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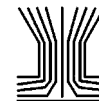
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Automated Measurement of the Size and Concentration of Airborne Particulate Nitrate

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A three-stage, cascaded integrated collection and vaporization system has been developed to provide automated, 10 min resolution monitoring of the size and concentration of fine particulate nitrate in the atmosphere. Particles are collected (7 min) by a humidified impaction process, and analyzed in place (3 min) by flash vaporization and chemiluminescent detection of the evolved nitrogen oxides. The three size fractions, $< 0.45 \mu\text{m}$, $0.45\text{--}1.0 \mu\text{m}$, and $1.0\text{--}2.5 \mu\text{m}$, are chosen to distinguish the condensation, droplet, and coarse components of $\text{PM}_{2.5}$. The size pre-cut at $2.5 \mu\text{m}$ is done at ambient conditions, while the size fractionation at $1.0 \mu\text{m}$ and $0.45 \mu\text{m}$ is done at a constant relative humidity of 65%. The system is calibrated with laboratory aerosols, including comparison of sizing for hygroscopic salt and hydrophobic organic aerosols. The complete system is tested with monodisperse ammonium nitrate aerosol generated with a high-flow differential mobility analyzer coupled with an impactor pre-cut and yields results consistent with the calibration of the individual stages.

INTRODUCTION

Although from a regulatory point of view $\text{PM}_{2.5}$ is considered one size class, in fact it is composed of several fractions. Whitby and Sverdrup (1980) identified three modes of the ambient aerosol, “nuclei,” “accumulation,” and “coarse,” roughly corresponding to the size ranges below $0.1 \mu\text{m}$, $0.1\text{--}1 \mu\text{m}$, and above $1 \mu\text{m}$, respectively. With work in the last twenty years the midsize range, or accumulation mode, has been further separated into the “condensation” and “droplet” modes, corresponding to particles from $0.1\text{--}0.5 \mu\text{m}$ and 0.5 to $1 \mu\text{m}$, respectively (John et al. 1990; Hering et al. 1997). The origins of particles in these size ranges differ (McMurry and Wilson 1983; Hering and Friedlander 1982).

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In past years, detailed size-resolved chemical composition was obtained through time-integrated collection of size-segregated samples collected by impaction. Rotating drum impactors have provided semicontinuous records of elemental composition (Flocchini et al. 1976; Malm et al. 1994; Bench et al. 2002). More recently, particle mass spectrometers have emerged that provide simultaneous data on particle composition and size. The system of Jayne et al. (2000) couples aerodynamic size classification with analysis of vaporized particles by quadrupole mass spectrometry. Noble and Prather (1996) measure the aerodynamic size and mass spectra for individual particles using a time-of-flight mass spectrometer. Time-resolved measurements of inorganic ions can be made using on-line ion chromatographic systems, such as those of Simon and Dasgupta (1993, 1995), Khlystrov et al. (1995), Slanina et al. (2001), and Weber et al. (2001). Although these ion chromatographic systems do not offer size resolution, they show precision comparable to that obtained from integrated filter methods (Weber et al. 2003).

Previously we reported on a method to provide 10 minute automated measurement of fine particle nitrate using an integrated collection and vaporization cell (ICVC, Stolzenburg and Hering 2000). We have now extended our method to make measurements in three size fractions using a cascaded ICVC system. The three fractions target the condensation, droplet, and coarse modes of $\text{PM}_{2.5}$. Analogous to the ion chromatographic systems, the ICVC is a semicontinuous method that can be field-calibrated using aqueous standards. As before, the time resolution is 10 min.

EXPERIMENTAL METHODS

Instrument Description

The cascaded ICVC has three impaction stages, designated “A,” “B,” and “C” and operated in series, as shown in Figure 1. The 0.9 L/min aerosol sample flow passes through a $2.5 \mu\text{m}$ pre-cut impactor and vapor denuder, operated at near-ambient temperature and relative humidity (RH), and is then humidified to 65% RH using a Nafion[®]-based humidity conditioner. A target of 65% RH was chosen to allow for enough humidification of

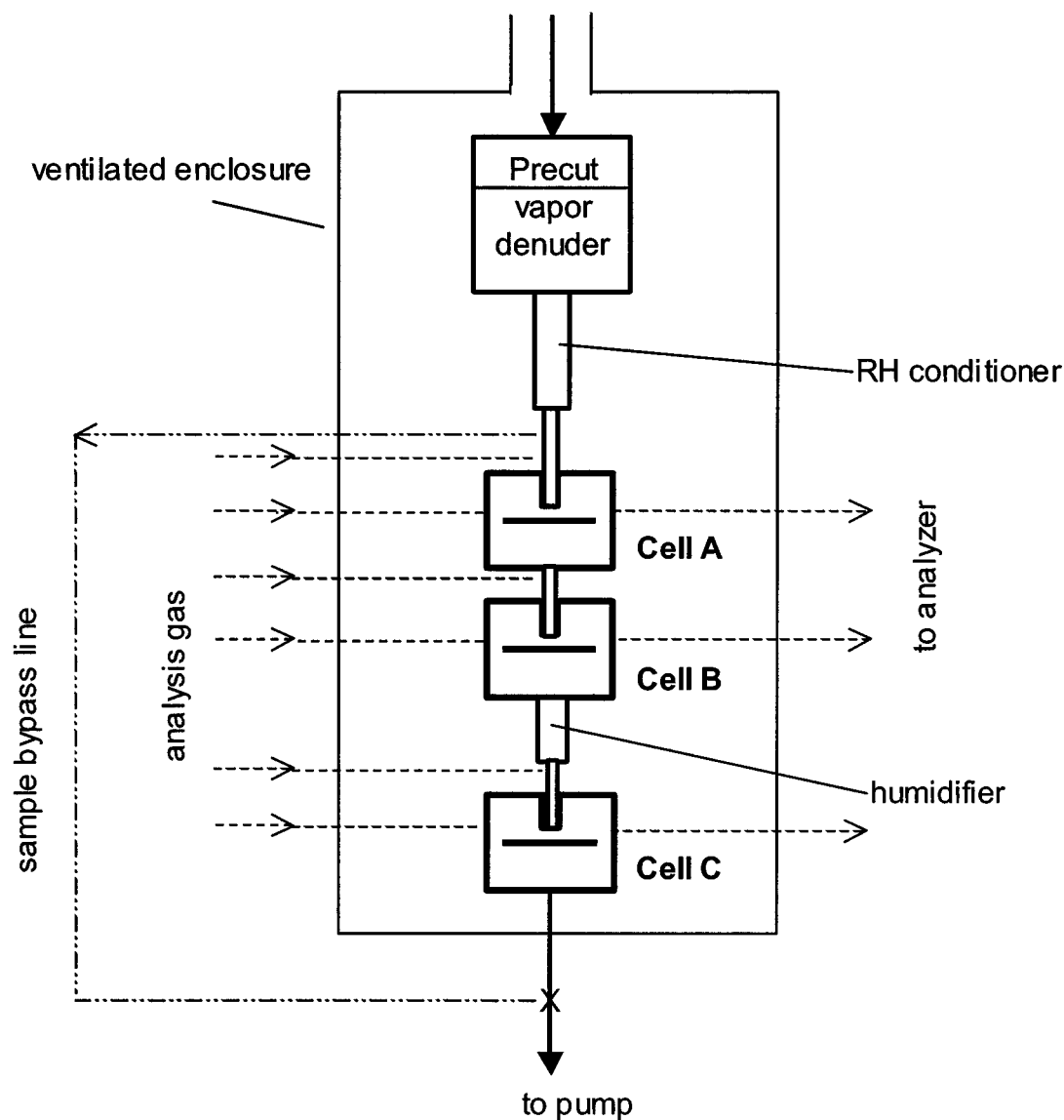


Figure 1. Schematic of the cascaded ICVC system for size-resolved analysis of $\text{PM}_{2.5}$ nitrate. Solid lines show the flow path during sampling. Dashed lines show the flow paths for ambient air bypass and the nitrogen carrier gas that are active during analysis.

the aerosol to prevent bounce, but not so much as to drastically increase particle size. Particles below the $2.5\ \mu\text{m}$ precut and above $1.0\ \mu\text{m}$ aerodynamic diameter at 65% RH are collected in Stage A. The humidity is not changed through Stage B, which collects particles above $0.45\ \mu\text{m}$ in aerodynamic diameter. The sample then passes through a Nafion[®] humidifier with a liquid water sheath to achieve humidity above 90% before collecting on Stage C.

The sample train, including the preimpactor, denuder, humidifiers, and the three collection-analysis cells are housed in an environmental enclosure that is ventilated with outdoor air by means of an exhaust blower. As deployed for these measurements, the sample line is 4 mm ID aluminum tubing ($1/4$ in OD) housed within a 75 mm diameter flexible duct through which

the ventilation air is drawn. The preimpactor is a single jet impactor with an oiled, sintered glass impaction surface and is used to exclude particles larger than $2.5\ \mu\text{m}$ in aerodynamic diameter. The denuder is an activated carbon-impregnated ceramic honeycomb manufactured by Corning, and is used to remove interfering vapors.

The humidity conditioner, which controls the RH of the sample stream at 65% for the first two cells, is based on the approach of Collins (2000). For our application, conditioning is done using a single Nafion[®] tube, 2.2 mm ID by 300 mm in length (PermaPure MH-110). The humidity is controlled by means of a PID-controlled valve that regulates the pressure of a flow, saturated with water at ambient pressure, through the sheath region of the humidifier. The volumetric flow through the humidifier

shell is limited to 4 L/min maximum by a downstream orifice, while the absolute pressure in the shell is controlled by an upstream fixed .28 mm orifice and a PID-controlled valve in parallel. The PID-controlled valve consists of a pressure controller (Alicat PC-40inHg-D-V94) with downstream pressure setpoint provided by a PID controller (Omega CNi3254). The PID input is from a humidity sensor (Vaisala Humitter 50Y) in the sample flow immediately below the humidifier. The pressure (and valve) is regulated to maintain a reading of 65% relative humidity of the sample flow. Laboratory measurements confirmed that there is very little change in the relative humidity between Cell A and Cell B. Prior to entering Cell C, the sample stream is humidified to above 90% RH using a second 2.2 mm $\times$ 300 mm Nafion[®] tube surrounded by a liquid water sheath. Temperature and RH of the sample stream are measured immediately above Cell A and Cell C.

Each of the collection cells measures 32 mm interior diameter by 19 mm interior height. Orifice diameters are 0.99 mm, 0.61 mm, and 0.37 mm, corresponding to flow Reynolds numbers of 1270, 2080, and 3400. In the final configuration, the jet-to-place spacing is 4, 5, and 5 jet diameters, respectively. The flow rate of 0.9 L/min is controlled by the final (Stage C) jet, which operates at sonic conditions. The collection substrates are 23 mm $\times$ 5.3 mm $\times$ 0.025 mm stainless steel strips held in place by metal posts that provide the electrical contact.

The analysis train employs a nitrogen source, chemiluminescence nitric oxide detector, and vaporization electronics. The analysis procedure is similar to that described previously for the single cell ICVC. The aerosol deposits from each cell are analyzed sequentially, beginning with Stage C. Vaporization electronics use a 6V gel cell battery with an infrared sensor cutoff, analogous to the approach used in the Rupprecht and Patashnick Co. 8400N (Rupprecht and Patashnick Co. 2001). The infrared sensor is mounted in the bottom of each collection cell facing the underside of the collection substrate. Current is supplied from the battery until the preset infrared cutoff is reached. Typical heating times are 50–80 ms. The nitrogen oxide detector is a commercial chemiluminescence analyzer that measures NO based on its chemiluminescent reaction with ozone (Model 42C, Thermo Environmental Instruments). The analyzer is used with a molybdenum converter for reducing higher nitrogen oxides to nitric oxide.

The system alternates between sampling and analysis modes through the switching of the various valves. During sampling the valve between the final cell and the pump is open, while the valves between the cells and the NO_x analyzer and between the cells and the nitrogen source are closed. Ambient, particle-laden air is drawn through the pre-impactor, denuder, humidifier and into the cascaded ICVC. The pressure in the final cell is regulated by a downstream valve to near one-half of atmospheric, to provide just-critical flow. There are no valves between the cells or elsewhere in the aerosol sample path. For sample analysis, the valve between the final cell and the pump switches to redirect the sample flow to bypass the cells, and the valves to the nitrogen

source and to the NO_x analyzer for each cell are opened in turn. Nitrogen enters the cell being analyzed through the pumping port at a flow rate slightly less than the 0.6 L/min required by the gas analyzer. The balance enters through the sample orifice above which the nitrogen is supplied in slight excess. After a preset flushing time of 20 s, the particle deposit is vaporized in place by rapid resistive heating of the metal strip, and the evolved vapors are transported by the nitrogen carrier gas to the NO_x analyzer. The gases pass through the molybdenum converter to reduce NO₂ and other nitrogen oxides to NO prior to detection. The resulting peak in NO_x concentration is integrated to yield the mass of nitrate collected. The detector baseline is read prior to each measurement, and nitrate is derived from the baseline-corrected nitrogen oxide concentration peak. To assure complete removal, the strip is heated a second time. Peak integration time is 15 s; the entire analysis takes 50 s for each cell. Cells are analyzed sequentially, beginning with the bottom cell, in a total of 160 s. After analysis the system returns to sampling mode and the cycle is reinitiated. For a 10 min cycle the sample collection time is 420 s.

The system and data acquisition are controlled by a Pentium computer equipped with a Keithley MetraByte card (DAS-1202). Recorded parameters include the sample flow rate and interval; flash strip heating performance parameters; the baseline, integral, and shape of each analysis peak; and other system operating parameters.

Cutpoint Evaluation

The size-dependent collection efficiencies for Stages A, B, and C were evaluated in the laboratory by measuring particle concentrations above and below each stage for various challenge aerosols. For Cell A, which has the largest cutpoint, testing was done using polydisperse challenge aerosol, with measurements downstream by an aerodynamic particle sizer (TSI 3320). Polydisperse polystyrene latex with a median diameter of 2 μ m was generated using a fluidized bed and dispersed into a plenum. The collection substrate was greased to prevent rebound of the test particles. Alternating 1 min measurements were taken directly from the plenum, or downstream of the cell, using the aerodynamic particle sizer. Cell collection efficiencies were determined from the downstream counts normalized with respect to the average of the immediately preceding and following upstream counts. Assurance of equal transport along the two sampling lines was evaluated by measurements without the collection substrate, and without the orifice. Each measurement was repeated at least three times.

The upper portion of the collection efficiency curve for Cell B was determined in the same manner as for Cell A. Below 0.8 μ m the collection efficiency for Cell B was measured using dioctyl sebacate particles generated by nebulization, and size classified using a high-flow differential mobility analyzer (HF-DMA, Stolzenburg et al. 1998). Upstream particle counts were measured with an optical particle counter (Climet Spectro .3) and condensation particle counter (TSI 3760). A laser particle

counter (Particle Measuring Systems LAS-X or LasAir 1003) sampled alternately from immediately upstream and downstream of the collection cell. For Cell C, the particle concentrations downstream of the cell were monitored with a second optical particle counter operated at low pressure (LP-OPC).

Calibration Checks with Aqueous Standards

In routine operation, the calibration for the analysis step is checked using aqueous standards applied directly to the collection substrate. Each of the three cells are opened, and a sub-microliter drop of the standard is applied directly to the center of each collection substrate using a graduated, 1 μL syringe. The droplets are allowed to airdry for 2 min, then the cells are closed and the samples are analyzed using the same purging and flashing conditions as in the actual operation. The response is the baseline-corrected integral, in ppb-s, of the resulting peak in NO_x concentration as measured by the analyzer. The response over a range of concentrations is obtained by varying the amount of standard applied.

Laboratory Aerosol Tests of the Integrated System

Ammonium nitrate particles were generated by nebulization, and a mono-mobility size fraction was selected from the nebulized aerosol using the HF-DMA. A single stage impactor was used ahead of the mobility analyzer to remove larger particles that would otherwise contribute a larger doubly charged particle fraction to the monodisperse particle output. The size of the challenge aerosol was varied from 0.1 to 1.1 μm diameter. The particle upstream concentration and size distribution was monitored with a condensation nucleus counter and an optical counter as described above. The nitrate deposited on each stage was determined by the flash-vaporization analysis.

RESULTS AND DISCUSSION

Approach

Many aspects of the cascaded ICVC system are similar to the single-stage ICVC system described earlier (Stolzenburg and Hering 2000). The third and final cell of the cascaded ICVC

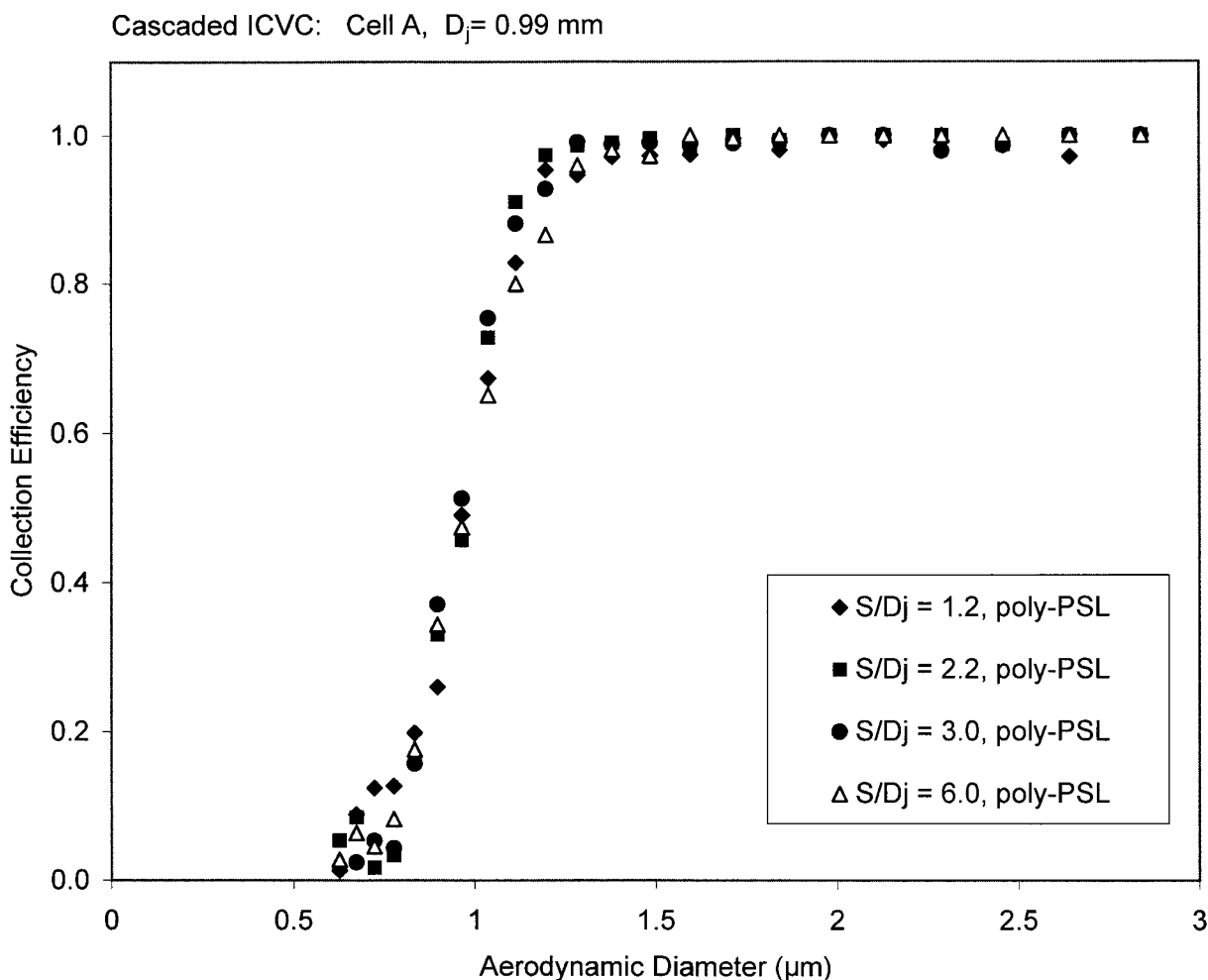


Figure 2. Collection efficiency, expressed as fraction of the challenge aerosol, for Cell A (jet diameter = 0.99 mm) at jet-to-plate spacing, S , equal to 1.2, 2.2, 3, and 6 jet diameters. All data are for a challenge aerosol of polydisperse polystyrene latex aerosol, with stage efficiency determined by upstream and downstream counting with an aerodynamic particle sizer.

system is identical to the single stage from that system. Likewise, the humidifier employed immediately above the final stage is identical to that in the single stage system. The cascaded system simply has an additional two cells and a humidity conditioner upstream of the existing cell for size-selection of the larger particles. The humidity conditioner ahead of the first collection cell is used to provide a well-defined humidity for the size separation while ensuring sufficient water on the particles to prevent particle bounce.

In our prior work we systematically investigated specific aspects of the system performance, including volatilization losses, vapor interferences, response to different nitrate compounds, and comparison with filter data in the field. Our current investigations have focused on the performance of the new components of the cascaded system, namely the size-segregation characteristics of the cascaded cells, and the stability of the humidity conditioner.

Individual Cell Collection Efficiencies

The particle size-dependent collection efficiency of Cell A is shown in Figure 2 for various jet-to-plate separations. The

challenge aerosol was polydisperse polystyrene latex, a nonhygroscopic solid, with collection onto a greased surface without the humidity preconditioner. These experiments focused on the influence of the jet-to-plate spacing. While impactor design criteria call for close jet-to-plate separation of approximately one jet diameter, the in situ analysis is best if a larger jet-to-plate spacing can be used. Tests were done for spacings of 1, 2, 3, and 6 jet diameters, as shown in Figure 2. The results all show a cutpoint of 1 μm aerodynamic. Little degradation of the curve is seen up to 3 jet diameters, in agreement with impaction theory (Rader and Marple, 1985). At the largest jet-to-plate separation of 6 jet diameters, the collection efficiency becomes less sharp, with slightly lower collection near 1.2 μm . In the final configuration, the Cell A jet-to-plate spacing is 4 jet diameters. Stage A was also tested using a liquid aerosol, dioctyl sebacate (DOS), to evaluate the efficiency of penetration of particles below the cutpoint. These data show that the submicrometer penetration is as good for the liquid particles as for the solid latex spheres.

Calibration curves for Cell B are shown in Figure 3 for four different challenge aerosols, polystyrene latex and DOS which

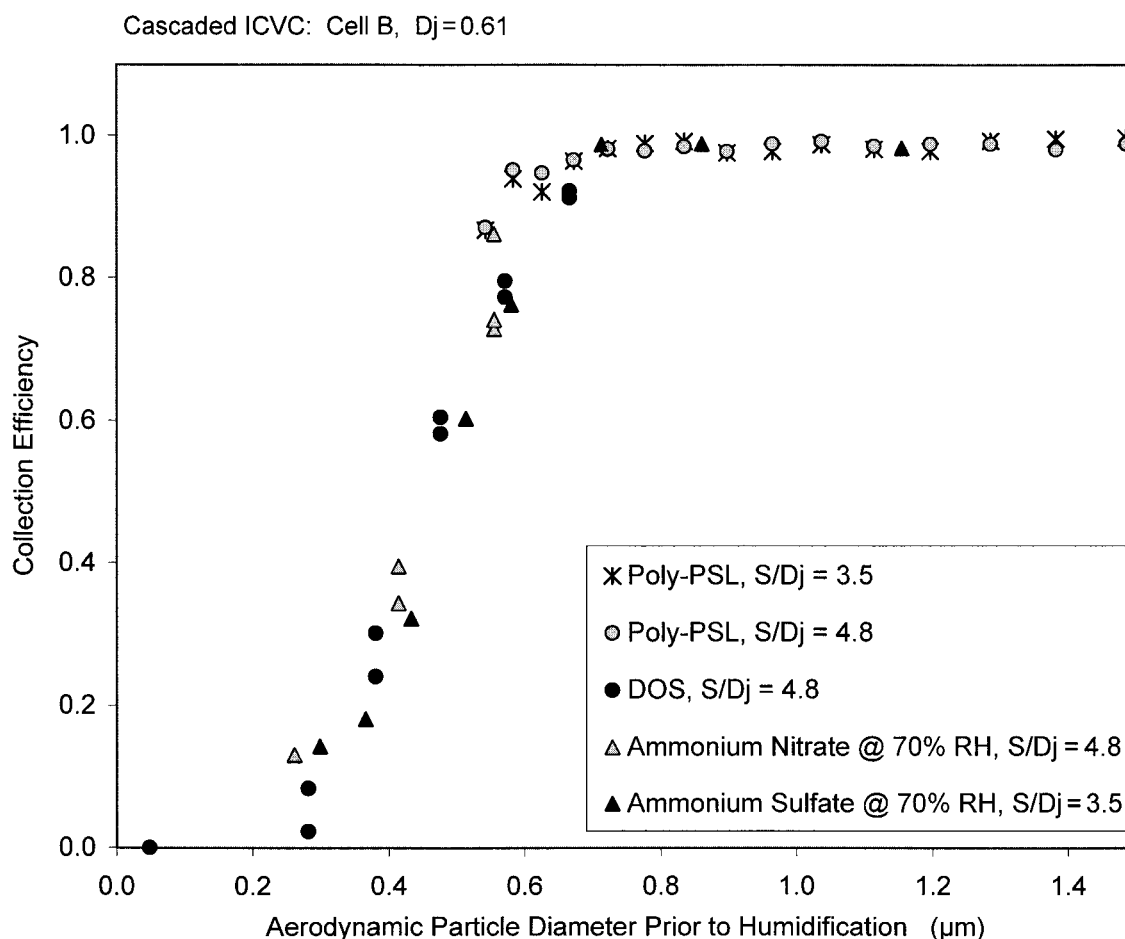


Figure 3. Collection efficiency for Cell B, with a jet diameter of 0.61 mm, for challenge aerosols of polydisperse polystyrene latex, dioctyl sebacate (DOS), ammonium nitrate, and ammonium sulfate. Particle size is shown as a function of aerodynamic diameter calculated from the Stokes diameter prior to humidification. Data are for jet-to-plate spacings, corresponding to 3.5 and 4.8 jet diameters.

are nonhygroscopic, and ammonium nitrate and ammonium sulfate which are hygroscopic. With the exception of the data for the polydisperse polystyrene latex, the measurements were made with the humidity conditioner immediately upstream of the cell. For DOS the aerodynamic diameter is calculated from the single charge mobility diameter (Stokes diameter) from the mobility analyzer, and from the bulk DOS density of 0.89 g/cm^3 . Data are shown for two jet-to-plate spacings with essentially equal results. The aerodynamic cutpoint obtained with the DOS challenge aerosol is $0.45 \mu\text{m}$.

The DOS calibration curve for Cell B is compared to that for the two hygroscopic salts, ammonium nitrate and ammonium sulfate. These particles were size selected by the mobility analyzer at a relative humidity of $30 \pm 5\%$, and then passed through the 65% RH conditioner and into the cell. Collection efficiency is shown as a function of the aerodynamic diameter calculated from the dry particle density and the mobility diameter, that is the Stokes diameter prior to humidification. The data indicate a slight shift in the collection efficiency curve to larger diameters.

The final collection stage, Cell C, is identical to that used in the single size fraction ICVC system. As in the single stage system, it is preceded by a humidifier. Collection efficiency

above $0.12 \mu\text{m}$ was measured using monodisperse ammonium sulfate particles. The jet-to-plate spacing is 5 jet diameters. Over the size range from 0.1 to $0.6 \mu\text{m}$ the collection efficiency is above 95%. With this experimental arrangement, which used a low-pressure optical counter as the downstream detector, it was not possible to extend the measurements to smaller particle sizes. Figure 4 shows these data together with that for the nonhygroscopic aerosol response for Cells A and B.

Size Cut Characteristics of the Integrated System

The assembled, cascaded ICVS system was tested using a laboratory challenge aerosol of ammonium nitrate aerosol, which was size-classified using the HF-DMA coupled with a single-jet preimpactor. The amount of nitrate collected by each cell was determined by flash vaporization analysis. Parallel optical particle counter data showed that for primary particle diameters of $0.6 \mu\text{m}$ and larger the preimpactor was effective in removing the larger, multiply charged particles. At a primary size of $0.3 \mu\text{m}$, the optical counter indicated that 3% of the aerosol number, or 15% of the mass, was due to doubly charged particles.

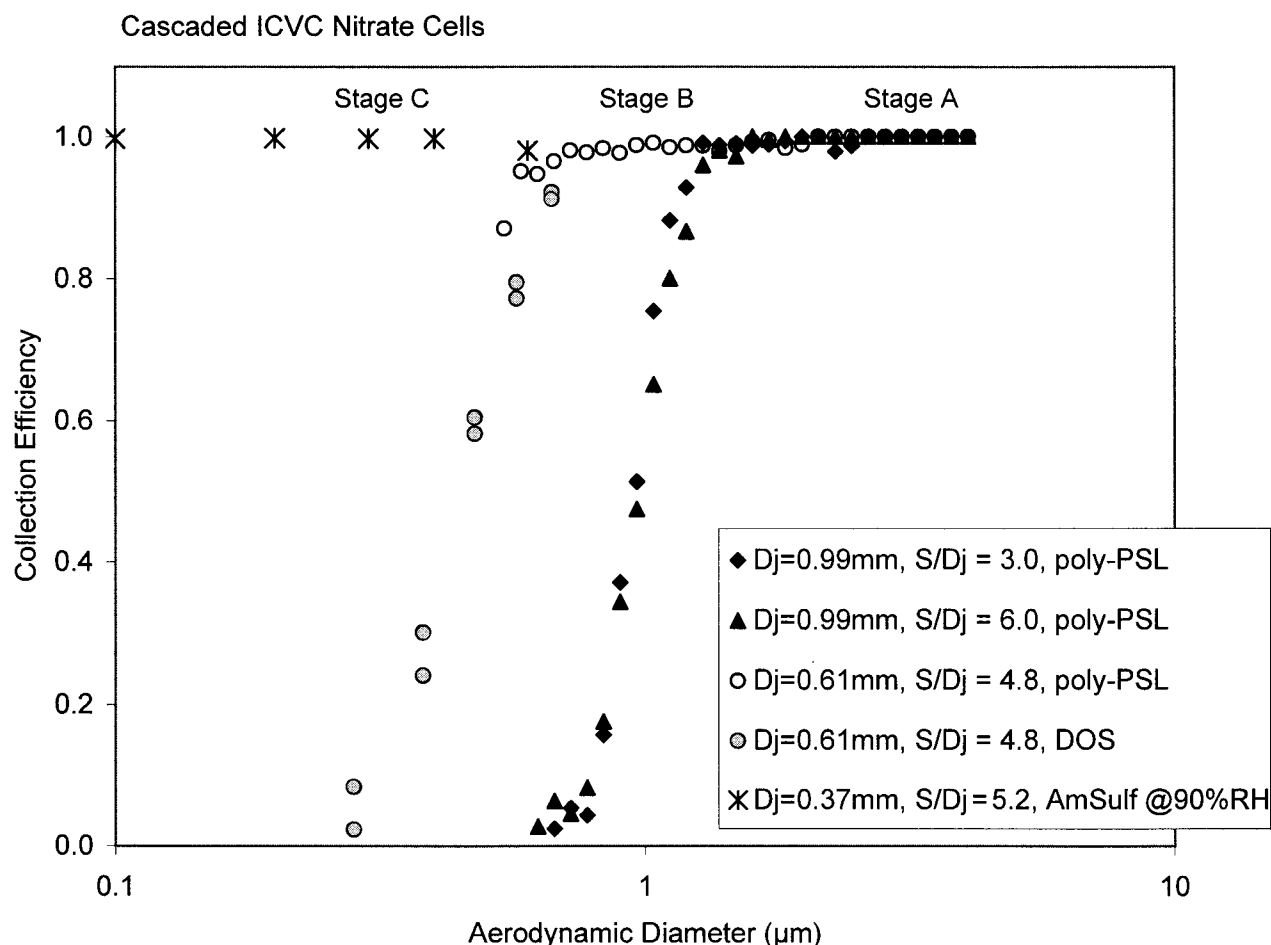


Figure 4. Combined stage collection efficiency data for all three ICVC cells.

To apportion the mass distribution at the primary size, it was assumed that the multiply charged particles deposited on Stage B. A similar 15% correction was made for triply charged particles at a primary size of $0.2\ \mu\text{m}$. No corrections were made for other particle sizes. Figure 5 shows the fraction of nitrate collected by each stage (with the correction for multiplets just noted) as a function of the monomobility, or Stokes, particle diameter determined by the HF-DMA, prior to humidification by the cascaded ICVC system. Lines are hand-drawn fits to the data. These data indicate size cuts at 0.41 and $0.95\ \mu\text{m}$ Stokes diameter, consistent with the single stage collection efficiency measurements of Figures 2–4.

Performance of the RH Conditioner

While some testing of the RH conditioner was done in the laboratory, the best assessment of its performance is from the field data, wherein the RH of the sample stream immediately downstream of the conditioner was monitored continuously. For the first five months of operation, from July 2001 through January

2002, the conditioner ahead of Stage A held the conditioned RH to a value of $63 \pm 5\%$, with a target set point of 65% . Approximately 9% of the data show values below 60% RH, while RH values in excess of 70% were rarely observed. We find that under dry summer conditions the conditioner was not always capable of sufficient humidification. This was attributed in part to the limited capacity of the humidifier, and in part to temperature differences between the ICVC system and the bubbler for saturating the humidifier sheath air flow. The ICVC system was housed in a ventilated chamber to achieve outdoor temperatures, while the bubbler was located in the airconditioned trailer. Under warm summertime conditions, the conditioner sheath air flow from the bubbler was no longer saturated after entering the warmer instrument enclosure, resulting in the inability to bring the sheath flow of the humidifier to sufficiently high RH.

Evaluation of Nitrate Recovery

Two factors influence the recovery of nitrate from the deposited particles: evaporative loss during collection and

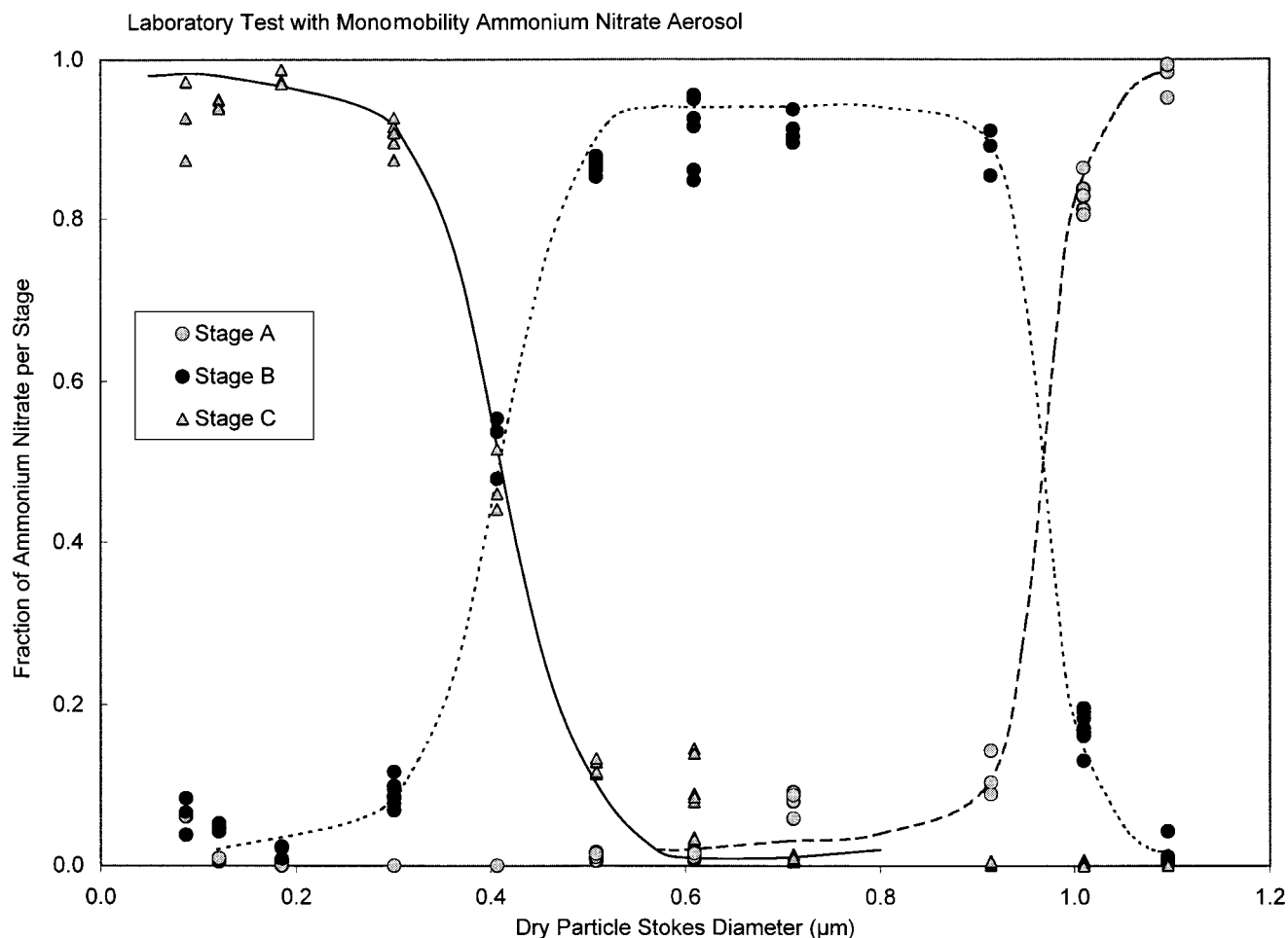


Figure 5. Fraction of ammonium nitrate measured on each of the three cascaded ICVC cells for monodisperse ammonium nitrate aerosol generated using a high-flow differential mobility analyzer. Data are shown as a function of the mobility diameter at 30% RH, prior to humidification by the conditioner.

analytical response. Vaporization losses are of greatest concern for the final stage, which operates at a pressure of approximately 0.5 atmospheres. In our previous work (Stolzenburg and Hering 2000) vaporization losses were evaluated in the laboratory and in the field. In the laboratory the system was challenged with monodisperse ammonium nitrate aerosol, with parallel measurements by the optical and condensation nucleus counters. Some samples were analyzed immediately at the end of the collection period. Other samples were collected for the same sampling time but then exposed to particle-free air prior to analysis. Average measured recovery, that is, the ratio of results for delayed analysis versus immediate analysis, was $98 \pm 4\%$ for 10 experiments. In the field, during a period of high nitrate concentrations, a special experiment was conducted wherein the sample duration was alternately varied between 4 min and 8 min. The nitrate concentration obtained with the longer sample duration was compared to the mean value from the immediately preceding and following shorter duration samples, yielding a mean recovery of $101 \pm 4\%$.

The issue of recovery of nitrate from the flash vaporization process is more difficult to evaluate in the context of the matrix of material present in ambient particles. The flash vaporization method for nitrate, as reported by Yamamoto and Kosaka (1994), showed that 96% to 100% of the nitrate deposited in the form of NaNO_3 , NH_4NO_3 , KNO_3 , $\text{Ca}(\text{NO}_3)_2$, or $\text{Fe}(\text{NO}_3)_3$ was recovered as NO_x by the catalyst-equipped chemiluminescent analyzer. For our system, we find recoveries for deposited aqueous standards of sodium nitrate are 5–10% higher than the response to ammonium nitrate.

For our laboratory experiments with mobility-selected ammonium nitrate aerosol, we compared the total measured nitrate concentration to the aerosol volume concentration. Total ICVC nitrate concentration is evaluated on the basis of the response to aqueous nitrate standards. The aerosol volume concentration is calculated from the number concentration measured by the CPC and the Stokes diameter from the mobility analyzer. Results shown in Figure 6 exclude those particle sizes for which the optical counter indicated a doublet concentration of greater than 10%

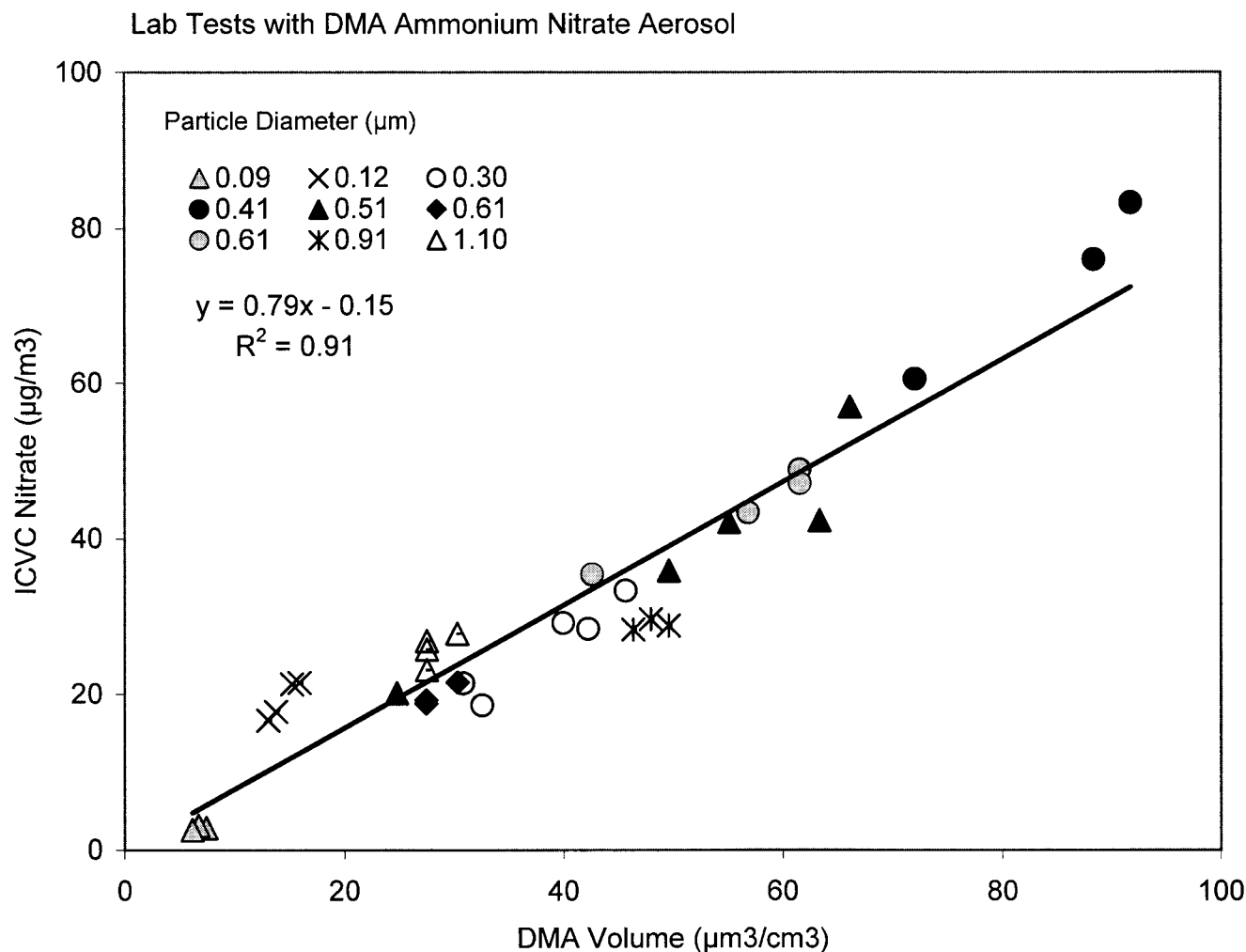


Figure 6. Comparison of nitrate concentration measured by the cascaded ICVC to the spherical-equivalent aerosol volume calculated from the mobility diameter for monodisperse ammonium nitrate challenge aerosols.

by volume. We find that the response for all particle sizes fall on a common line. The slope of the line, 0.8 g/cm^3 , is the same obtained in our earlier experiments (Stolzenburg and Hering 2000), but lower than the theoretical nitrate mass-to-volume ratio of 1.3 g/cm^3 for pure, dry ammonium nitrate. Several uncertainties are associated with the mass-to-volume comparison. As our size selection in the mobility analyzer was done at relative humidity of 35–40%, associated water could be contributing to the aerosol volume but not the nitrate mass. Alternatively, as noted by Tobias and Ziemann (1999), if a particle is cubic rather than spherical, then its volume will be 30% smaller than the spherical equivalent diameter calculated from the Stokes diameter.

For measurements of atmospheric nitrate, the analytical recovery could be influenced by the complex matrix in the ambient aerosol. Given these uncertainties, we have relied on field comparisons to integrated filter-based measurements to evaluate nitrate recovery. Nitrate concentrations from the ICVC system calculated on the basis of the response to aqueous ammonium nitrate standards have been compared to other methods. In Riverside, Mira Loma, and Bakersfield, California, measurements with our original single stage system yielded regression slopes between 0.96 and 1.06 in comparison to integrated filter systems (Stolzenburg and Hering 2000). In Atlanta the single stage ICVC gave regression slope of 0.94 ± 0.05 by comparison

to the mean of other automated nitrate measurement methods (Weber et al. 2003).

For the field deployment in Rubidoux and Claremont, California, the nitrate concentrations measured by the cascaded ICVC are compared to parallel filter and impactor measurements conducted by the University of Southern California. Again, the ICVC nitrate was calculated on the basis of the response to aqueous ammonium nitrate standards. Fine et al. (2003) report that the $\text{PM}_{2.5}$ nitrate concentrations measured by the cascaded ICVC system were 10% lower, on average, than filter-based concentrations obtained with the HEADS (Harvard EPA annular denuder sampler) sampler, but 26% to 43% higher than nitrate concentrations measured by a MOUDI (micro-orifice uniform deposit impactor). These field comparisons indicate that the aqueous standards provide a reasonable surrogate for the response of the system to atmospheric nitrate aerosol.

Example Data

Initial field data from Rubidoux, California, are displayed in Figure 7. Diurnal peaks in total nitrate are observed near noon daily, with occasional smaller increases in the early morning hours. This is similar to the diurnal pattern observed for August 1997 in Riverside by the single-size ICVC System (Stolzenburg

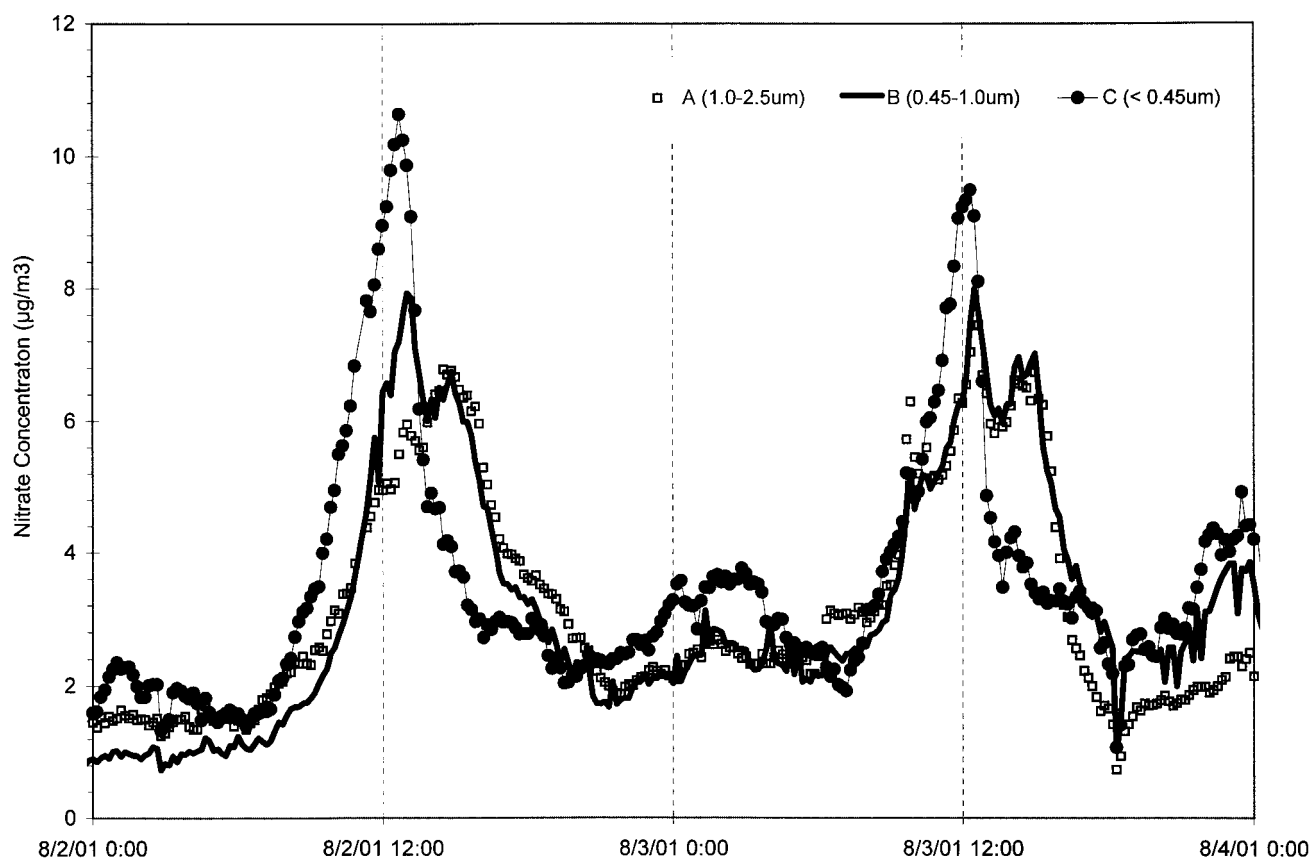


Figure 7. Cascaded ICVC data from Rubidoux, California, showing nitrate concentrations for each of the three size fractions for a two-day period in August 2001.

and Hering 2000). It is interesting to note that Stage C, the smallest size range, often increases first, followed by the larger Stages A and B 1–3 h later. On these days, the mass balance shifts toward larger particles immediately following a peak in total nitrate mass. On some days we observed a dominance of coarse particle nitrate, as has been reported by the aerosol time-of-flight mass spectrometer for Riverside (Liu et al. 2000).

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