

A Particle-into-Liquid Collector for Rapid Measurement of Aerosol Bulk Chemical Composition

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We report on a new instrument developed for rapid automated on-line and continuous measurement of ambient aerosol bulk composition. The general approach is based on earlier devices (Khlystov et al. 1995; Simon and Dasgupta 1995) in which ambient particles are mixed with saturated water vapor to produce droplets easily collected by inertial techniques. The resulting liquid stream is analyzed with an ion chromatograph to quantitatively measure the bulk aerosol ionic components. In this instrument, a modified version of a particle size magnifier (Okuyama et al. 1984) is employed to activate and grow particles comprising the fine aerosol mass. A single jet inertial impactor is used to collect the droplets onto a vertical glass plate that is continually washed with a constant water diluent flow of nominally 0.10 ml min^{-1} . The flow is divided and then analyzed by a dual channel ion chromatograph. In its current form, 4.3 min integrated samples were measured every 7 min. The instrument provides bulk composition measurements with a detection limit of approximately $0.1 \mu\text{g m}^{-3}$ for chloride, nitrate, sulfate, sodium, ammonium, calcium, and potassium. Results obtained during its deployment in the August 1999 Atlanta EPA Supersite study are presented.

BACKGROUND

Process studies aimed at understanding sources, atmospheric transformation, and fate of ambient aerosols require knowledge of particle chemical composition. To date, quantitative composition measurements are typically performed off-line on particles collected onto substrates by filtration or inertial impaction. The collected sample is then manually extracted and analyzed. For example, measurements of ionic aerosol components involve collection on denuder-filter pack assemblies, extraction of the collected aerosol into water, and analysis of

the extract for various ionic species using the ion chromatography (IC) technique. Although widely used, this approach has many drawbacks. Depending on flow rates and ambient concentrations, sampling intervals are long, typically hours to days. Faster measurements are possible but often impractical due to the labor involved in filter preparation and sample extraction. This is particularly true in long-term air quality monitoring programs. Since the turn-around time for processed results also tends to be long, immediate insights and interpretations are generally not available for in-the-field adjustment and modifications of experiment sampling strategies and protocols.

Off-line techniques are also prone to potential sampling artifacts, particularly for volatile aerosol components. Artifacts that lead to measurement errors are due to interactions between particles, gases, and the substrate (Chow 1995). These interactions occur because particles are removed from the gas, concentrated on the substrate, and then exposed to different conditions for extended periods during sampling and storage. During sampling, volatile chemical components can be adsorbed or lost resulting from changes in temperature, relative humidity, and ambient particle and gas composition. Pressure drops within the sampler can also contribute to volatility losses. These artifacts have led to complicated filter pack sampling systems using multiple filters of various types to capture volatile aerosol components. Artifacts may also be introduced in the manual preparation and extraction of filters. Combined, these processes can lead to significant uncertainties, particularly when measuring mass concentration of volatile or easily contaminated aerosol chemical components, such as nitrate, ammonium, and semivolatile organics.

Advanced instruments for real-time size-resolved measurements of particle chemical composition involving mass spectrometers have been developed (Carson et al. 1995; Hinz et al. 1994; Jayne et al. 1998; Marijnisson et al. 1988; McKeown et al. 1991; Prather et al. 1994; Reents et al. 1995). These techniques provide important and unique insights into particle composition at single particle resolution. However, they tend to be complex and costly, and the measurements generally do not give quantitative information on particle composition.

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Other approaches involving automated bulk composition measurements have been developed. These approaches provide faster measurements and minimize many sampling artifacts associated with the off-line techniques. Although they do not provide size-resolved information like the mass spectrometer-based instruments, these approaches are quantitative. One common approach is to convert the aerosol particles to a vapor and measure selected evolved gases. For example, Turpin et al. (1990) developed a technique for carbonaceous aerosols by measuring the quantity of carbon dioxide produced when a loaded filter is heated to various temperatures. Stolzenburg and Hering (1999) developed an instrument that collects particles by impaction and measures various evolved gases when the deposited aerosol is flash vaporized. This approach has been successfully used to measure nitrate and also shows promise for sulfate and carbonaceous aerosol components.

Other devices have been developed that essentially bypass the filter or impactor sampler used in the off-line approaches for measurement of aerosol ionic species. In this case, the same analytical technique is employed, except the particles are collected directly into a liquid for automatic analysis by the IC technique. Approaches for capturing the particles vary. Automated systems have been developed that collect particles onto a filter that is periodically washed (Buhr et al. 1995); in other systems, particles are directly impacted into a flowing liquid (Karlsson et al. 1997). In another approach, ambient particles are first grown to large water droplets by mixing with saturated water vapor. The large droplets are then captured onto surfaces by various inertial techniques and combined with condensed water vapor to produce the liquid stream for analysis. A variety of instruments have been developed using this approach (Ito et al. 1998; Khlystov et al. 1995; Liu and Dasgupta 1996; Poruthoor and Dasgupta 1998; Simon and Dasgupta 1995; Zellweger et al. 1999).

We report here on a new instrument similar to the particle growth devices, but designed specifically for rapid measurement of the ionic component of ambient aerosols. The approach combines two proven aerosol technologies, particle growth in a mixing condensation particle counter, and droplet collection by a single jet inertial impactor. Initial field studies with this device suggest that it is an effective analytical tool for characterizing ambient aerosols.

INSTRUMENT DESCRIPTION AND CALIBRATION

The Particle Size Magnifier

To accurately measure the total bulk aerosol composition, the particle size magnifier must activate the aerosol particles comprising the majority of the total aerosol mass. These particles must grow to sizes that can be efficiently transported, yet can be easily captured by a simple inertial impactor. This requires activating all particles larger than approximately 80 nm in diameter and growing them to sizes on the order of 1–10 μm in diameter. The complete system consists of three main components.

The first two components, referred to as a particle-into-liquid sampler (PILS), consist of a particle growth device and an impactor/collection component. A variety of techniques could be employed to analyze the liquid. In this study we used an IC to analyze the aerosol particle ionic components. The complete system is referred to as a PILS-IC.

Particle Growth Chamber. To activate and grow the ambient particles, we employed a modified version of the basic particle size magnifier (PSM) developed by Okuyama et al. (Kousaka et al. 1982; Okuyama et al. 1984). These devices were originally developed as aerosol detectors (Kogan and Burnasheva 1960), were similar to condensation particle counters (CPCs), and were used for studies of condensational particle growth. In this study the PSM is employed for a different application. Ideally, the PSM grows particles in a supersaturated atmosphere created by adiabatic mixing of a hot saturated stream with an ambient aerosol flow. The temperatures, saturation ratios, and mass flow rates of the hot and ambient streams control the degree of supersaturation. This determines the minimum particle size activated and the amount of vapor available for condensation.

We altered the PSM of Okuyama et al. (1984) for operation at higher flow rates while minimizing aerosol losses. As shown in Figure 1, the PILS is composed of three sections: a saturator, a mixing region, and a particle growth region. Here, the saturator is simply a 1/8 inch stainless tube through which a steady flow of purified water is pumped. This tubing is coiled around a temperature-controlled cartridge heater. Changing the temperature and the water feed flow rate control the output steam temperature and flow. We used a water flow rate of nominally 0.4 mL min^{-1} to generate the steam. The steam is injected into the PILS mixing chamber and immediately encounters the ambient aerosol drawn in from the side at a rate of 5 L min^{-1} . Rapid mixing of the hot saturated flow with the cooler aerosol flow creates the supersaturated atmosphere needed for particle activation and growth.

To minimize potential volatility loss associated with altering the ambient aerosol temperature, sample air entering the mixing chamber is held to near ambient temperature by a temperature controlled water jacket. To operate at higher flows, and for simplicity, the PSM mixer in the original device (Okuyama et al. 1984) was removed and the steam and ambient flows were simply directed at a 90° angle to each other; neither flow was accelerated to promote turbulent mixing. As shown in the following section, this tended to limit activation to only particles larger than ~ 50 nm in diameter. However, for our urban study this was found to be sufficient to capture most of the PM_{2.5} mass.

Following the mixing chamber, the supersaturated vapor and aerosol pass through a 16 cm long tube with a wall temperature held at 10°C with a thermostatic-controlled water jacket. The residence time in this tube is approximately 0.6 s. The walls were cooled to maintain the supersaturation necessary for particle growth and yet remove as much water vapor as possible prior to the droplet collection region. This is a fundamental difference between our approach and the other droplet growth

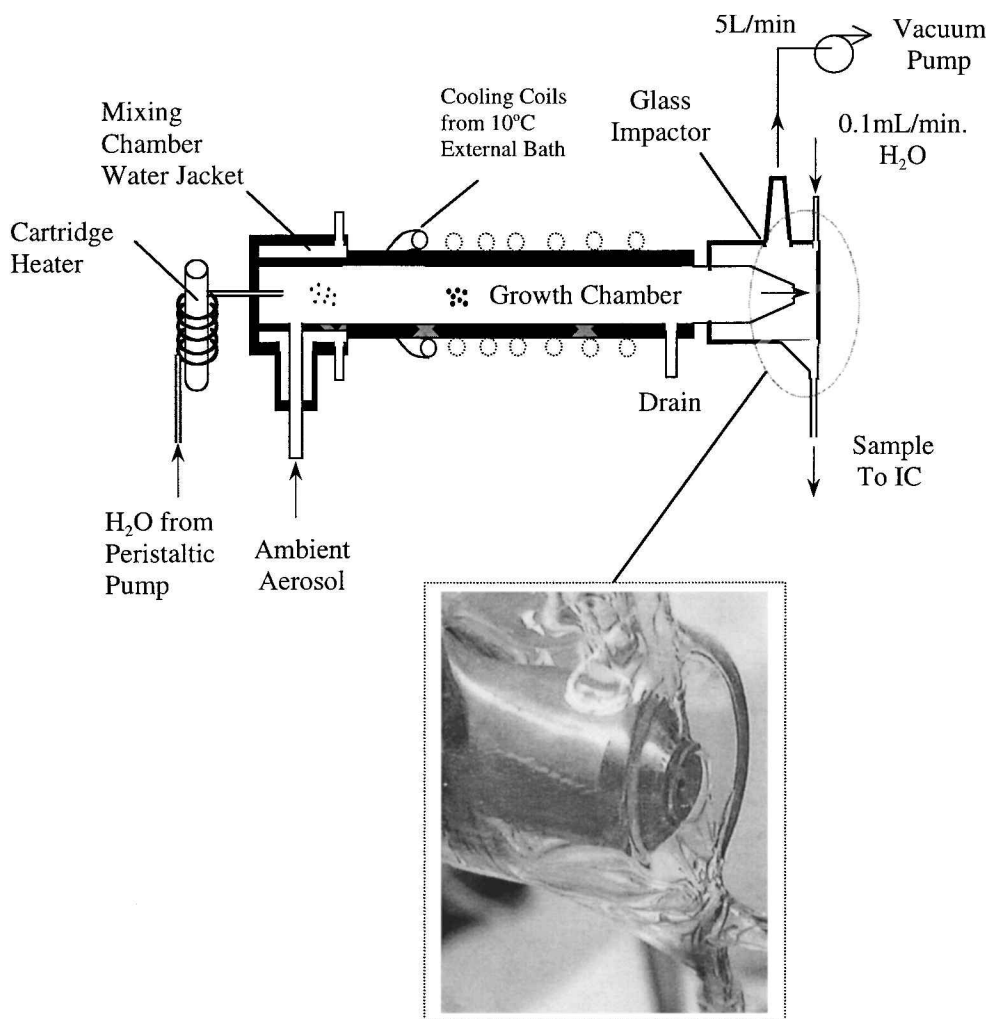


Figure 1. Schematic diagram of the PILS, which is composed of a saturated vapor generating system, a chamber for mixing vapor and ambient air, a condenser, and the impaction region for collecting the droplets into a flowing liquid stream. The insert shows the impactor nozzle, glass impactor housing, and the stable liquid ring formed by the impinging air jet.

devices. We attempt to separate the drops from the vapor to allow better control of the total liquid stream containing the captured particles. In the other devices, much of the steam is condensed and added to the total sample liquid flow (Khlystov et al. 1995; Simon and Dasgupta 1995). The PILS was operated with the condenser horizontal so that a drain at the bottom of the condenser (Figure 1) could be used to remove condensation from the walls. The horizontal arrangement has the potential disadvantage of losing large droplets to settling during transport. However, measurements indicated that particles in the condenser reached final diameters of nominally 2–3 μm , resulting in few particles lost by gravitational settling during transit through the condenser.

Inertial Impactor. To collect the droplets into a flowing stream of water, sample airflow containing the droplets was directed through a single circular nozzle impactor which was designed for a 1 μm diameter cut size based on published impactor

design criteria (Marple and Willeke 1976; Rader and Marple 1985). The aerosol jet impinged onto a flat vertical glass plate. The impactor nozzle consisted of a 1.27 cm (0.50 inch) outside diameter (OD) stainless-steel tube with 1.04 cm (0.41 inch) inside diameter (ID) that tapered down through a 45° angle to a nozzle diameter of 0.119 cm (3/64 in). Sample air is drawn through the PSM and impactor from a port at the top of the impactor housing (see Figure 1). Droplets impacted onto the plate flowed radially out from the jet stagnation line, and at a diameter of roughly 1 cm, the liquid collected in an observable ring (see insert in Figure 1). The ring's shape and stability depended on the external shape of the nozzle and the jet-to-plate distance. The latter was adjusted manually so that a stable ring was achieved. A peristaltic pump was used to regulate a carrier water flow of 0.10 mL min^{-1} introduced at the top of the ring. This flow drained down either side of the ring and allowed the collected drops to be flushed off the impaction surface. The

resulting liquid containing the ambient particles flows to a low point in the glass impaction-plate housing where it is continually pumped off. The ring provided a convenient visual gauge of the impactor operation; it showed that the liquid was not splashing and that a minimal wetted area was achieved, both of which are essential for a highly time resolved quantitative measurement.

Liquid Transport. The liquid sample collected at the base of the impaction plate housing was pumped out at a rate faster than the rate at which it accumulated, resulting in entrainment of air bubbles into the liquid stream. The bubble segments formed in the liquid transport tubing help to minimize the axial mixing of the sample liquid during transport. Prior to injecting into the IC, the bubbles were removed by a debubbler consisting of a glass tee in which the intersection was expanded to a volume of roughly 0.25 cm^3 . The air bubbles, along with a small fraction of the sample liquid, were pumped off from the top leg, and the sample liquid, free of air, was transported from the bottom of the debubbler to the IC at approximately 0.07 mL min^{-1} . This flow was then split and directed into two $150 \mu\text{l}$ sample loops for injection into a dual channel IC. The time to fill a sample loop is the integration time of the ambient air sample. For a sample aerosol flow rate of 5 L min^{-1} , and a carrier liquid flow of 0.10 mL min^{-1} , our arrangement resulted in 4.3 min integrated samples. In all cases, 0.159 cm (1/16 inch) OD Teflon tubing with 0.051 cm (0.02 inch) ID was used to transport the liquid. The small ID minimized the time for liquid transport from the collector to the IC sample loops.

Ion Chromatography Analysis

The concentrations of the major inorganic ionic components of the collected aerosol samples were analyzed using a computer-controlled dual channel ion chromatograph (Dionex, Model 300DX), which permitted both the cations and anions to be determined on-line and continuously. Each analysis channel consisted of a 6 port valve injector fitted with a $150 \mu\text{L}$ sample loop, a dual piston pump, an analytical separation column (IonPac CS12A, $4 \times 250 \text{ mm}$, for cations; IonPac AS11, $4 \times 250 \text{ mm}$, for anions, both from Dionex), a membrane suppressor, and a conductivity meter (Figure 1). The analysis was performed with isocratic elution using a $40 \text{ mN H}_2\text{SO}_4$ eluent for the cations and a 7.0 mN NaOH eluent for the anions, both at a flow rate of 1.0 mL min^{-1} . The analysis was automated using a computer interface (Dionex, Model ACI450) and the associated software running on a PC, which controlled the sample injection, data collection, data storage, and chromatographic analysis. This arrangement resulted in approximately 7 min long chromatograms for both anions and cations. This 7 min duty cycle was the limiting factor controlling the sampling frequency. During our first field operation, the IC system was calibrated every 2 to 3 days using standard solutions of 4 different concentrations of all the ions being analyzed.

To calculate the concentrations of the chemical components of the ambient aerosol, the total liquid sample flow rate must be

known. Although the carrier water flow rate was known from the pump speed, the amount of additional water introduced by the collected water droplets and condensed water vapor was not directly measured. However, tests showed that the final sample liquid flow remained fairly constant ($\pm 3\%$) for ambient aerosol concentrations ranging from 5000 to 10000 cm^{-3} , which is well within the range of ambient concentrations at the Atlanta EPA Supersite study. This results from the droplets comprising a small fraction of the total liquid volume and because we minimize the contribution of steam condensate to the total liquid flow. Thus the total flow was controlled primarily by the carrier flow introduced to the impactor region. In our current version of this instrument, the liquid added to the top of the impactor is spiked with a known amount of lithium fluoride and the IC measurement of the lithium concentration is used to continually determine the total liquid flow rate.

Limit of Detection and Measurement Uncertainties

The limit of detection (LOD) and uncertainty of the PILS-IC can be estimated from the expected IC sensitivity and measured flow rates of the sample air and liquid stream. With an IC sensitivity of roughly $0.1 \mu\text{M}$ for nitrate, sulfate, sodium, ammonium, calcium, and potassium, a sample flow rate of 5 L min^{-1} , and a carrier liquid flow of 0.10 mL min^{-1} , the PILS-IC is estimated to have a limit of detection near $0.1 \mu\text{g m}^{-3}$ for the various ionic components. We also estimated the limits of detection from ambient measurements during the Atlanta Supersite Study. Because of the instrument's rapid sampling rate, the integration of the chromatogram peaks was automated. The limits of detection based on the smallest peak we could reliably integrate were similar to the calculated limits of detection, ranging from $0.18 \mu\text{g m}^{-3}$ for sulfate to $0.05 \mu\text{g m}^{-3}$ for ammonium.

The uncertainty associated with the mass measurements was estimated by combining the uncertainties in flow rates and IC calibrations. Uncertainties of both liquid and air flow rates are approximately $\pm 4\%$. Uncertainties in the IC calibration for sulfate, nitrate, and ammonium were determined by comparisons with measurements of independent NIST traceable standards (Fisher Scientific). Comparisons immediately following IC calibrations were within 3–5%, and 5–10% after running for an extended period. The overall uncertainty of the measured ionic species is estimated to be about $\pm 10\%$.

Particle Collection Efficiency

To determine the minimum size of particles activated, and the overall droplet transport and collection efficiency, the mass collection efficiency of the PILS was calibrated. In these laboratory experiments, aerosol particles of known chemical composition and size were generated using the standard technique of atomizing an aqueous solution, neutralizing and diffusion drying the aerosol, and selecting a specific size with a differential mobility analyzer (DMA; Knutson and Whitby 1975; Figure 2). The mass concentration of the calibration aerosol was measured with the PILS-IC and compared to the mass concentration measured

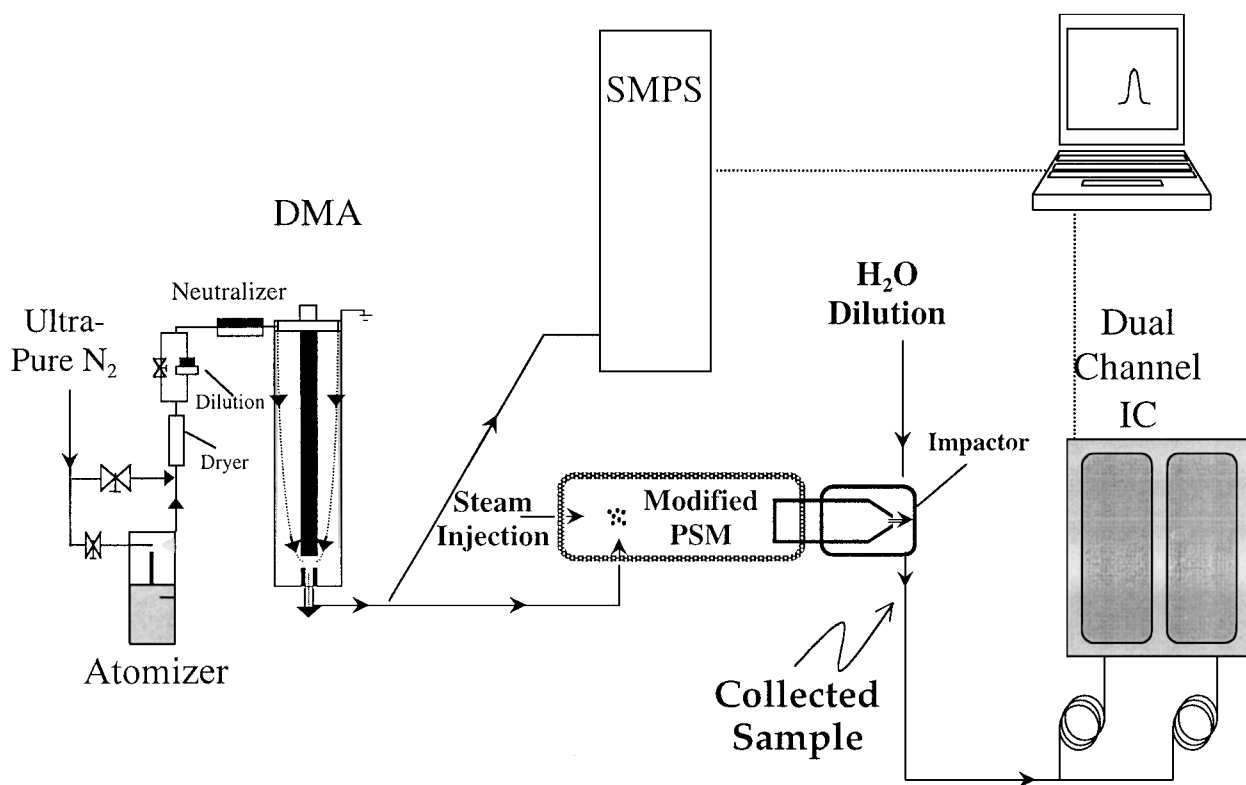


Figure 2. Schematic diagram for mass collection efficiency calibration of the PILS coupled to a dual channel ion chromatograph. Monodisperse ammonium sulfate aerosol is generated with a nebulizer and DMA. The mass of this calibration aerosol measured by the PILS-IC is compared to the mass monitored by a SMPS.

with a scanning mobility particle spectrometer (SMPS; TSI Inc, St Paul MN; Wang and Flagan 1990). The SMPS measures the particle number distribution. This was converted to total aerosol mass concentration from the known particle density and by assuming that the particles were dry spheres. The assumption that the particles are dry is valid since the relative humidity (RH) of the calibration aerosol was about 20%, well below the efflorescence point of 40% RH for a calibration aerosol of ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$). The validity of the assumption that the particles are spherical is unknown. If the particles were cubic, by assuming they are spherical we could overestimate the mass by up to roughly 80% since the side length of a cubic particle of the same electric mobility (e.g., particles classified by the DMA) is about 0.75 times the diameter of a spherical particle (Dahneke 1973). Because the large particle collection efficiencies approached 100%, we believe that most particles were likely close to being spherical. We have not included this in the experimental uncertainty associated with this measurement. Note that the SMPS measurement also accounts for single and multiple charged particle contributions to total mass. Calibration results for sulfate generated from $(\text{NH}_4)_2\text{SO}_4$ are shown in Figure 3. Measured concentration ratios are compared to the size of the single charged particle generated. (At the smaller sizes where concentration ratios are sensitive to size, contributions of

multiply charged particles to the total mass are small since most particles are singly charged.) Selected calibration particle diameters ranged from 25 to 300 nm with total number concentrations varying between 150 and 10^5 particles cm^{-3} depending on particle size. This corresponds to sulfate mass concentrations between 0.5 and $40 \mu\text{g m}^{-3}$, typical of ambient urban aerosol concentrations.

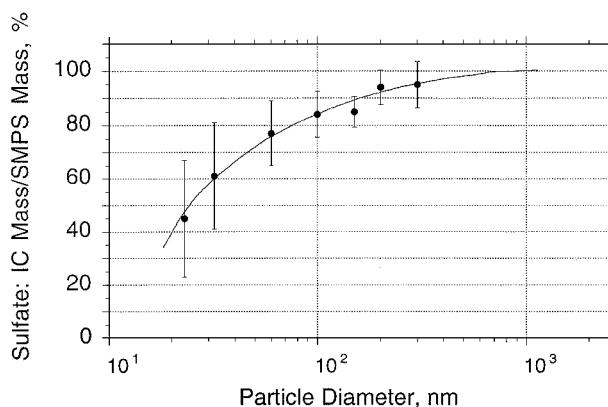


Figure 3. Results of the PILS-IC mass collection efficiency tests for sulfate.

From Figure 3, a maximum collection efficiency of 94% was measured and over 80% of all particles larger than approximately 50 nm were collected. Below 50 nm, the collection efficiency drops rapidly with decreasing size. We attribute the drop in collected mass primarily to nonactivation of smaller nuclei, a result of our limited mixing of saturated water vapor and sample air. Note that to achieve measurable masses for the smaller particle sizes tested (i.e., 25 nm diameter size), number concentrations of the order of 10^5 particles cm^{-3} were required. Since the activated drops grow to similar final sizes, during the experiments we were concerned that the unrealistically high concentrations necessary for the calibrations at the smaller sizes could lead to underestimation of the activation efficiencies due to vapor depletion. This was found, however, to be a minor effect since tests with increased steam-water flow rates had little influence on the lower size collection efficiencies. These tests demonstrated that the PILS collection efficiency was not significantly influenced by particle concentration for concentrations up to 10^5 cm^{-3} .

Although the activation efficiency shown in Figure 3 is likely sufficient for collecting most of the ambient aerosol mass in the EPA Supersite study, a better mixer could easily be designed to activate much smaller particles. In a new version of the PILS we have developed an efficient mixer for operation at high sample flow rates.

PRELIMINARY RESULTS FROM THE ATLANTA EPA SUPERSITE STUDY

The PILS was developed specifically for the metro Atlanta EPA Supersite study of August 1999. As the first EPA Supersite, the campaign was aimed at intercomparing various techniques for measuring chemical composition of particles smaller than $2.5 \mu\text{m}$ diameter, so-called $\text{PM}_{2.5}$. A secondary goal was to study the chemical and physical properties of urban $\text{PM}_{2.5}$ aerosol particles in the southeastern United States. Findings from extensive instrument measurement intercomparisons will be published elsewhere. Preliminary results showed that the PILS agreed well with other semicontinuous techniques and was in general agreement with filter measurements of nonvolatile species, such as sulfate.

The $\text{PM}_{2.5}$ sampling system, including the PILS-IC, is shown in Figure 4. The sampling inlet consisted of an inverted stainless-steel tube connected to a 10 L min^{-3} , $2.5 \mu\text{m}$ cut University Research Glass (URG) Cyclone to permit measurements of $\text{PM}_{2.5}$. Inside the sampling trailer, the 10 L min^{-3} aerosol flow passed through two URG annular denuders in series, one coated with citric acid and the other calcium carbonate, to remove gaseous NH_3 , SO_2 , and HNO_3 , respectively. The denuders were regenerated approximately every 2 days.

Focusing on nitrate, sulfate, and ammonium, Figures 5, 6, and 7 show the data collected during a 10 day sample period,

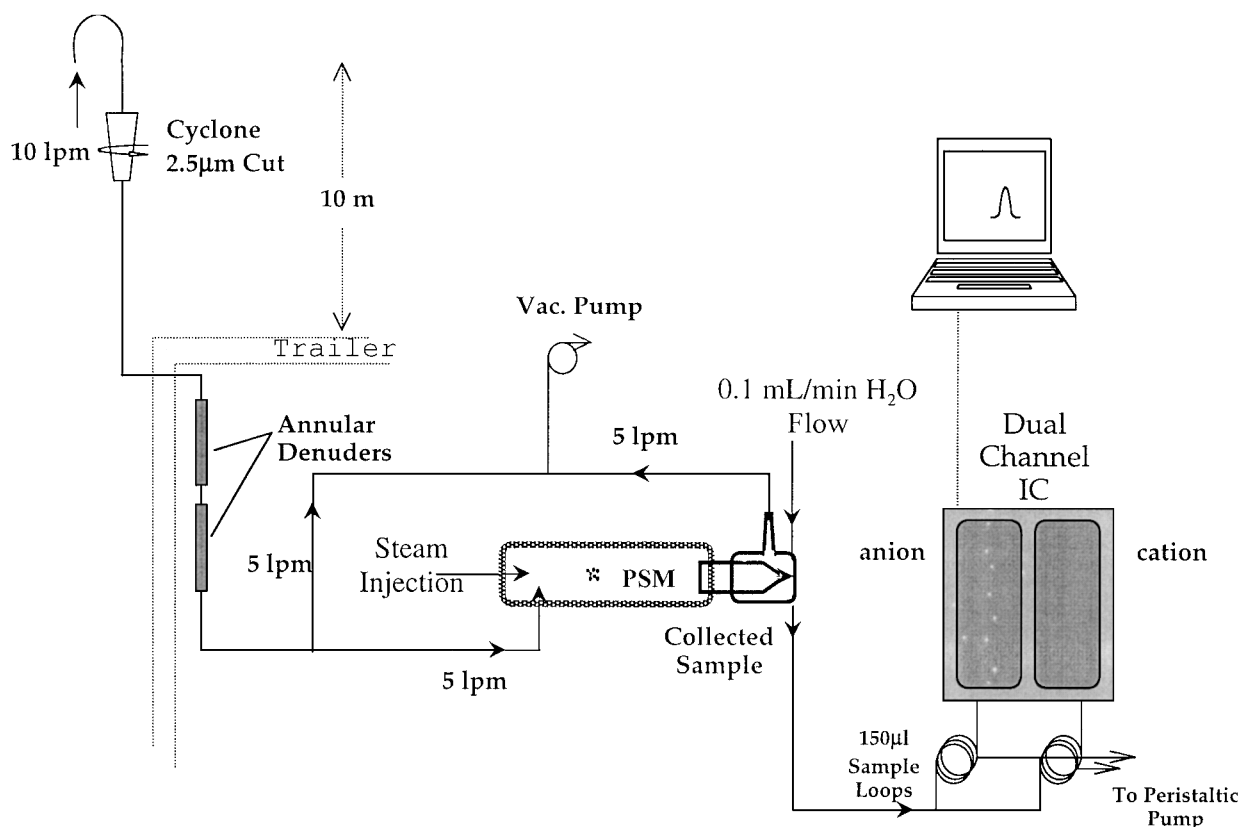


Figure 4. Schematic of the PILS-IC deployed for the EPA Atlanta Supersite measurements in August 1999 for rapid measurements of bulk aerosol ionic species.

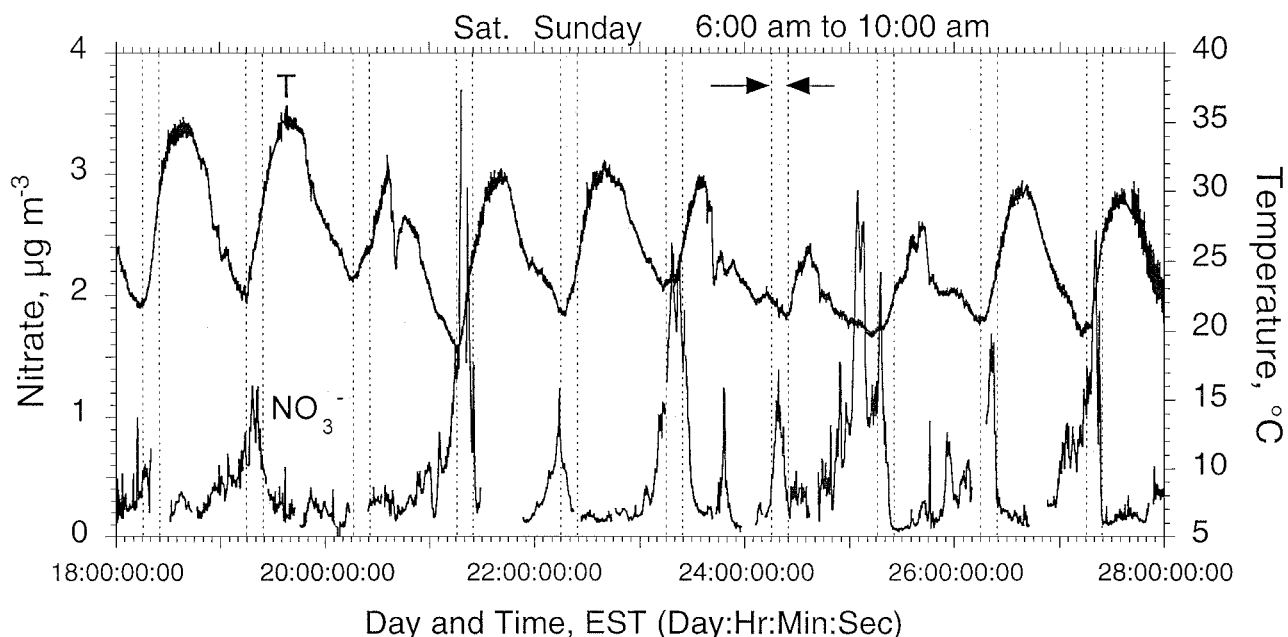


Figure 5. PILS-IC measurements of nitrate and ambient temperature recorded at the Atlanta Supersite from August 18 to August 28, 1999. Nitrate was observed to peak between 6:00 and 10:00 Eastern Standard Time on practically every morning. The peaks coincided with minimums in daily temperature. The data demonstrate how rapid measurements can provide insights into processes that would not be observed with samplers employing long integration intervals (e.g., standard filter sampling approaches).

August 19–August 28, 1999. Figure 5 shows nitrate levels ranging between roughly the LOD of the system, i.e., 0.1, to $3.0 \mu\text{g m}^{-3}$ during this time. The nitrate measurements demonstrate how highly time-resolved measurements can provide insights into processes controlling ambient aerosol concentrations. Figure 5 shows that practically every day, nitrate peaked in early

morning between 6:00 and 10:00 Eastern Standard Time. Although this coincides with morning rush hour, peaks were also observed on Saturday and Sunday when there is no rush hour traffic. These peaks correlate with periods of minimum daily temperatures, which are also times of maximum RH. It is known that partitioning of nitric acid between the gas and condensed

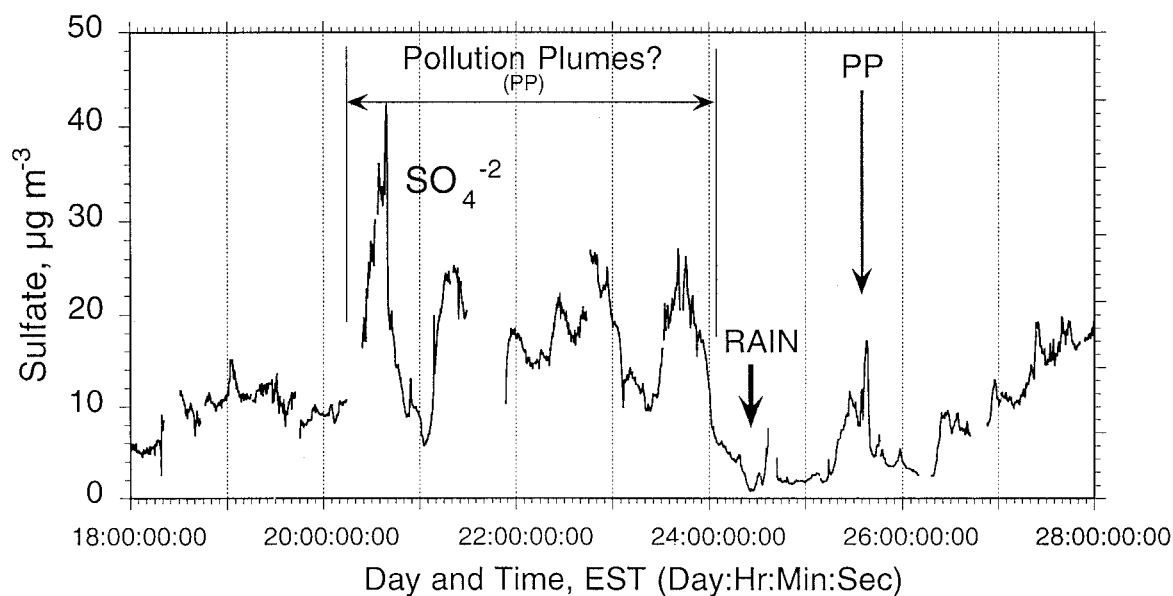


Figure 6. PILS-IC measurements of sulfate recorded at the Atlanta Supersite from August 18 to August 28, 1999.

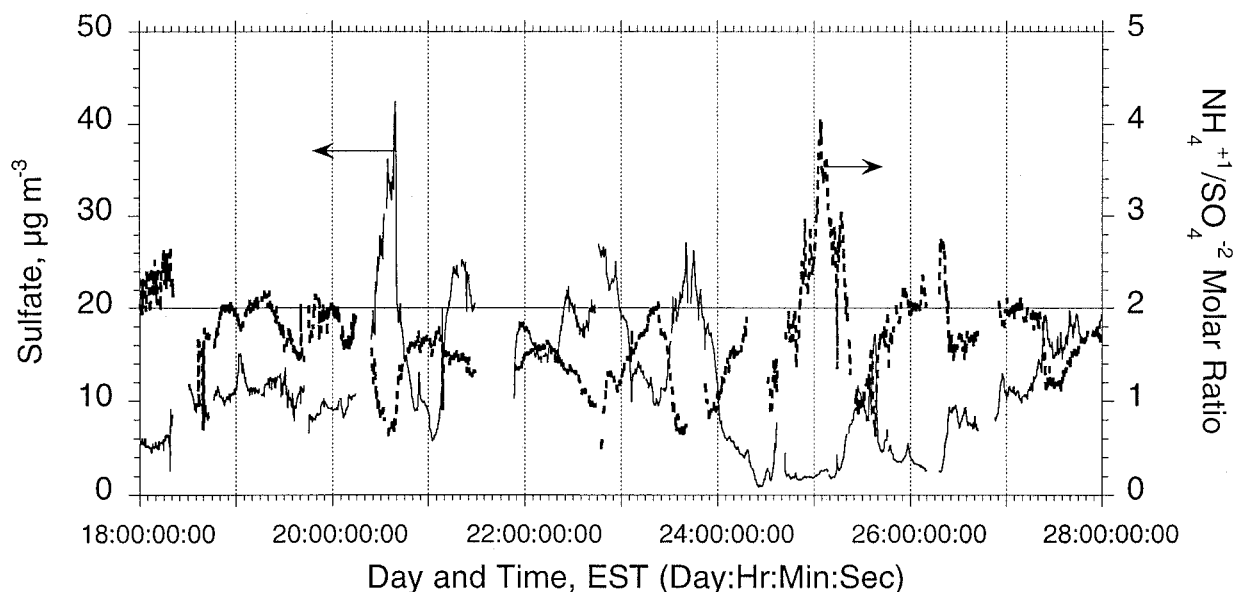


Figure 7. PILS-IC measurements of sulfate concentrations and ammonium to sulfate molar ratios recorded at the Atlanta Supersite from August 18 to August 28, 1999. Peaks in sulfate are associated with pollution plumes and a minimum in molar ratios.

phase is highly sensitive to temperature, RH, and aerosol composition. Consistent nitrate peaks following minimum temperatures and maximum daily RH suggest that these thermodynamic effects may play a major role in the formation of the early morning nitrate peaks.

During the period of August 18–28, other ancillary measurements showed that total PM_{2.5} mass concentrations varied

between 5 and 60 $\mu\text{g m}^{-3}$ (M. Bergin 2000; TEOM with inlet heated to 50°C, Rupprecht and Patashnick Co., Albany, NY). As is typical of the eastern United States, sulfate was found to be a major component and nitrate a minor component of total PM_{2.5} aerosol mass. Figure 6 shows the sulfate concentration measured during this period. Sulfate concentrations ranged from about 2 to 40 $\mu\text{g m}^{-3}$, with the highest levels

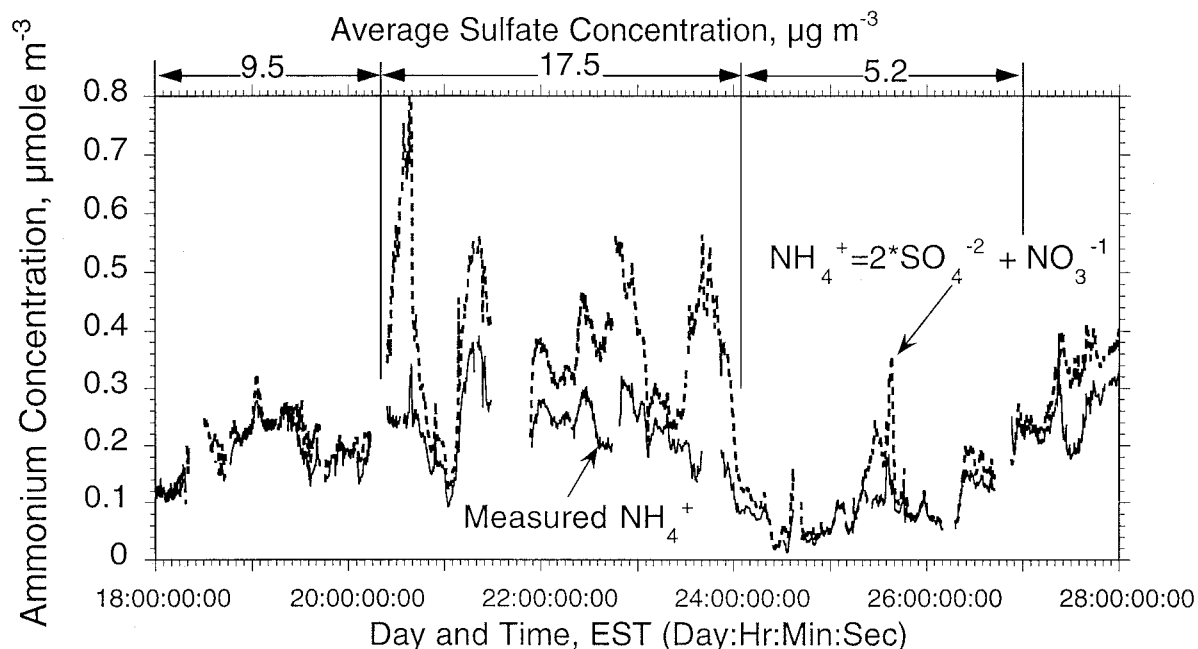


Figure 8. PILS-IC measurements of the ammonium molar concentration and the calculated ammonium molar concentration necessary to neutralize the measured aerosol sulfate and nitrate. The plot shows that typically the aerosol is nearly completely neutralized, except during periods of high sulfate concentrations.

corresponding to pollution episodes, possibly associated with power plant plumes or other local sources. During this period these plumes were observed primarily between August 20 and August 24.

Sulfate concentration and ammonium to sulfate molar ratios are plotted in Figure 7. The molar ratios are of interest since they provide insights into aerosol gas-to-particle conversion processes and also served as an internal check on our measurement accuracy. Under typical conditions, ammonium-sulfate molar ratios were near 2, suggesting that sulfate was usually completely neutralized, assuming most of the ammonium was associated with sulfate. However, during pollution episodes, molar ratios often dropped below 1, arising most likely from the fact that the available ammonia present was insufficient to neutralize the unusually large amount of sulfuric acid produced in the plume. There were also periods when molar ratios exceeded 2. This typically occurred when the total aerosol mass concentrations were very low. For example, molar ratios peaked near 4 just at the beginning of August 25. During these times, PM_{2.5} levels were unusually low at 10 $\mu\text{g m}^{-3}$. At these times ammonium associated with additional acidic species may be a significant contribution to the total aerosol ammonium. To test this we plot in Figure 8 the measured ammonium molar concentration and the concentration calculated from measured sulfate and nitrate, assuming that these are the major acidic species and that they are completely neutralized by ammonium. The graph shows that the measured and calculated ammonium concentrations agree remarkably well, except under high sulfate concentrations associated with pollution plumes. During these times there appears to be insufficient ammonia to neutralize the aerosol. These data attest to the accuracy of the independent anion and cation measurement results.

CONCLUSIONS

Our preliminary investigations with a newly designed PILS coupled with an IC suggest that it is a powerful tool for rapid quantitative measurements of aerosol particle ionic composition. The instrument is simple and robust. Sampling artifacts associated with filter techniques are minimized since particles are rapidly stabilized by formation of water drops collected into a flowing liquid. Data is obtained in near real-time, with a 4.3 min integrated sample at a duty cycle of 7 min. With an IC sensitivity of roughly 0.1 μM , a sample flow rate of 5 L min^{-1} , collecting particles into a liquid flow of 0.10 ml min^{-1} , the PILS-IC had a limit of detection near 0.1 $\mu\text{g m}^{-3}$ for nitrate, sulfate, sodium, ammonium, calcium, and potassium. We are currently developing and testing an improved PILS with a better steam-air mixer to activate smaller particles, a higher sample flow rate, and improved droplet collection geometry. In current laboratory work we have achieved measurement cycles down to 3 min with sensitivities approaching 0.01 $\mu\text{g m}^{-3}$. Although at this point we have only focused on coupling the PILS to an IC, other analytical techniques could also be employed to quantitatively measure additional aerosol chemical components and properties.

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REFERENCES

- Bergin, M. (2000). *Private Communication*.
- Buhr, S. M., Buhr, M. P., Fehsenfeld, F. C., Holloway, J. S., Karst, U., Norton, R. B., Parrish, D. D., and Sievers, R. E. (1995). Development of a Semi-Continuous Method for the Measurement of Nitric Acid Vapor and Particulate Nitrate and Sulfate, *Atmos. Environ.* 29:2609–2624.
- Carson, P. G., Neubauer, K. R., Johnston, M. V., and Wexler, A. S. (1995). On-Line Chemical Analysis of Aerosols by Rapid Single-Particle Mass Spectrometry, *J. Aerosol Sci.* 26:535–545.
- Chow, J. C. (1995). Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles, *J. Air Wast Mang.* 45:320–382.
- Dahneke, B. E. (1973). Slip Correction Factors for Nonspherical Bodies—I Introduction and Continuum Flow, *Aerosol Sci.* 4:139–145.
- Hinz, K. P., Kaufmann, R., and Spengler, B. (1994). Laser-Induced Mass Analysis of Single Particles in the Airborne State, *Anal. Chem.* 66:2017–2076.
- Ito, K., Chasteen, C. C., Chung, H., Prouthor, S. K., Genfa, Z., and Dasgupta, P. K. (1998). A Continuous Monitorings System for Strong Acidity in Aerosols, *Anal. Chem.* 70:2839–2847.
- 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, *J. Aerosol Sci.* 33:49–70.
- Karlsson, A., Irgum, K., and Hansson, H. (1997). Single-Stage Flowing Liquid Film Impactor for Continuous On-Line Particle Analysis, *J. Aerosol Sci.* 28:1539–1551.
- Khlystov, A., Wyers, G. P., and Slanina, J. (1995). The Steam-Jet Aerosol Collector, *Atmos. Environ.* 29:2229–2234.
- Knutson, E. O., and Whitby, K. T. (1975). Aerosol Classification by Electrical Mobility: Apparatus, Theory, and Applications, *J. Aerosol Sci.* 6:443–451.
- Kogan, Y. I., and Burnasheva, Z. A. (1960). Growth and Measurement of Condensation Nuclei in a Continuous Stream, *J. Phys. Chem.* 34:1240–1243 (in Russian).
- Kousaka, Y., Niida, T., Okuyama, K., and Tanaka, H. (1982). Development of a Mixing Type Condensation Nucleus Counter, *J. Aerosol Sci.* 13:231–240.
- Liu, S., and Dasgupta, P. K. (1996). Automated System for Chemical Analysis of Airborne Particles Based on Corona-Free Electrostatic Collection, *Anal. Chem.* 68:3638–3644.
- Marjijnissen, J. C. M., Scarlett, B., and Verheijen, P. J. T. (1988). Proposed On-Line Aerosol Analysis Combining Size Determination, Laser-Induced Fragmentation and Time-of-Flight Mass Spectroscopy, *J. Aerosol Sci.* 19:1307.
- Marple, V. A., and Willeke, K. (1976). Impactor Design, *Atmos. Environ.* 10:891–896.
- McKeown, P. J., Johnston, M. V., and Murphy, D. D. (1991). On-Line Single-Particle Aerosol Analysis by Laser Desorption Mass Spectrometry, *Anal. Chem.* 63:2069.
- Okuyama, K., Kousaka, Y., and Motouchi, T. (1984). Condensation Growth of Ultrafine Aerosol Particles in a New Particle Size Magnifier, *Aerosol Sci. Technol.* 3:353–366.
- Poruthoor, S. K., and Dasgupta, P. K. (1998). Automated Particle Collection and Analysis. Near-Real Time Measurement of Aerosol Cerium (III), *Anal. Chem. Acta* 361:151–159.

- Prather, K. A., Nordmeyer, T., and Salt, K. (1994). Real-Time Characterization of Individual Aerosol Particles Using Time-of-Flight Mass Spectrometry, *Anal. Chem.* 66:1403.
- Rader, D. J., and Marple, V. A. (1985). Effect of Ultra-Stokesian Drag and Particle Interception on Impaction Characteristics, *Aerosol Sci. Technol.* 4:141-156.
- Reents, W. D. J., Mujsce A. M., Muller, A. J., Siconolfi, D. J., and Swanson, A. G. (1995). Real-Time Elemental Analysis of Individual Submicron Particles by Laser Ablation Time-of-Flight Mass Spectrometry, *J. Aerosol Sci.* 23:263.
- Simon, P. K., and Dasgupta, P. K. (1995). Continuous Automated Measurement of the Soluble Fraction of Atmospheric Particulate Matter, *Anal. Chem.* 67:71-78.
- Stolzenburg, M. R., and Hering, V. (2000). A Method for the Automated Measurement of Fine Particle Nitrate in the Atmosphere, *Environ. Sci. Technol.* 34:907-914.
- Turpin, B. J., Cary, R. A., and Huntzicker, J. J. (1990). An In Situ, Time-Resolved Analyzer for Aerosol Organic and Elemental Carbon, *J. Aerosol Sci.* 12:161-171.
- Wang, S. C., and Flagan, R. C. (1990). Scanning Electrical Mobility Spectrometer, *Aerosol Sci. Technol.* 13:230-240.
- Zellweger, C., Ammann, M., Hofer, P., and Baltensperger, U. (1999). NOy Speciation with a Combined Wet Effluent Diffusion Denuder-Aerosol Collector Coupled to Ion Chromatography, *Atmos. Environ.* 33:1131-1140.