

A PARTICLE-INTO-LIQUID COLLECTOR FOR RAPID MEASUREMENT
OF AEROSOL BULK CHEMICAL COMPOSITION

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ABSTRACT

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 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 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 0.10 ml min^{-1} . The flow is divided and analyzed by a dual channel ion chromatograph. In its current form, 4.3-minute integrated samples were measured every 7 minutes. 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 involves 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 particle/gas, particle/particle, gas/substrate, and particle/substrate interactions. 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 concentrations of volatile or easily contaminated aerosol chemical components, such as nitrate, ammonium, and semi-volatile organics.

Advanced instruments for real-time size-resolved measurements of particle chemical composition involving mass spectrometers have been developed . 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.

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. 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 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 bypass the filter or impactor sampling 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. Techniques for capturing the particles vary. Automated systems have been developed that collect particles onto a filter that is periodically washed , or particles are directly impacted into a flowing liquid . In another approach, ambient particles are first grown to large water droplets by mixing with saturated water. The large droplets are then captured onto surfaces by various inertial techniques, and combined with condensed water vapor, produce the liquid stream for analysis. A variety of instruments have been developed using this approach .

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 easily captured by a simple inertial impactor. This requires activating all particles larger than approximately 80 nm diameter, and growing them to sizes on the order of a 1 to 10 microns 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 can be employed to analyze the liquid, and 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. . These devices were originally developed as aerosol detectors , 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 air stream with an ambient aerosol flow. The degree of supersaturation, which is controlled by the temperatures, saturation ratios, and mass flow rates of the hot and ambient air, determine minimum particle size activated the vapor available for condensation.

We altered the PSM of Okuyama et al. for operation at higher flow rates while minimizing aerosol losses. 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} . Ideally, 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 was removed and the steam and ambient flows were simply directed at a 90° angle to each other, and neither flow was accelerated to promote turbulent mixing. As shown in the following section, this tended to limit activation to only particles larger than $\sim 50 \text{ nm}$ diameter. However, for our urban study, this was found to be sufficient to capture most of the $\text{PM}_{2.5}$ mass.

Following the mixing chamber, the supersaturated vapor and aerosol pass through a 16 cm-long tube with a wall temperature kept at 10°C with a thermostated 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 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. 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 to 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 air flow 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. 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-degree 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 rings 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 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 thus formed helped to minimize the axial mixing of the sample liquid during transport. Prior to injecting into the IC, the bubbles were removed by a debubber 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 to the IC at approximately 0.07 mL min^{-1} from the bottom. This flow was then split and directed into two 150 (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 mLmin^{-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 (L sample loop, a dual piston pump, an analytical separation column (IonPac CS12A, 4x250mm, for cations; Dionex IonPac AS11, 4x250mm, for anions, both from Dionex), a membrane suppressor, and a conductivity meter (Figure 1). The analysis was performed with isocratic elution using a 40 mN H_2SO_4 eluant for the cations and a 7.0 mN NaOH eluant 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-minute long chromatograms for both anions and cations. This 7-minute duty cycle was the limiting factor controlling the sampling frequency. The IC system was calibrated daily using standard solutions of 4 different concentrations of all the ions being analyzed.

In these instruments, the total sample liquid flow must be known to calculate the concentrations of the chemical components of the ambient aerosol. Although the carrier water flow rate was known, the amount of additional volume introduced by the collected water droplets was not directly measured. However, tests showed the final sample liquid flow remained fairly constant ($\pm 3\%$) for ambient aerosol concentrations ranging from 5000 to 10000 cm^{-3} , 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.

Measurement Uncertainties and Limit of Detection

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} , 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. 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 follow IC calibrations were within 3 to 5%, and 5 to 10% after running for an extended period. The overall uncertainty of the measured ionic species is estimated to be $\pm 10\%$.

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 was 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) (Figure 2). The mass concentration of the calibration aerosol was measured with the PILS-IC and compared to the mass concentration measured with a scanning mobility particle spectrometer (SMPS; TSI Inc, St Paul MN,). Note that 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. This is a valid assumption 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 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 g m^{-3} , typical of ambient urban aerosol concentrations.

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 non-activation of smaller nuclei, a result of our limited mixing of saturated water vapor and sample air. Note, 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 underestimating 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 μm diameter, so-called PM_{2.5}. A secondary goal was to study the chemical and physical properties of urban 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 semi-continuous techniques, and was in general agreement with filter measurements of non-volatile species, such as sulfate.

The PM_{2.5} sampling system, including the PILS-IC, is shown in Figure 4. The sampling inlet consisted of an inverted stainless steel tube connect to a 10 L min⁻³, 2.5 μm cut URG (University Research Glass) cyclone to permit measurements of 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 NH₃, and SO₂ and HNO₃ 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, Aug. 19 to Aug. 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 on practically every day, nitrate peaked in early morning between 600 and 1000 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 relative humidity. It is known that partitioning of nitric acid between the gas and condensed 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 play a major role in the formation of the early morning nitrate peaks.

During the period of Aug. 18 to 28, other ancillary measurements showed that total PM_{2.5} mass concentrations varied between 5 to 50 $\mu\text{g m}^{-3}$ (Bergin, personal communication; 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 highest levels corresponding to pollution episodes, possibly associated with power plant plumes or other local sources. During this period these plumes were observed primarily between Aug. 20 to Aug 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 two, 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 one, 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 two. These typically occurred when the total aerosol mass concentrations were very low. For example, molar ratios peaked near 4 during periods near midnight on Aug. 26 and Aug. 27. During these times PM_{2.5} levels were unusually low at 10 $\mu\text{g m}^{-3}$. At these times ammonium may also be associated with other acidic species. 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 acidic species are 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 particle-into-liquid sampler (PILS) coupled with an ion chromatograph (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 near real-time with a 4.3 minute 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 minutes with sensitivities near 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 components and properties.

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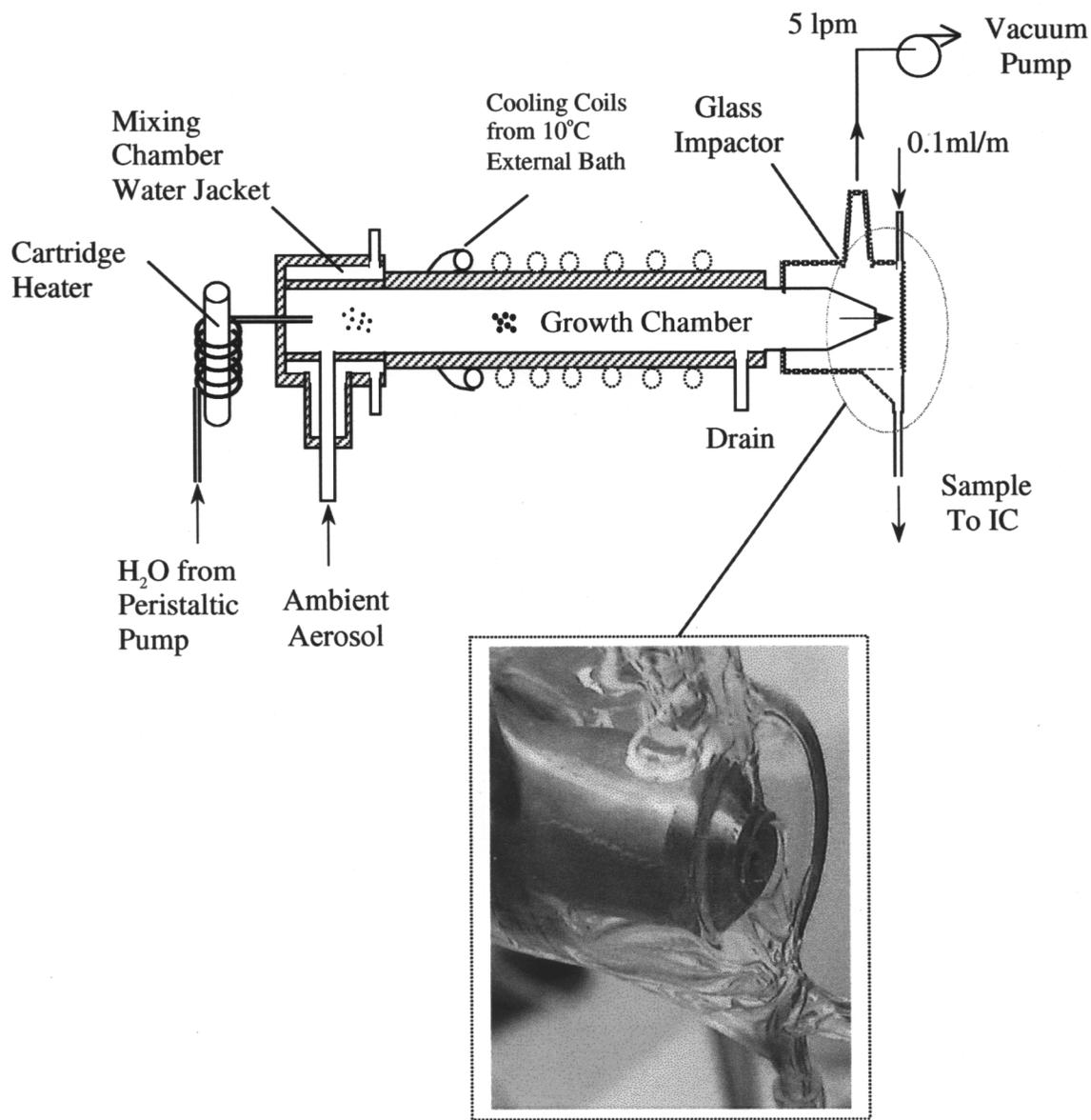


Figure 1. Schematic diagram of the particle-in-liquid collector (PILS) which is composed of a saturated vapor generating system, a chamber for mixing vapor and ambient air, a condenser, and the impaction region for collecting the droplets into a flowing liquid stream. The insert shows the impactor nozzle,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

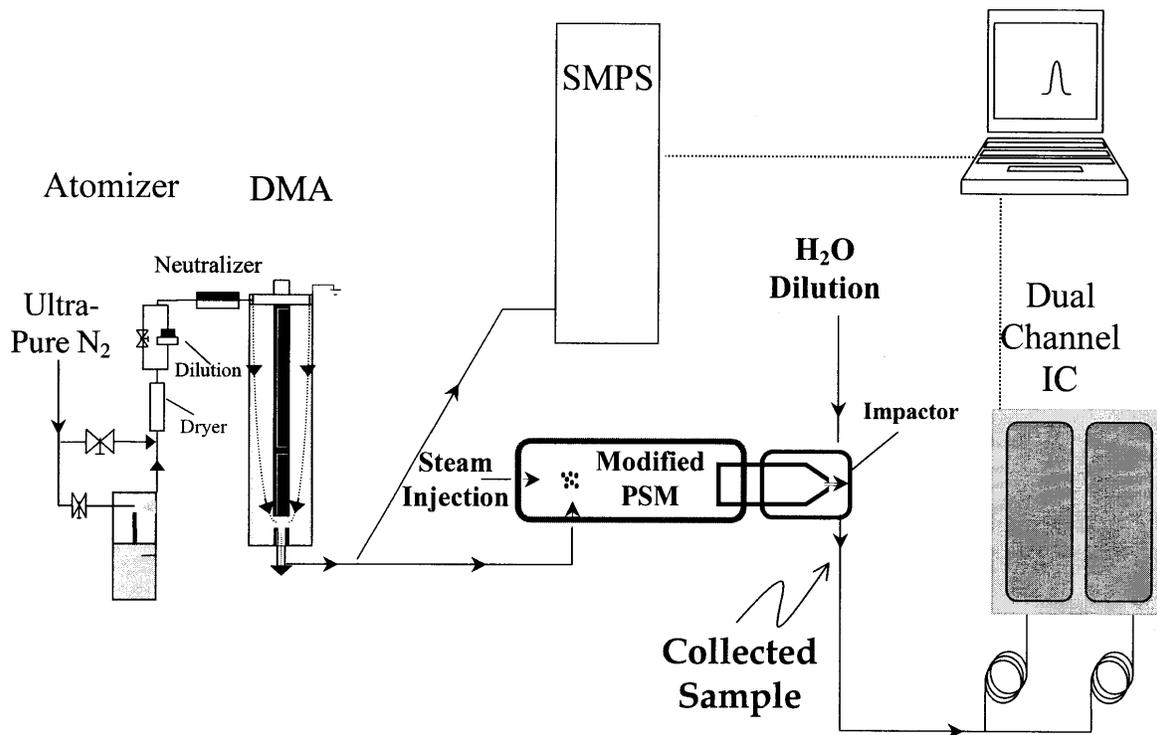


Figure 2. Schematic diagram for mass collection efficiency calibration of the PILS coupled to a dual channel ion chromatograph. Monodisperse ammonium sulfate aerosol is generated with a nebulizer-differential mobility analyzer (DMA). The mass of this calibration aerosol measured by the PILS-IC is compared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

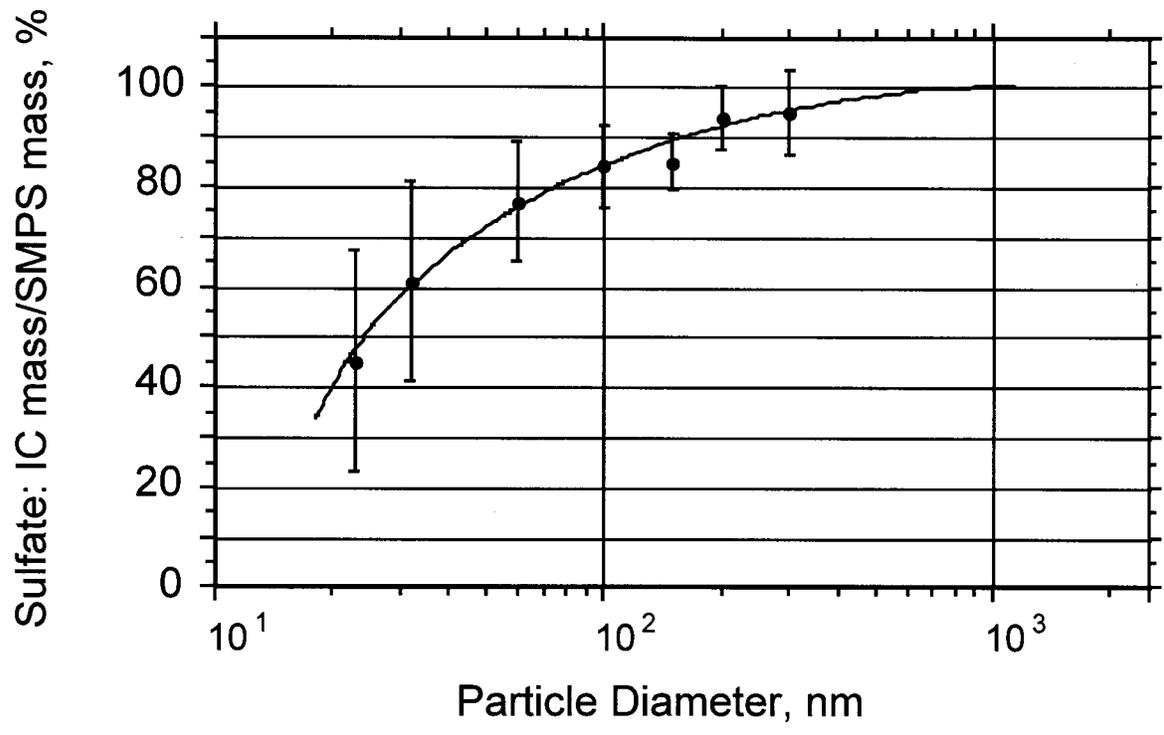


Figure 3. Results of the PILS-IC mass collection efficiency tests for sulfate.

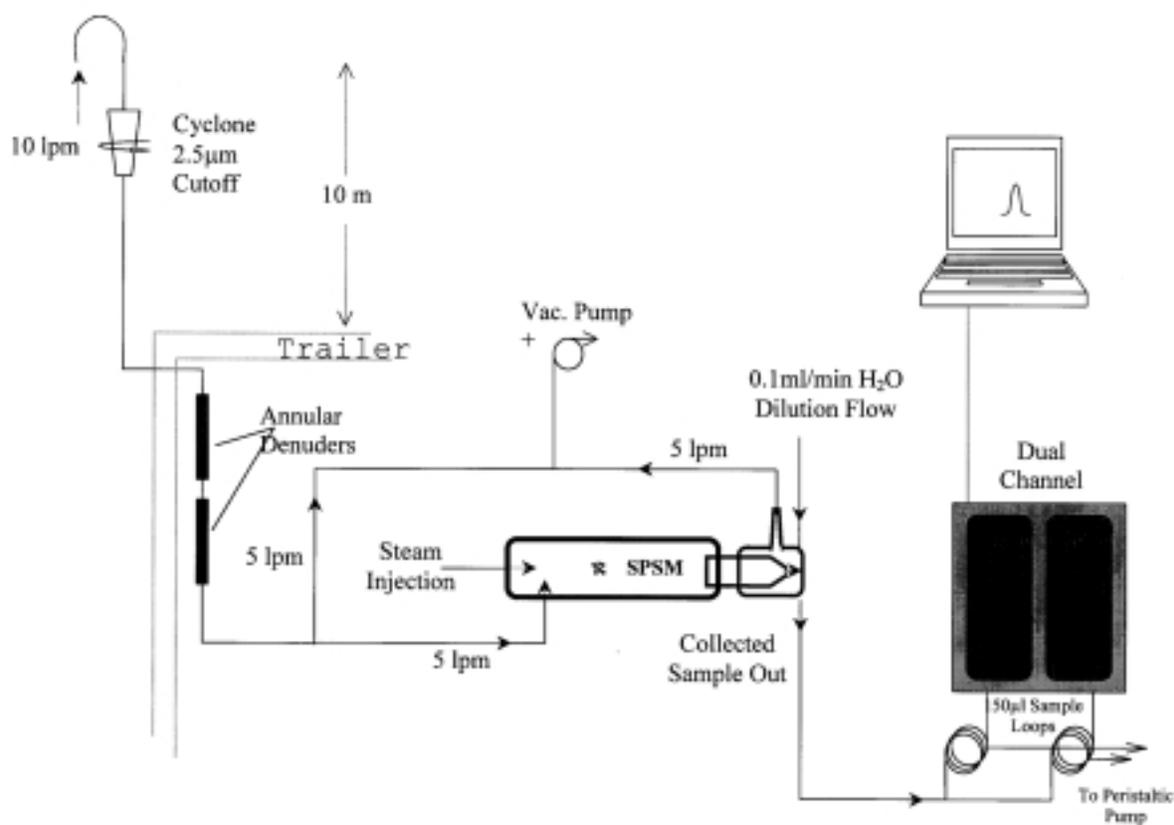


Figure 4. Schematic of the PILS-IC deployed for the EPA Atlanta Supersite measurements in August 1999 for rapid measurements of bulk aerosol ionic species.

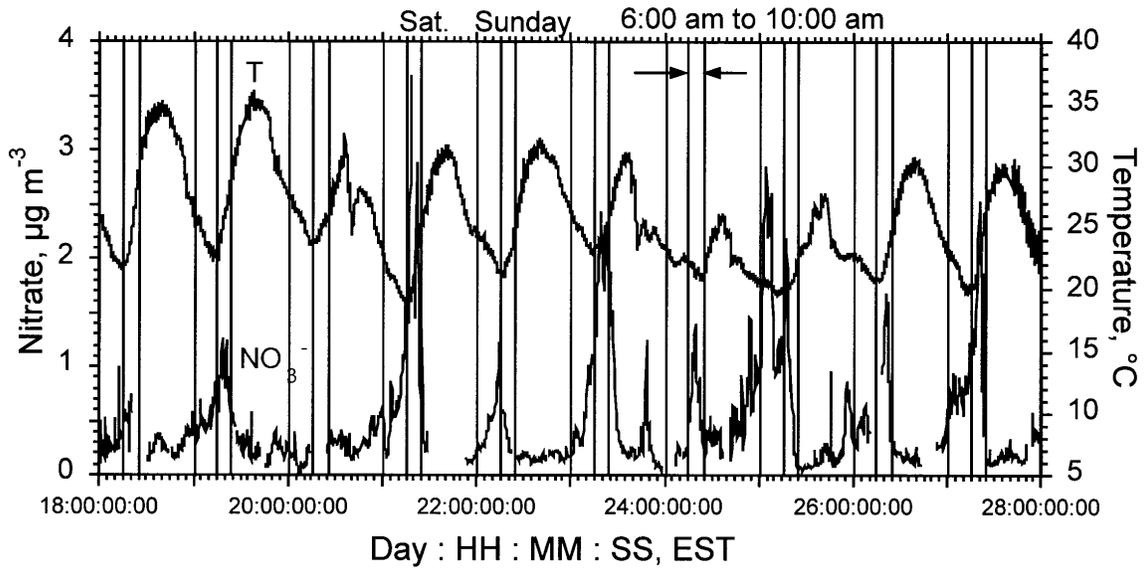


Figure 5. PILS-IC measurements of nitrate and ambient temperature recorded at the Atlanta Supersite from August 18, 1999 to August 28, 1999. Nitrate was observed to peak between 0600 and 1000 Eastern Standard Time (EST) on practically every morning. The peaks coincided with minimums in daily temperature. The data demonstrate how rapid measurements can provide insights into processes that would not be observed with long integration intervals associated with standard filter measurement approaches.

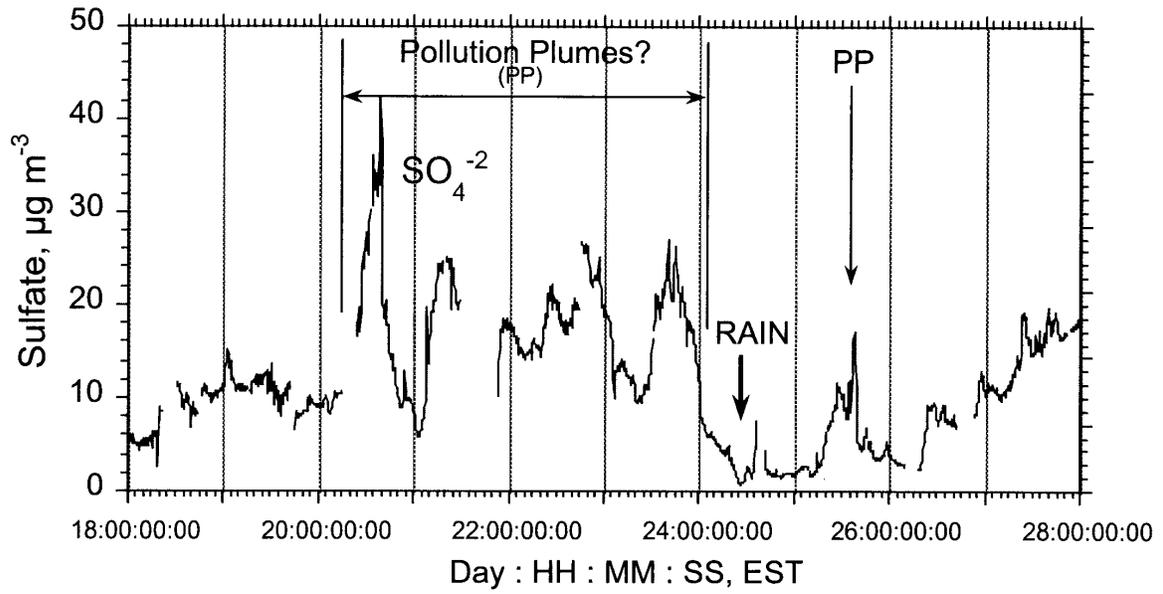


Figure 6. PILS-IC measurements of sulfate recorded at the Atlanta Supersite from August 18, 1999 to August 28, 1999.

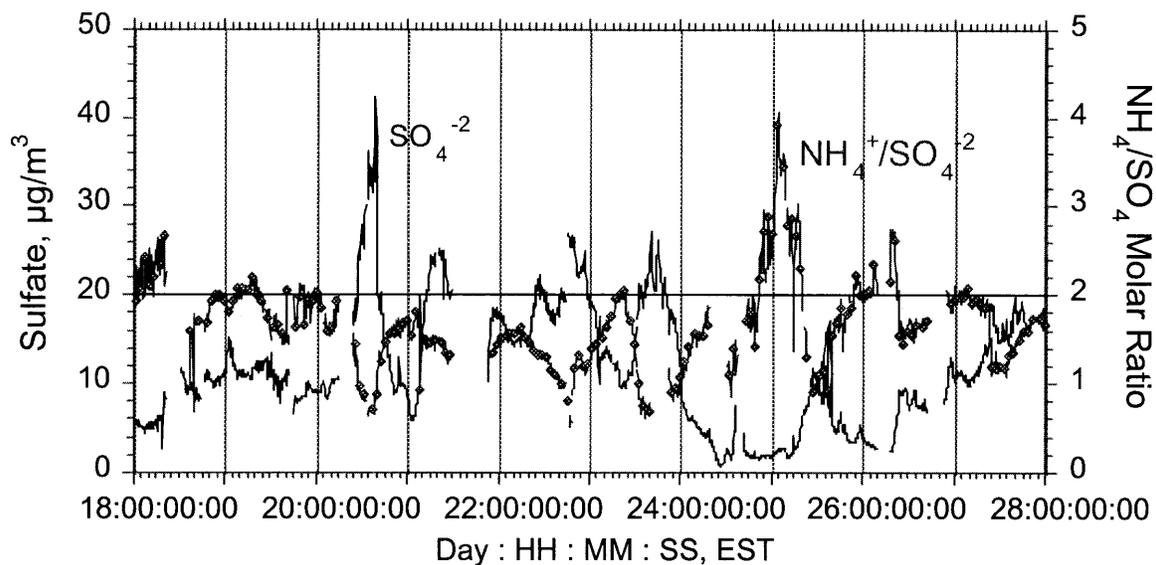


Figure 7. PILS-IC measurements of sulfate concentrations and ammonium to sulfate molar ratios recorded at the Atlanta Supersite from August 18, 1999 to August 28, 1999. Peaks in sulfate are associated with pollution plumes and a minimum in molar ratios.

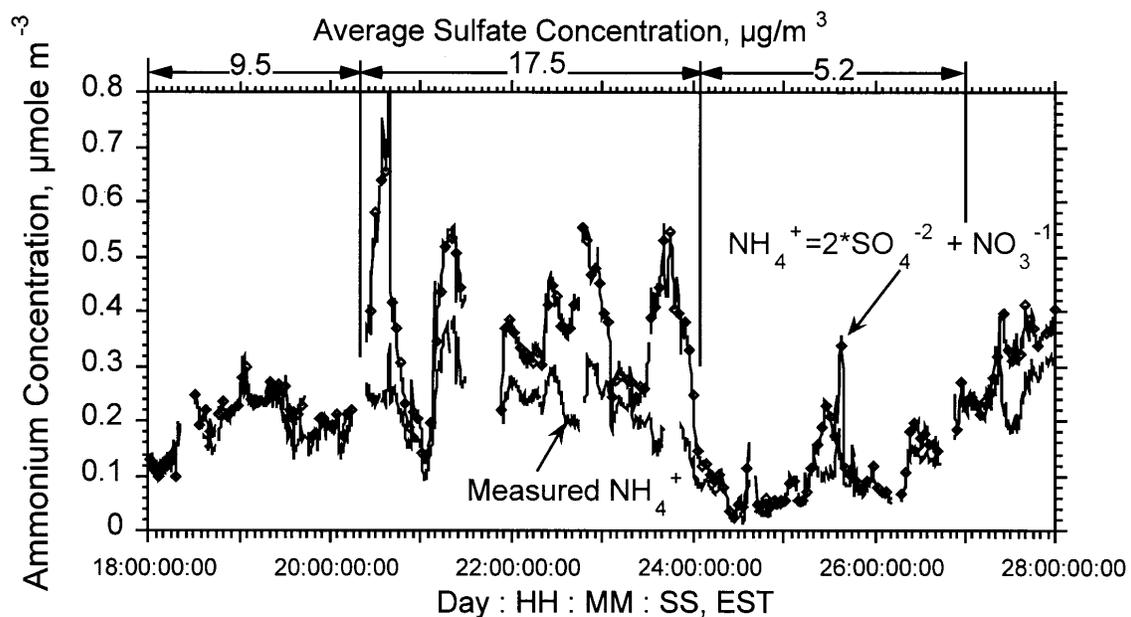


Figure 8. PILS-IC measurements of the ammonium molar concentration and the calculated ammonium molar concentration necessary to neutralize the measured aerosol sulfate and nitrate. The plot shows that typically the aerosol is nearly completely neutralized, except during periods of high sulfate concentrations.