined in the field by comparison of a limited data set of the AMS sulfate with another semicontinuous technique

(Drewnick et al. 2004a) to be 2.30 (with an estimated uncertainty of 10%:  $\pm 0.20$ ).

Subsequent to the field measurements in the PMTACS-NY 2001 campaign, experiments in the PMLab were conducted to obtain additional information about the sulfate particle focusing properties and the evaporation and ionization process in the AMS in order to investigate the sulfate correction factor. Mixed ammonium nitrate and ammonium sulfate particles were generated from aqueous solutions of different ratios of these salts using the constant output atomizer. With the DMA, 200 nm particles were selected from the polydisperse aerosol and passed through an aerosol dryer before transport to the AMS inlet. In the AMS these mixed particles were measured with the mass spec mode.

For every mixing ratio, the ratio of sulfate-to-nitrate mass in the particles was calculated assuming that the ammonium-sulfate-to-ammonium-nitrate ratio in the particles is the same as in the solution. In the mass spectra  $m/z$  30 and 46 amu were used for calculation of the nitrate signal and  $m/z$  48, 64, and 80 amu were used for the sulfate signal. In Figure 11 the measured signal ratio of sulfate to nitrate is plotted versus the sulfate-to-nitrate mass ratio in the particles.

The linear correlation of the signal ratio versus mass ratio with intercept forced through zero has a slope of  $0.658 \pm 0.004$ . After correction for the omitted sulfate fragments, it is  $1.164 \pm 0.009$ . This means that the sulfate ionization efficiency is 16.4% larger than the ionization efficiency of nitrate (only  $m/z$  30 and 46 amu used, as in the ionization efficiency calibration of the AMS). Therefore, measured sulfate mass concentrations have to be corrected for ionization efficiency by a factor of



**Figure 11.** Ratio of  $\text{SO}_4$  (only  $m/z$  48, 64, and 80 amu) to  $\text{NO}_3$  (only  $m/z$  30 and 46 amu) signal in the mass spectra plotted versus sulfate-to-nitrate mass ratio in the particles.

$0.859 \pm 0.006$ . This also enables us to calculate the correction factor used to correct for incomplete focusing of the sulfate particles into the evaporation and ionization chamber from the total correction factor determined during PMTACS-NY 2001. The particle collection correction factor for these sulfate particles is  $2.327 \pm 0.233$ , while most of this uncertainty is due to the uncertainty of the instrument intercomparison during PMTACS-NY 2001.

## SUMMARY AND CONCLUSIONS

An aerosol generation, calibration, and research facility has been developed at the Atmospheric Sciences Research Center, University at Albany. The aerosol generation, dilution, and equilibration systems are quite flexible and can be used and modified, if necessary, to produce and handle aerosol with a wide range of specified properties (size, concentration, volatility, composition, etc.). Prominent features of the facility include: equilibration of aerosols at a controlled relative humidity in a large (450 l) slow-flow chamber, and controlled addition and monitoring of reactive trace gases ( $O_3$ ,  $NO_x$ ,  $SO_2$ , and VOCs). Aerosol mass concentration measurements are NIST traceable through the use of a calibrated microbalance for gravimetric measurements of filter samples. The facility maintains and operates a wide variety of commercial aerosol mass, mass-concentration, chemical speciation, sizing, and counting instruments, as well as research-grade instruments (e.g., AMS and the PILS-IC), which provide extensive capabilities for characterizing the chemical and physical properties of generated aerosols.

The combination of generation and analytical capabilities and the applications discussed demonstrate the uniqueness of the aerosol facility and its utility for basic experimental aerosol research. The aerosol facility as currently equipped has served in evaluating aerosol instrumentation, including quality assurance testing, and the intercomparison, performance evaluation, and calibration of aerosol instrumentation. Instruments calibrated and/or evaluated to date include the SMPSs and the CPCs, the standard TEOM mass monitor, the SES TEOM mass monitor, the Differential TEOM mass monitor with the ESP, the ambient particulate sulfate, nitrate, and carbon monitors, the PILS-IC, and the AMS.

## LIST OF ABBREVIATIONS

|               |   |
|---------------|---|
| 8400N (8400S) | Ambient Particulate Nitrate (Sulfate) monitor |
| AMS           | Aerosol Mass Spectrometer                     |
| amu           | atomic mass unit                              |
| APS           | aerodynamic particle sizer                    |
| ASRC          | Atmospheric Sciences Research Center          |
| CNC           | condensation nuclei counter                   |
| COA           | constant output atomizer                      |
| CPC           | condensation particle counter                 |
| DD water      | distilled/deionized water                     |
| DMA           | differential mobility analyzer                |
| EAG           | electrospray aerosol generator                |

|          |  |
|----------|--|
| EC       | electrostatic classifier                             |
| ESP      | electrostatic precipitator                           |
| FDMS     | Filter Dynamics Measurement System                   |
| FRM      | Federal Reference Method                             |
| ID       | internal diameter                                    |
| LDMA     | differential mobility analyzer with a long column    |
| Nano-DMA | differential mobility analyzer with a nano-column    |
| OPC      | optical particle counter                             |
| PILS-IC  | Particle-Into-Liquid Sampler with Ion Chromatographs |
| PSL      | polystyrene latex                                    |
| R&P      | Rupprecht and Patashnick Company, Inc.               |
| SES      | Sample Equilibration System                          |
| SMPS     | scanning mobility particle sizer                     |
| TEOM     | tapered element oscillating microbalance             |
| VOAG     | vibrating orifice aerosol generator                  |
| VOCs     | volatile organic compounds                           |

## REFERENCES

- Buzorius, G. (2001). Cut-Off Sizes and Time Constants of the CPC 3010 Operating at 1–3 Lpm Flow Rates, *Aerosol Sci. Technol.* 35:577–585.
- Charlson, R. J., Schwartz, S. E., Hales, J. M., Cess, R. D., Coakley, Jr., J. A., Hansen, J. E., and Hofmann, D. J. (1992). Climate Forcing by Anthropogenic Aerosols, *Science* 255:423–430.
- Chen, B. T., and John, W. (2001). Instrument Calibration. In *Aerosol Measurement. Principles, Techniques and Applications*, edited by P. A. Baron and K. Willeke. John Wiley and Sons, Inc., New York, pp. 627–666.
- Cheng, Y.-S., and Chen, B. T. (2001). Aerosol Sampler Operation. In *Air Sampling Instruments*, edited by B. S. Cohen and C. S. McCammon, Jr. ACGIH Worldwide, Cincinnati, OH, pp. 177–199.
- Chow, J. C. (1995). Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles, *JAWMA* 45:320–382.
- Drewnick, F., Schwab, J. J., Jayne, J. T., Canagaratna, M., Worsnop, D. R., and Demerjian, K. L. (2004a). Measurement of Ambient Aerosol Composition during the PMTACS-NY 2001 Using an Aerosol Mass Spectrometer Part I: Mass Concentrations, *Aerosol Sci. Technol.* 38:92–103.
- Drewnick, F., Jayne, J. T., Canagaratna, M., Worsnop, D. R., and Demerjian, K. L. (2004b). Measurement of Ambient Aerosol Composition During the PMTACS-NY 2001 Using an Aerosol Mass Spectrometer Part II: Chemical Speciated Mass Distributions, *Aerosol Sci. Technol.* 38:104–117.
- Drewnick, F., and Demerjian, K. L. (2004c). Investigation of the Evaporation and Ionization Process in the Aerosol Mass Spectrometer, *Aerosol Sci. Technol.* (in preparation).
- Finlayson-Pitts, B. J., and Pitts, J. N. (1986). *Atmospheric Chemistry: Fundamentals and Experimental Techniques*. John Wiley and Sons, Inc., New York.
- Hogan, A. W. (1979). Aerosol Detection by Condensation Nucleus Counting Techniques. In *Aerosol Measurement*, edited by D. A. Lundgren, F. S. Harris, Jr., W. H. Marlow, M. Lippmann, W. E. Clark, and M. D. Durham. The University Presses of Florida, Gainesville, FL, pp. 497–514.
- Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. R. (2000). Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles, *Aerosol Sci. Technol.* 33:49–70.
- Jimenez, J. L., Jayne, J. T., Shi, Q., Kolb, C. E., Worsnop, D. R., Yourshaw, I., Seinfeld, J. H., Flagan, R., Zhang, X., Smith, K. A., Morris, J., and Davidovits, P. (2003). Ambient Aerosol Sampling Using the Aerodyne Aerosol Mass Spectrometer, *J. Geophys. Res.-Atmospheres* 108:8425–8437.

- McMurry, P. H. (2000). A Review of Atmospheric Aerosol Measurements, *Atmos. Environ.* 34:1959–1999.
- Meyer, M. B., Patashnick, H., Ambs, J. L., and Rupprecht, E. (2000). Development of a Sample Equilibration System for the TEOM Continuous PM Monitor, *JAWMA* 50:1345–1349.
- NIST. (2002). *Building and Fire Research Laboratory Monthly Highlights*. Available at: [http://www.bfrl.nist.gov/bfrlnews/monthly\\_highlights/january\\_2002.htm](http://www.bfrl.nist.gov/bfrlnews/monthly_highlights/january_2002.htm)
- Patashnick, H., Rupprecht, G., Ambs, J. L., and Meyer, M. B. (2001). Development of a Reference Standard for Particulate Matter Mass in Ambient Air, *Aerosol Sci. Technol.* 34:42–45.
- Patashnick, H., and Rupprecht, E. G. (1991). Continuous PM-10 Measurements Using the Tapered Element Oscillating Microbalance, *JAWMA* 141:1079–1083.
- Pope, C. A., Burnett, R. T., Thun, M. J., Calle, E. E., Krewski, D., Ito, K., and Thurston, G. D. (2002). Lung Cancer, Cardiopulmonary Mortality, and Long-Term Exposure to Fine Particulate Air Pollution, *JAMA* 287:1132–1141.
- Rupprecht, G., Patashnick, H., Beeson, D. E., Green, R. N., and Meyer, M. B. (1995). A New Automated Monitor for the Measurement of Particulate Carbon in the Atmosphere. In *Proceedings, Particulate Matter: Health and Regulatory Issues*, edited by J. A. Cooper and L. D. Grant. Pittsburgh, PA, pp. 262–267.
- Samet, J. M., Dominici, F., Curriero, F. C., Coursac, I., and Zeger, S. L. (2000). Fine Particulate Air Pollution and Mortality in 20 U.S. Cities, *N. Engl. J. Med.* 343:1742–1749.
- Schwab, J. J., Hogrefe, O., Demerjian, K. L., and Ambs, J. (2004). Laboratory Characterization of Modified TEOM<sup>®</sup> Samplers, *JAWMA* in press.
- Seinfeld, J. H., and Pandis, S. N. (1998). *Atmospheric Chemistry and Physics*. John Wiley and Sons, Inc., New York.
- Stolzenburg, M. R., and Hering, S. V. (2000). A New Method for the Automated Measurement of Atmospheric Fine Particle Nitrate, *Environ. Sci. Technol.* 34:907–914.
- Weber, R. J., Orsini, D., Daun, Y., Lee, Y.-N., Klotz, P. J., and Brechtel, F. (2001). A Particle-into-Liquid Collector for Rapid Measurement of Aerosol Bulk Chemical Composition, *Aerosol Sci. Technol.* 35:718–727.