AUTOMATED FINE-PARTICLE NITRATE AND PM$_{2.5}$ FRM MEASUREMENTS FOR METHOD EVALUATION AND SECONDARY AEROSOL CHARACTERIZATION DURING SCOS'97

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Executive Summary

Study Overview

The concentration of airborne fine particle nitrate was measured with 10-min time resolution over a six-week period from August 16, 1997 until October 1, 1997. Measurements were made using a new, automated method developed by Aerosol Dynamics Inc. With this technique particles are collected by a humidified impaction process and analyzed in-place by flash vaporization. Deposited nitrate mass is quantitated by the chemiluminescent detection of the evolved nitrogen oxides.

For the period until September 3 the automated nitrate system was deployed in Riverside, CA alongside several other particle measurement techniques. From September 3 through October 1, 1997 the system was deployed in Mira Loma, California, located to the west of Riverside. These field measurements were done with the combined support of EPRI, the Coordinating Research Council and National Renewable Energy Laboratory. They were made in conjunction with the Southern California Oxidant Study (SCOS’97), conducted under the auspices of the California Air Resources Board.

With the support of CRC, NREL and the South Coast Air Quality Management District (SCAQMD), Federal Reference Samplers for PM$_{2.5}$ were operated at each of three sites on selected study days. Two samplers were collocated at each site. One sampler was operated with a single Teflon filter and the other was operated with a Teflon-nylon filter pair in series. This was done to evaluate nitrate evaporative losses. Filters were analyzed for mass and ions by the SCAQMD.

With the support of EPRI, the methodology for automated, particle nitrate measurement was evaluated through a series of laboratory studies. Tests were done to evaluate the various components of the system including: particle penetration through the inlet; particle collection efficiency in the cell; evaporative losses of deposited particles; and interferences from various gaseous compounds. The complete system was tested with laboratory-generated monodisperse ammonium nitrate aerosol. Tests of collection efficiency, evaporative losses and interferences were conducted in the field as well as in the laboratory.

Results from Laboratory and Field Performance Tests

Various aspects of the automated nitrate system were tested in the laboratory, and where applicable these tests were repeated in the field. Results are, as follows.

Particle transmission through the inlet and humidifier: Measured particle transmission through the humidifier was 98±1% for submicrometer ammonium nitrate particles and 99±3% for submicrometer ambient laboratory aerosols. For the inlet used in
this study the transmission of submicrometer particles through the combined inlet and humidifier was 91±2%, and the data were corrected for this loss.

**Particle collection efficiency:** With the automated nitrate monitor, particles are humidified, and then collected by impaction within an integrated collection and vaporization cell. The collection efficiency of the cell was measured with monodisperse, laboratory-generated ammonium nitrate and ammonium sulfate particles. The average collection efficiency for 6 particle sizes between 0.1 and 0.8 µm was 99±2%. For ambient particles the collection efficiency for all particles above 0.1 µm ranged from 89% on a day of low nitrate concentrations, to 99% for days of high nitrate. The data were reduced assuming 100% collection efficiency.

**Evaporative losses.** In the laboratory, evaporative losses were assessed by exposing deposited nitrate samples to particle-free air prior to analysis. Measurements were made on several different days. Average loss was 2±4%. In the field the sample collection times were varied. The results for 8-min collection periods were compared to the average of 4-min samples collected immediately prior, and immediately following, the 8-min sample. For four such measurements the ratio of long to short sample concentrations was 1.01±4%. We conclude that nitrate evaporative losses were less than 2%.

**Interference from non-nitrate compounds.** Interference from ammonium ion in the nitrate measurement was tested through the analysis of ammonium sulfate standards. The mean response to a 80 ng standard of ammonium sulfate was 0.1 ppm-s, which was the same as the substrate blank, and less than 3% of the response nitrate on an equivalence basis. Similarly, no response above the substrate blank was observed for oxalic acid.

**Interference from gaseous compounds.** Interference from nitric acid was tested in the laboratory. The measured signal was less than 0.3±0.1 µg/m³ for exposure to 150-320 ppb of nitric acid. However, in the field measurable interference was found from gaseous compounds in ambient air, as determined by the response to Teflon-filtered ambient air. At Riverside samples were collected using a potassium hydroxide coated denuder, and the response to filtered air was 1.3±0.8 µg/m³. At Mira Loma samples were collected using an activated carbon denuder, and measured responses were 0.7±0.4 µg/m³. We concluded that neither ammonium ion nor nitric acid caused a positive interference. However, positive interference was seen for filtered ambient air on some days. This interference was minimized by use of an activated carbon denuder.

**System response to laboratory ammonium nitrate:** The response of the complete system to laboratory-generated monodisperse ammonium nitrate aerosol was compared to that calculated particle number concentrations and size. The response increased systematically and linearly with the amount of nitrate sampled. Measurements at different particle sizes and concentration yielded similar results.
Field Performance of the Automated Particle Nitrate System

The nitrate system provided nearly uninterrupted data over the six-week sampling period. Dynamic field blanks and calibration standards were run at least once weekly. Twenty-four hour averaged nitrate values from the automated system were compared to three different filter-based methods.

The performance of the system was compared to data quality goals that were prepared prior to the beginning of the study. These goals set specified values for accuracy, precision, lower quantifiable limit and data completeness. In each case the stated goals were met, as described below.

Accuracy: Accuracy was assessed by comparison to traditional filter-based methods. For three types of filter-based measurements the regression slopes were 0.88, 0.96 and 1.06, with R² values of 0.96, 0.99 and 0.94 respectively. The corresponding systematic bias in the automated nitrate measurement varied from -12%, to -4% to +6%, depending on the comparison. The differences between the 24-hr average of the automated nitrate and the filter-based measurements were no more than among the filter based measurements themselves. We conclude that no systematic bias could be detected in the measurement of particle nitrate using the automated system.

Precision: Precision was assessed by replicate standards. The pooled standard deviation of replicate ammonium nitrate standards run on the same day was 3%. The overall deviation in standards throughout the entire study period was 10%. These standards corresponded to concentrations from 5 to 40 µg/m³. We conclude that the precision of the method is 10% or better for levels above 5 µg/m³.

Lower Quantifiable Limit: The largest source of uncertainty in the data was the variability of the field blank. For measurements at Riverside using the KOH denuder one-sigma uncertainty arising from the field blanks was 0.8 µg/m³. For measurements at Mira Loma using the activated carbon denuder the one-sigma uncertainty was 0.4 µg/m³. Corresponding lower quantifiable limits, based on 3-sigma uncertainties, are 2.4 and 1.2 µg/m³.

Data Completeness: Instrument difficulties resulted in a down time of 30 hours over the 45 days of sampling. Apart from power outages and periods of calibration, the data recovery was 97%. On average, instrument calibrations took the instrument off-line another 4% of the time. Validated data were reported for 93% of the 10-min periods over the 45 day study period.

Results from the Federal Reference Method Sampler

Two Federal Reference Method samplers for PM2.5 were operated at each of three sites on selected days. One had a single Teflon filter, the other had a Teflon and nylon filter pair in series. No systematic difference was seen for the gravimetric mass or ion concentrations on the Teflon filters of the two samplers. Collocated precision for sulfate, nitrate and ammonium ions on the Teflon filters was 0.1 to 0.3 µg/m³. Precision for gravimetric mass was not as good as for ions.
The nitrate captured by the nylon backup filter varied from 1 to 9 µg/m³. The fractional loss was greater on days of lower nitrate concentration. Comparisons with the automated nitrate sampler discussed above indicate that the Teflon-nylon filter sum from the FRM sampler is a more accurate representation of the particle nitrate concentration than the Teflon filter alone. We conclude that the nitrate mass was underreported by the FRM sampler operated with a single Teflon filter.

**Observed Patterns in Ambient Nitrate Concentrations**

The field measurements showed strong diurnal variation in nitrate concentrations, with peak concentrations at midday. At times the concentrations would increase by a factor of 3 or more within a single hour. Many of the days in Riverside exhibited a double peak, with maxima in midmorning and again in the afternoon. The maximum observed hourly-averaged nitrate concentration was 32 µg/m³ between 0800-0900 August 31 in Riverside, and 46 µg/m³ between 1200-1300 on September 30 in Mira Loma. The highest concentrations were associated with the midmorning nitrate maxima.

At Riverside, the sub-hourly variations were compared to the nephelometer and to the ATOFMS. Sub-hourly variations closely followed fluctuations in the nephelometer measurements of particle scattering at Riverside. Time variation in the number of nitrate-containing particles detected by the ATOFMS was similar to that of the automated nitrate monitor. These comparisons lend credence to the time variation in nitrate concentrations reported by the automated nitrate monitor.

**Conclusions**

The automated nitrate monitor performed well, with no observable bias by comparison to denuder-filter methods, with a precision of better than 10% and a three-sigma lower detectable limit of 1.2 µg/m³.

The instrument was reliable, and could be left unattended in the field. Data loss due to instrument failure was 3%. Overall data recovery, including time off-line for calibrations, was 93%.

Results from laboratory testing of components of the system were satisfactory. Laboratory testing show less than 2% loss due to particle deposition in the humidifier, greater than 98% particle collection efficiency, and less than 2% evaporative losses. 9% losses were observed for the inlet used in this study, a problem that has since been rectified.

Further work is needed to reduce and quantify positive interferences found from sampling of filtered ambient air. The interference was lower when using an activated carbon denuder. Additional work could reduce this further.
The FRM samplers produced precise data, but showed evaporative losses for nitrate when using a Teflon filter only. The use of a nylon-Teflon filter pair with cleaned inlets reproduced the nitrate values reported by the automated nitrate monitor. Direct comparison of the FRM to the Harvard sampler was not possible due to a difference in sampling periods, however the Harvard sampler results also agreed with the automated nitrate system.

For this summertime study period in Riverside and Mira Loma, the nitrate concentrations were usually largest during daytime hours. Often two nitrate peaks were observed, one midmorning and a second in the afternoon. The largest nitrate concentration events were associated with the morning nitrate peak, when ozone concentrations were low and relative humidity was high. The data are suggestive of a heterogeneous formation of nitrate under some conditions.

**Recommendations for Future Work**

The automated nitrate method shows promise of providing nearly uninterrupted particle nitrate data. Refinements of the system could lead to improved detection limits, lower interferences and a more compact and portable system. Most needed are tests in other regions of the country with comparison to traditional filter based methods, and evaluation of precision with collocated systems.

Greater understanding of the formation of particle nitrate could be gained through air trajectory modeling of existing data set, and through additional experiments with multiple nitrate monitors located along likely air trajectories. Modeling of the existing data set would also provide the basis for efficient design of future experiments. Collocated testing to establish and improve the precision of the nitrate monitor would provide the basis for knowing the uncertainties with measurements along air trajectories.

Finally, it is possible to extend the existing measurement technology of nitrate to other aerosol constituents such as sulfate and possibly carbon. Such measurements would be a powerful tool in identifying the sources and origins of PM$_{2.5}$, and for better understanding possible relationships between fine particles and human health.
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1.1 Study Overview

The Southern California Oxidant Study (SCOS’97) was designed to provide a database to understand ozone formation and transport. Measurements included upper air ozone and meteorology, as well as ground-based data of ozone, ozone precursors and meteorological parameters. With the interest in fine particles generated through the anticipated regulation of fine particles by EPA (PM$_{2.5}$), SCOS’97 was expanded to include concurrent measurements of particles as well as ozone.

Two concurrent atmospheric particle studies were conducted as part of SCOS’97. A Methods Evaluation Study, supported through EPRI, provided a field comparison of numerous particle measurements at Riverside. Methods included daily denuder-filter collectors for inorganic ions and vapors, a variety of denuder-filter methods for measurements of organic particles, and real-time indicators of particle mass and light scattering. In addition, some methods were evaluated through controlled, laboratory experiments.

A Particle Trajectory study funded through ARB, CRC and NREL, with in-kind support from SCAQMD, examined upwind-downwind particle relationships through simultaneous particle measurements at three locations. Measurements were made on selected days during August and September, 1997. For August these sites were located at downtown Los Angeles, Azusa and Riverside. For September they were located at Diamond Bar, Mira Loma and Riverside. Measurements at these sites included filter and impactor collection for PM$_{2.5}$ and size-resolved particle chemistry conducted by Dr. Glen Cass of Caltech, and single particle composition measurements with the Aerosol Time of Flight Mass Spectrometer (ATOFMS) designed and operated by Dr. Kimberly Prather and her group at UC Riverside.

While the objectives for each of these programs differed, the measurement programs overlapped. Both included measurements at Riverside, California. Both were coordinated with SCOS’97.

Aerosol Dynamics Inc. participated in both programs, with automated, near-continuous measurements of particle nitrate at Riverside during August 1997, and at Mira Loma during September. In addition, as part of the Trajectory Study we provided Federal Reference Method (FRM) PM$_{2.5}$ measurements at three sites during the selected intensive study days. As part of the Methods Evaluation Study we conducted a laboratory evaluation of our automated nitrate system through tests with known aerosols. Results for each of these activities are given in this combined report.
1.2 Motivation

While particle mass is the parameter that is subject to regulation, data on particle chemical composition and size are needed to understand their origins and sources, and to evaluate the relationships between specific chemical constituents and potential environmental consequences.

Automated monitoring methods, such as are now available for specific gaseous pollutants such as ozone and carbon monoxide, have made it possible to obtain high-time resolution, continuous ambient concentration data for these gases at reasonable cost. Equivalent monitoring methods are needed for fine particles. Filter-based particle collection and analysis as is now done is costly, and often results are not known until some months after the samples were collected. As the need for particle data grows with new regulation, advances in particle measurement methods will become essential. It will be quite costly to continue with manual particle measurement methods. However, before automated methods can be used routinely, they must be better developed and tested against the more traditional filter-based approaches, and to the new Federal Reference Method for PM$_{2.5}$. This study provides the opportunity for these comparisons.

1.3 Objectives

The objectives of our work are:

(1) to improve and validate our automated particle nitrate method through laboratory and field evaluation;

(2) to provide continuous, near real-time data on nitrate concentrations in particles below 2.5 µm for comparison with the ATOFMS; and

(3) to provide PM$_{2.5}$ federal reference measurements for comparison with conventional sampling techniques.

1.4 Report Outline

In this report we describe the measurement approach for automated nitrate (Section 2), its evaluation through laboratory experiments (Section 3), and its deployment for SCOS’97 (Section 4). The FRM measurements are described in Section 5. Chapter 6 presents the study results, with comparison among measurements, and comparisons of the diurnal nitrate profiles to those for ozone and nitrogen oxides. Section 3 and Section 5 have been kept separate because the funding for these aspects of the project was distinct: EPRI funded the laboratory and system testing while the Coordinating Research Council and National Renewable Energy Laboratory funded the FRM measurements. The FRM measurements were also supported through in-kind contribution from South Coast Air Quality Management District (SCAQMD).
Section 2.
Method Description: Automated Particle Nitrate Measurement

2.1 Approach

The Automated Nitrate Monitor developed by Aerosol Dynamics Inc. is designed to provide the automated measurement of PM$_{2.5}$ nitrate concentrations, with a time resolution of 10 minutes. The objectives are (1) to capture the 10-minute variation in the atmospheric concentration of fine particle nitrate, and (2) to provide immediate results with unattended operation. The primary motivation is to provide an uninterrupted data set for nitrate concentrations at reduced labor costs while providing immediate identification of high concentration events. A second motivation is to provide a data set suitable for source attribution based on the correlation in short-term fluctuations in gas, particle and meteorological data.

The monitor uses an integrated collection and vaporization cell (ICVC) whereby particles are collected by a humidified impaction process and analyzed in place by flash vaporization (Stolzenburg and Hering, 1999). The approach is similar to the manual method that has been used for over twenty years to measure the size distribution of sulfate aerosols (Hering and Friedlander, 1982). The difference is that the particle collection and analysis have been combined into a single cell, allowing the system to be automated. Particles are humidified prior to impaction to eliminate the rebound of particles from the collection surface without the use of grease (Winkler, 1974 and Stein et al. 1994). Interference from vapors such as nitric acid is minimized by use of a denuder upstream of the humidifier. Analysis is done by flash-vaporization into a nitrogen carrier gas with quantitation by a chemiluminescent NO$_x$ analyzer, similar to that described by Yamamoto and Kosaka (1994). The flow system is configured such that there are no valves on the aerosol sampling line.

The measurement is a two-step process. Particles are first collected onto the metal strip in the collection and vaporization cell. The typical collection period is 8 minutes. Then by switching appropriate valves on the nitrogen and pumping lines, the cell is purged with nitrogen. The sample is vaporized into the nitrogen stream and carried to a chemiluminescent analyzer for quantitation. The integral of the resulting NO$_x$ peak is proportional to the deposited aerosol nitrate. The time for analysis is about 90 seconds. The system then returns to sample collection mode, initiating the next 8-min sample at the beginning of the next 10-min period.

2.2 Instrument Description

A schematic of the instrument is shown in Figure 1. The system consists of pre-impactor, a multicell denuder, a humidifier, a collection and vaporization cell, a nitrogen
source, a chemiluminescence nitric oxide detector, vaporization electronics, pump, data system and various sensors, flow meters and valves.

The pre-impactor has a single diameter jet with an oiled frit impaction surface. The denuder used during initial measurements was a KOH-coated glass honeycomb. This was changed midway in the study to an activated carbon impregnated ceramic honeycomb manufactured by Corning (Corning, NY). The humidifier consists of a 30 mm long, 1 mm diameter tube of Nafton® surrounded by a jacket of water (Perma Pure). The water jacket is kept full by means of the water reservoir.

The integrated collection and vaporization cell has a single orifice that operates under sonic flow conditions. A stainless steel strip mounted 1.9 mm below the orifice exit collects the particles. The dimensions of the integrated collection and vaporization cell are 32 mm in diameter by 19 mm high. The strip is held in place by metal mounting posts which provide the electrical contact as well as mechanical stability.

The pre-impactor, denuder, humidifier and collection-analysis cell are housed in an environmental enclosure consisting of a wooden and plexiglass box measuring 14x16x36 inches. The enclosure was ventilated with outdoor air through a 4” diameter line by means of an exhaust blower. Temperature and relative humidity of the sampled air were measured between the humidifier and collection cell.

The flash vaporization electronics contain a bank of capacitors that may be charged to a preselected voltage and discharged through a silicon controlled rectifier switch. The total capacitance is 0.315 farads. The charge and discharge cycles can be triggered manually or by computer. The nitrogen oxide analyzer is a commercial chemiluminescence analyzer, that analyzes for NO based on the chemiluminescent reaction with ozone (Thermo Environmental Instruments, Franklin, MA). It has a molybdenum converter for reducing higher nitrogen oxides to nitric oxide.

The instrument has two modes of operation: sampling and analysis. During sampling particles are collected by impaction onto a small area at the center of the metal strip mounted inside the collection and vaporization cell. At the end of the collection period the instrument switches to the analysis mode. The particle deposit is vaporized in place by rapid resistive heating of the metal strip and the evolved vapors are transported by a nitrogen carrier gas to a commercial gas phase analyzer. The resulting peak in the gas-phase concentration is integrated to give the mass of the nitrate collected. After the analysis is complete the system returns to sampling mode and the cycle is reinitiated.

In the sampling mode the valve between the cell and the pump is open, while the valves between the cell and the NOx analyzer and between the cell and the nitrogen source are closed. Ambient, particle-laden air is drawn through a pre-impactor, denuder, humidifier and into the collection and vaporization cell. The sample flow rate is 1 L/min.
Figure 1. Schematic of the ADI Automated Nitrate Monitor.
The pre-impactor has a calculated cutpoint of 3 µm, and removes coarse particles from the sample stream to provide an approximate PM$_{2.5}$ sample. The denuder removes interfering vapor species including nitric acid and peroxy-acetyl nitrate. The humidifier increases the relative humidity of the sample stream to a value between 70% and 99% so that the sampled particles become wet. The cell collects the humidified particles onto the metal strip by impaction. Particle bounce is minimized by the humidification prior to impaction. The sample flow rate is controlled by the cell orifice.

In analysis mode the valve between the cell and the pump is closed, and the valves to the nitrogen source and to the NO$_x$ analyzer are open. Nitrogen enters through the pumping port and through the orifice tube, and exits into the NO$_x$ analyzer. Nitrogen enters the cell through the pumping port at a flow rate slightly less than the 0.6 L/min required by the gas analyzer. The balance of the analyzer flow is supplied through the sample orifice above which the nitrogen is supplied in slight excess. There are no valves on the sample line.

After a preset flushing time (typically 20 s) the collection strip is rapidly heated to a dull red color by capacitor discharge through the strip. The evolved nitrogen oxides are quantitated by the chemiluminescence analyzer. The analyzer is operated in manual NO$_x$ mode whereby the sampled stream passes through a molybdenum converter to reduce NO$_2$ and other nitrogen oxides to NO prior to detection. To assure complete removal of nitrates, the strip is heated a second time. The time required for the analysis step is 90 seconds. Then the system is returned to the sampling mode.

The system is controlled by a PC-based computer with a Keithley Metrabyte analogue to digital input - output card. This program controls the operation of the valves and vaporization electronics, and captures the analogue signals from the NO$_x$ analyzer, and temperature and relative humidity probe. During sampling the analogue signals are read and recorded every 60 s. During analysis the system reads the NO$_x$ baseline just prior to each vaporization analysis. The system captures and integrates the NO$_x$ peak. Data are recorded in two files. The primary file contains sample times, analogue signals and analysis peak integrals. A second file contains the NO$_x$ signal–time profile for each flash analysis. A third file, the configuration file, contains default system parameters such as the time between analogue readings, the cell flushing time prior to analysis, the integration time for the flash analysis, and the compression factor for storage of the flash integration peaks.

The system has three modes of operation: sample mode, analysis mode, and a cycle mode. Sample and analysis modes allow for single sample collection or analysis under the direct control of the operator. These modes are used for system checks and calibrations. Cycle mode automatically switches between the sample collection and analysis modes, and is used for automated data collection. The sample duration is user-selectable, and the program is set so that sampling begins on the hour.
Section 3.
Laboratory Evaluation and Field Performance Tests

3.1 Overview of Laboratory and Field Performance Tests

The testing and calibration of the Automated Nitrate Monitor encompassed a variety of measurements. Some experiments assessed particle penetration through the inlet components, others examined collection efficiency in the cell, and others determined the extent, if any, of nitrate vaporization losses and interferences. Most of the testing was done in the laboratory using monodisperse ammonium nitrate aerosol. As appropriate, some tests were repeated in the field with ambient aerosol. Results from both are reported here.

Specific parameters that were measured are:

1. analytical response to liquid standards;
2. particle penetration through denuder and humidifier;
3. particle collection efficiency in the collection cell;
4. vaporization loss for ammonium nitrate and ambient particles;
5. interference from ammonium ion, nitric acid and filtered ambient air; and
6. system response to laboratory, monodisperse aerosols.

Measurements of particle collection efficiency, vaporization loss and interferences were made in the field as well as in the laboratory. We refer to these specific field evaluations as “field performance” tests.

3.2 Experimental Methods

Calibration with Aqueous Standards

The analysis step is calibrated using aqueous standards applied directly to the collection substrate. The collection cell is opened, and a sub-microliter aliquot of a known standard is placed in the center of the collection substrate and allowed to dry. The cell is then closed and the standard is analyzed using the automated purge and vaporization cycle employed for the analysis of ambient particles. The response is the integral, in ppb-s, of the resulting peak in NOx concentration as measured by the analyzer. Tests were done with four compounds: ammonium nitrate, sodium nitrate, ammonium sulfate and oxalic acid. The applied mass is in the range from 20 to 170 ng of nitrate (or sulfate).

Laboratory Aerosol Tests

The configuration for aerosol tests is shown in Figure 2. Ammonium nitrate particles are generated by nebulization, and a mono-mobility size fraction was selected from the nebulized aerosol using a high-flow differential mobility analyzer. The particle concentration upstream of the collection cell was monitored with a condensation nucleus
counter (CNC) and an LAS-X optical counter. The particle concentrations downstream of the collection cell were monitored with a second optical particle counter operated at low pressure (LP-OPC). The LAS-X counter allowed us to correct for larger doubly charged particles in the test aerosol, while the CNC provided redundancy for evaluating counting efficiency, and for evaluating the response for particles below the optical counter detection limit.

Particle collection efficiency was measured from the ratio between the LP-OPC counts during collection, to that when sample flowed through the bypass line, as during sample analysis or standby modes. The bypass line has a 1 L/min critical orifice so that the absolute pressure in the optical counter is the same for both measurements. Care was taken to minimize the excess nitrogen flow introduced above the orifice during analysis so that the dilution of the test aerosol through the bypass was less than 5%. Particle collection efficiency was measured as a function of particle size for ammonium nitrate and ammonium sulfate test aerosols.

Particle penetration through the humidifier was measured with monodisperse particles from the HF-DMA. Concentrations above and below the humidifier were counted using the condensation nucleus counter. Experiments were done with

---

**Figure 2. Schematic of aerosol testing system for the automated nitrate monitor.**
CNC = condensation nucleus counter, LAS-X = laser optical particle counter and LP-OPC is a second laser optical particle counter operated at low pressure below the cell. Nitrogen lines for analysis are not shown.
monodisperse fractions of ambient laboratory air particles, and with monodisperse nebulized ammonium nitrate particles.

Vaporization losses for ammonium nitrate were evaluated by exposing a deposited sample to particle free air. The particle-free air exposure was obtained by stopping the sampling, adjusting the DMA voltage to zero, and then restarting the sampling once the particle counts dropped to zero. The expected response was calculated from the LAS-X and CNC counts during particle collection. The measured response from the flash vaporization analysis was compared to that expected as a function of the exposure time to particle-free air.

The overall response to monodisperse ammonium nitrate particles was evaluated by comparison of the measured nitrate from the flash-vaporization to that calculated from the HF-DMA size, upstream particle counting instruments, and sample duration. The nitrate from flash-vaporization was calculated on the basis of the liquid ammonium calibration standards. The sampled particle volume was calculated using the total number concentration given by the upstream CNC, and the particle size calculated from the flow rate and applied voltage in the HF-DMA. This particle volume was corrected to account for the presence of larger, doubly charged particles based on the size distributions from the LAS-X. For some particle sizes as much as 50% of the aerosol mass was in the doubly charged particles. Measurements were done for varying concentrations and sampling times at selected particle sizes.

Laboratory Interference Tests

Possible interference from other compounds in the flash-vaporization analysis of the nitrate was tested by measuring the response to aqueous standards of ammonium sulfate and oxalic acid. This was done following the procedure for the calibration with standards, described above. Standards of ammonium sulfate were run routinely to test that the ammonium ion was not detected as nitrate.

Interference from nitric acid was tested in the laboratory by using a permeation source. Nitrogen gas was passed through a particle filter and then through a glass cell containing the permeation source (VCI Metronics, Santa Clara, CA). The nitric acid concentration was calculated from the temperature and permeation tube emission rate, and checked using the response of a chemiluminescent analyzer in NOx mode. The particle-free nitric acid source was sampled by using the automated nitrate system, with and without a denuder in place.

Field Performance Tests

Particle collection efficiency was measured in the field using the LP-OPC to detect particles penetrating through the cell during sample collection. As with the laboratory experiments the efficiency was calculated from the ratio between particle counts during collection to that measured during analysis mode, when the LP-OPC samples ambient air immediately downstream of the humidifier. The ambient air sample line has a 1 L/min critical orifice so that the absolute pressure in the optical counter is the same for upstream ambient air sampling as for the downstream, post-collection cell
sampling. Unlike the laboratory tests these measurements were not made as a function of particle size.

Evaporative losses were evaluated under field conditions by alternating between 4-min and 8-min sample collection during a period of relatively high nitrate concentrations. One experiment was done by passing filtered air over the sample prior to analysis. The measured result for longer sample duration and for the filtered-air exposed sample were compared to the average of that for shorter-term samples collected just prior, and just after the test sample.

Interferences from gaseous species were checked in the field by placing a Teflon filter in a Teflon filter housing, at the inlet of the sampling line. Sampling continued as during normal operation, and the indicated nitrate values compared to that obtained from the system blank. The system blank is that obtained by passing nitrogen gas or clean laboratory air through the cell.

3.3 Results

Response to Aqueous Standards

The analysis step of the nitrate monitor was calibrated using liquid standards applied directly to the collection substrate. Calibrations are routinely done at three concentrations, and with both sodium and ammonium nitrate. An example calibration response is shown in Figure 3. The response is approximately linear, with a slope of 0.036 ppm-s-ng\(^{-1}\) of nitrate for the ammonium salt. As was generally observed, the response to sodium nitrate is slightly (5-10\%) higher, especially at the highest standard levels.

The measured response to known nitrate standards can be compared to that expected on the basis of the NO\(_X\) calibration of the chemiluminescent analyzer and its sample flow rate. The integral of the NO\(_X\) concentration \(C\) is related to the mass of the deposited nitrate \(S\) by the mass balance equation:

\[
S = Q_c \frac{MW}{\nu} C \, dt \tag{1}
\]

where:

- \(S\) is the mass of particle nitrate in ng,
- \(Q_c\) is the carrier gas flow rate into the gas phase analyzer in liters/sec,
- \(MW\) is the molecular weight of species in g/mole,
- \(\nu\) is the molar volume of carrier gas in liters,
- \(C\) is the gas phase concentration of NO\(_X\) in ppb, and
- \(t\) is the integration time in seconds.

This equation assumes that the entire particle nitrate is converted to NO\(_X\) upon vaporization and efficiently transported to and quantitated by the analyzer.
For an analyzer gas flow rate of 0.6 L/min, the theoretical response for nitrate corresponds to 0.04 ppm-s-ng\(^{-1}\), compared to a measured value of 0.036 ppm-s-ng\(^{-1}\) in Figure 3. The corresponding recovery efficiency is 90%.

Response to Non-nitrate Compounds.

In the design of the system the flash vaporization conditions were selected to minimize the response to ammonium ion, as indicated by the analysis of ammonium sulfate standards, while providing approximately equal response to sodium nitrate and ammonium nitrate. The possible interference from ammonium ion was tested repeatedly using aqueous ammonium sulfate standards. This was done routinely as a part of each calibration procedure, as shown in Figure 3. For a mass of applied ammonium sulfate equivalent to 65 ng of sulfate, the response was less than 0.1 ppm-s, or less than 4% of the response to nitrate. Similarly, tests with an aqueous standard of oxalic acid showed less than 0.1 ppm-s for 300 ng of oxalic acid.

![Figure 3. Response of flash-vaporization analysis to liquid standards of sodium nitrate, ammonium nitrate and ammonium sulfate, plotted as a function of the mass of nitrate (or sulfate) applied.](image)
Particle Transmission through the Inlet and Humidifier

Components of the system upstream of the ICVC are the inlet and the humidifier. For the 1997 field campaigns the inlet was a single-jet aluminum impactor and denuders housed inside a 47-mm Teflon filter cassette holder (Savillex, Minnetonka, MN). This was followed by a single-tube, 30.5 mm (12-inch) long Nafion humidifier.

Results are shown in Table 1. Indicated precisions are derived from replicate measurements. We find that particle losses through the humidifier alone are less than 2%. However, with the impactor-denuder inlet added to the system, the losses increase to 10%, independent of particle diameter. Likely the losses are due to electrostatic losses on the Teflon housing used to hold the impactor and denuder.

Table 1. Particle Penetration Through Humidifier and Inlet

Penetration through Humidifier Alone:

<table>
<thead>
<tr>
<th>Particle Type</th>
<th>Diameter</th>
<th>Penetration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient</td>
<td>0.10 µm</td>
<td>98 ± 1 %</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>97 ± 1</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>102 ± 6</td>
</tr>
<tr>
<td>NH₃NO₃</td>
<td>0.40</td>
<td>98 ± 1</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>97 ± 1</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>98 ± 1</td>
</tr>
</tbody>
</table>

Penetration through Inlet and Humidifier:

<table>
<thead>
<tr>
<th>Particle Type</th>
<th>Diameter</th>
<th>Penetration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃NO₃</td>
<td>0.40 µm</td>
<td>91 ± 1 %</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>89 ± 1</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>92 ± 1</td>
</tr>
</tbody>
</table>

Particle Collection Efficiency

The collection efficiency in the ICVC was measured in the laboratory for ammonium sulfate and ammonium nitrate particles of known size. Measurements were made in the field for all particle sizes detected by the LP-OPC. Results are given in Table 2; uncertainties are the 2-sigma deviation from replicate measurements. The errors are greater for the larger particles due to lower particle concentrations.

Particle collection efficiencies for humidified ammonium sulfate and ammonium nitrate are above 95% for particle diameters ranging from 0.1 µm to 0.8 µm. These tests are for a jet-to-plate spacing of 1.9 mm (approximately 5 jet diameters). The relative humidity immediately upstream of the cell was 88%. Tests with ammonium sulfate aerosol at jet-to-plate spacings of approximately 1 jet diameter showed many particles with diameters smaller than those of the test particles reaching the LP-OPC detector. This indicated that the test particles tended to “splatter” upon impact at small jet-to-plate spacings. Results are shown for the spacing that yielded the highest collection efficiency.

Particle collection efficiencies were measured for ambient particles in two locations in southern California (Riverside in August 1997, and in Mira Loma in
September 1997). This was done by comparing the counts at the LP-OPC during sample collection to those during analysis when the LP-OPC was sampling ambient air immediately downstream of the humidifier. Measured collection efficiency for ambient particles ranged from 89% to 99%. As shown in Table 2, the lower collection efficiency values were observed during a period of lower nitrate concentration. This may be due to the presence of a higher percentage of non-hygroscopic particles when nitrate was low.

Table 2. Particle Collection Efficiency

<table>
<thead>
<tr>
<th>Ammonium Sulfate Particles</th>
<th>Particle Diameter</th>
<th>Collection Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 µm</td>
<td>99.7± .2%</td>
</tr>
<tr>
<td></td>
<td>0.2 µm</td>
<td>99.8± .2 %</td>
</tr>
<tr>
<td></td>
<td>0.3 µm</td>
<td>99.7± .2 %</td>
</tr>
<tr>
<td></td>
<td>0.4 µm</td>
<td>99.7± .4 %</td>
</tr>
<tr>
<td></td>
<td>0.6 µm</td>
<td>98. ± 2 %</td>
</tr>
<tr>
<td></td>
<td>0.8 µm</td>
<td>95. ± 6 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ammonium Nitrate Particles</th>
<th>Particle Diameter</th>
<th>Collection Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2 µm</td>
<td>98.6± .2 %</td>
</tr>
<tr>
<td></td>
<td>0.3 µm</td>
<td>99.8± .2 %</td>
</tr>
<tr>
<td></td>
<td>0.5 µm</td>
<td>99.0± 1. %</td>
</tr>
<tr>
<td></td>
<td>0.8 µm</td>
<td>97. ± 2 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ambient Southern California Aerosols</th>
<th>Ambient Collection Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Date</td>
<td>Nitrate (µg/m³)</td>
</tr>
<tr>
<td>8/22</td>
<td>3.</td>
</tr>
<tr>
<td>8/23</td>
<td>17.</td>
</tr>
<tr>
<td>9/30</td>
<td>20.</td>
</tr>
</tbody>
</table>

Evaluation of Interferences from Vapor Compounds

The magnitude of interferences from vapor compounds is evaluated by pulling particle-free air through the sampling cell and measuring the resulting signal. Similarly, field measurements of filtered ambient air are used to assess dynamic blanks. During testing of the first prototype system in Denver, Colorado, we found that these filtered air blanks were frequently greater than that obtained by repeated analysis of the same substrate. Furthermore, the blank values tended to be higher on days of elevated pollutant concentrations, suggestive of a gaseous interference. Therefore, for this study the question of positive artifacts from adsorbed gases was investigated further.

Results of various tests, both in the laboratory and the field are summarized in Table 3. All tests were done with the humidifier in place. Some were done without a denuder, as indicated. For exposure of the sampling substrate to a stream of nitrogen, no measurable blank is observed. For collection of filtered, laboratory air the resulting signal is less than 3 ng of nitrate even when no denuder was used. This corresponds to less than 0.4 µg/m³ for the eight-minute sample duration used in this study.
Tests with nitric acid in a nitrogen carrier gas in the range from 150 to 300 ppb yielded a measurable signal equivalent to 6 - 17 ng NO\textsubscript{3} when no denuder was used. Use of a KOH-coated glass denuder ahead of the humidifier reduced this signal to 2-3 ng, equivalent to 0.25 - 0.3\mu g/m\textsuperscript{3} nitrate for an 8-min sample. Yet for measurements of filtered ambient air using the same KOH-coated denuder in Riverside, California during August 1997, the blank values were high, as much as 10 ng. The blank values tended to be higher during periods of elevated NO\textsubscript{x} concentrations ($R^2=0.65$). Based on the laboratory testing, one infers this interference is from some vapor compound other than nitric acid.

For the latter portion of the study, an activated carbon impregnated ceramic honeycomb was used. Field blanks for this denuder were lower by a factor of two on average than for measurements with the KOH denuder. The ambient levels of NO\textsubscript{x} were 30% higher and particulate nitrate values were a factor of 3 higher when filtered air samples were collected with the carbon denuder, as compared to the periods of filtered air with the KOH denuders. While a direct comparison between the two types of denuders was not made, the indication is that the activated carbon denuder is more effective at removing interfering vapor compounds and reducing blank values. Efforts continue to find a yet more effective denuder to further reduce this artifact.

### Table 3. Summary of Vapor Interference Measurements

<table>
<thead>
<tr>
<th>Sample</th>
<th>Denuder</th>
<th>Exposure Time</th>
<th>Equivalent NO\textsubscript{3} Concentration (\mu g/m\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen Gas Stream</td>
<td>none</td>
<td>700 s</td>
<td>0.0± 0.0</td>
</tr>
<tr>
<td>Filtered lab air</td>
<td>none</td>
<td>300-2200 s</td>
<td>0.4± 0.2</td>
</tr>
<tr>
<td>HNO\textsubscript{3} in N\textsubscript{2}, 150 -320 ppb</td>
<td>none</td>
<td>600-700 s</td>
<td>1.4± 1.0</td>
</tr>
<tr>
<td>HNO\textsubscript{3} in N\textsubscript{2}, 150 -320 ppb</td>
<td>KOH Coated Glass</td>
<td>200-700 s</td>
<td>0.3± 0.1</td>
</tr>
<tr>
<td>Filtered Ambient Air: Riverside, Aug 17-30, 1997</td>
<td>KOH Coated Glass</td>
<td>480 s</td>
<td>1.3± 0.8</td>
</tr>
<tr>
<td>Filtered Ambient Air: Mira Loma, Sept 4 - 30, 1997</td>
<td>Activated Carbon</td>
<td>480 s</td>
<td>0.7± 0.4</td>
</tr>
</tbody>
</table>

\textsuperscript{1} calculated for 8-min sample collection period.
Evaluation of Vaporization Losses

For sampling ammonium nitrate, loss due to evaporation of the nitrate during sample collection is always a concern. For filter sampling, losses as high as 80% have been reported (Hering and Cass, 1999). Much smaller losses have been observed for nitrate measurements made with the Berner impactor (John et al, 1988; Zhang and McMurry, 1992). For the automated nitrate monitor, the short sampling times (8-12 minutes) and the high relative humidity during collection will tend to minimize losses. On the other hand, the use of denuders upstream of the collection point will tend to increase losses. Thus this issue required experimental investigation.

In the laboratory, evaporative losses were evaluated by collecting monodisperse ammonium nitrate with parallel measurements by the optical and condensation nucleus counters. Some samples were analyzed immediately at the end of the collection period, to provide a value for the expected nitrate response. Other samples were collected for the same sampling time, but then exposed to particle-free air prior to analysis. This was done by stopping the sample collection, setting the HF-DMA voltage to zero, waiting for the particle concentration to drop to zero, and then sampling the resulting particle-free air. Recovery is calculated as the ratio of the nitrate measured after exposure to particle-free air to that measured immediately after collection, normalized to the particle number concentrations measured during the collection period. Correction was also made for the blank value corresponding to the sampling of particle free air.

Results are shown in Figure 4. Particle collection periods were varied from 1 min to 8 mins. Exposure time is the duration of the subsequent of sampling of particle-free air, which was a factor of 1, 4 or 8 times longer than the initial sample collection period. These experiments mimicked the situation in which all of the nitrate was collected at the beginning of a collection period, and then was exposed to the air stream throughout the remaining period. Indicated recovery ranged from 91% to 102%, with a mean value from ten experiments of 98 ± 4%. Measured recovery was independent of the exposure time.

In the field, evaporative losses were evaluated through variation of the sample duration. The high particle nitrate concentrations found in Mira Loma made these experiments possible. As shown in Figure 5, samples of 4-min duration yielded the same results as those of 8-min duration. One point was taken using a 4-min collection followed by a 4-min filtered air, with the same indicated nitrate concentration as for an 8-min sample. If nitrate were volatilized during collection, then the samples of longer duration, or with exposure to filtered air, would yield lower values. The consistency of these data indicate that particle nitrate was not lost during sampling.
Figure 4. Laboratory measurements of nitrate recovery from samples exposed to particle free air after sample collection.

Figure 5. Comparison of ambient nitrate concentration measurements made with varying sample duration.
Laboratory Evaluation with Monodisperse Ammonium Nitrate Aerosols

The automated nitrate system was tested with monomobility nitrate aerosols generated using the HF-DMA, as shown in Figure 2. The nitrate concentration measured by flash vaporization is compared to the volume concentration for the test aerosol indicated from the measurement of number concentration during sample collection and from the particle size indicated by the flow and voltage settings of the mobility analyzer. Calibration for the flash vaporization is derived from the liquid standards, as described above. Calculation of the total aerosol volume took into account the presence of larger, doubly charged particles with the same mobility diameter. The number concentration of the doubly charged particles was obtained from the LAS-X optical counter. At 0.61 µm the doublets were 20% of the aerosol volume; at 0.41 µm the doublets accounted for 50% of the volume.

Results are presented in Figure 6 for primary particle sizes of 0.32 and 0.41 µm and in Figure 7 for 0.55, 0.61 and 0.86 µm. The nitrate measured by flash vaporization is shown as a function of the sampled aerosol volume derived from the particle number concentrations, mobility diameters and sample duration. Larger particle deposits were obtained by increasing the sampling times at approximately the same particle concentration. Results from different days of experiments are shown separately. The correlation between the two measurements is excellent, with $R^2 > 0.95$. A small change in the slope is observed for measurements at different particle sizes, but this could be easily accounted for by systematic differences between the two experiments, such as in the magnitude of the correction for doubly charged particles in the test aerosol.

Theoretically, the slope of the regression line is the product of the fraction of the particle mass that is nitrate and the particle density, in units of g/cm$^3$. For perfectly dry ammonium nitrate particles, the expected slope is $(62/80)*1.7 = 1.3$ g/cm$^3$. Our measured values are consistently lower, in the range 0.87-0.97 g/cm$^3$. This difference may in part be due to residual water associated with the particles, or impurities in the nebulization process. Both of these factors would lower the measured response.

The experiments with laboratory ammonium nitrate show consistency between the measured nitrate and the calculated volume of sampled aerosol. The nitrate response increases systematically with the mass of nitrate sampled. Measurements at different particle sizes and concentrations yield similar results.
Figure 6. Response of nitrate monitor to laboratory ammonium nitrate particles with primary sizes of 0.41 and 0.32µm.

Figure 7. Response of nitrate monitor to laboratory ammonium nitrate particles with primary sizes of 0.55, 0.61 and 0.87µm.
Section 4.  
Field Measurements:  Automated Nitrate System

4.1 Deployment

The ADI Automated Particle Nitrate Monitor was operated for a total of six weeks. From August 16 until September 3, the system was located at the University of California, Riverside (UCR) monitoring station, immediately alongside the measurement systems of Harvard University and Brigham Young University. This site was located at the Agricultural Operations facility about 1 mile (straight line) from the Chemistry Building at UCR where the Caltech measurement systems and the UCR Aerosol Time of Flight Mass Spectrometer were located. At noon on September 3, the automated nitrate system was moved to Mira Loma at a site provided by ARB on the grounds of the Union Pacific transfer facility, where it operated from Sept 4 - 30. At Mira Loma, the nitrate monitor was collocated with the measurement systems of Caltech and UCR’s field-portable Aerosol Time of Flight Mass Spectrometer. Both sites are next to sites used for the ARB Children's Health Study, with continuous PM$_{10}$, ozone and nitrogen oxides monitoring by the South Coast Air Quality Management District.

As described in Section 2, the automated nitrate system uses an integrated collection and vaporization cell whereby particles are collected by a humidified impaction process and analyzed in place by flash vaporization. A two step process is employed with 8-min particle collection followed by a 90-s analysis step. The measurements in southern California represent the second field deployment of this prototype system. Several changes were made to the system prior to the SCOS’97 study. These included increasing the ventilation for the environmental chamber housing the sampling cell; stopping the nitrogen carrier gas flow during sampling, relocating the pumping bypass line to downstream of the humidifier, and directly reading of the NO$_x$ baseline prior to each vaporization step. Additionally, the sampling time was decreased from 10 to 8 minutes, providing 6 measurements per hour.

With the exception of the type of denuder employed to remove interfering gases, the same configuration was used at the Riverside and Mira Loma sites. For Riverside, a KOH-coated glass multi-tube denuder was used; but some interferences were found. For Mira Loma, the denuder was changed to an activated carbon impregnated ceramic honeycomb, which proved to be more effective. The same collection strip was used throughout the study.

4.2 Performance Objectives

Data quality objectives for the study in Riverside were:
Accuracy: four-hour average of 10 minute nitrate concentrations from the nitrate flasher to agree within 25% of denuded nylon filter values from the sequential sampler at the same site.

Precision: at least ±10% (= 1 sigma) as determined by replicate standards.

Lower Quantifiable Limit: at least 20 ng, or 2µg/m³ for a 10 min sample.

Completeness: at least 88% data completeness during designated intensive.

4.3 Quality Assurance

Several tests were done in the field to evaluate the system performance. These included: (1) analysis of nitrate and ammonium sulfate standards applied directly to the particle collection strip; (2) collection and analysis of filtered air samples to check for positive interferences; (3) measurement of particle collection efficiencies for ambient particles; and (4) variation of sample duration to check for consistency and volatilization. We met with the EPRI field audit team for a check of flow rates and field operational procedures.

The running of standards (item 1) was done at the beginning and end of each aerosol intensive measurement period, or at least weekly. Checks for positive artifacts, with sampling of filtered air, were done weekly.

4.4 Field Calibration Procedures

The analytical step of the system was calibrated once or twice weekly while in the field. Calibrations were made using solutions of known concentrations of sodium nitrate, ammonium nitrate or ammonium sulfate. Each solution was prepared in the laboratory from a high-purity grade reagent purchased from Aldrich in dry solid form. Standards were prepared at a concentration of approximately 2000 µg/ml using a Mettler analytical balance, doubly distilled water and volumetric flasks. These standards were subsequently diluted to approximately 200 µg/ml.

Using a graduated, 1-µL syringe, a sub-microliter drop of the standard was applied directly to the center of the strip mounted in the cell. By removing the orifice, access to the strip was gained through the top of the cell. After application, the droplet was allowed to air-dry, as determined by visual inspection (usually less than 1 minute), and then the orifice was replaced and the strip analyzed using an "auto-flash-cycle". This mode is a computer-controlled analysis that provides exactly the same purging and flashing conditions as in the actual operation of the instrument.

The customary calibration set consisted of 13 standards, as shown in Table 4. The two types of nitrate salts tested for equality of response for these species. The sulfate standard was used to test for a null response for the ammonium ion. For the eight-minute sampling periods used in this study, these corresponded to 5 to 20 µg/m³ of nitrate.
Higher standards at 360 ng were run at the end of the study to encompass the highest ambient concentrations measured.

### Table 4. Nitrate Calibration Standards.

<table>
<thead>
<tr>
<th>Number</th>
<th>Volume applied</th>
<th>Solution</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.2 µL</td>
<td>NaNO₃</td>
<td>42 ng of NO₃⁻</td>
</tr>
<tr>
<td>2</td>
<td>0.4 &quot;</td>
<td>&quot;</td>
<td>83 &quot;</td>
</tr>
<tr>
<td>2</td>
<td>0.8 &quot;</td>
<td>&quot;</td>
<td>165 &quot;</td>
</tr>
<tr>
<td>2</td>
<td>0.2 µL</td>
<td>NH₄NO₃</td>
<td>43 ng of NO₃⁻</td>
</tr>
<tr>
<td>2</td>
<td>0.4 &quot;</td>
<td>&quot;</td>
<td>86 &quot;</td>
</tr>
<tr>
<td>2</td>
<td>0.8 &quot;</td>
<td>&quot;</td>
<td>173 &quot;</td>
</tr>
<tr>
<td>1</td>
<td>0.4 &quot;</td>
<td>(NH₄)₂SO₄</td>
<td>65 ng of SO₄²⁻</td>
</tr>
</tbody>
</table>

Blanks for the analytical step were determined in the laboratory by application of distilled water droplets to the strip. These were found to give no response. Similarly, the ammonium sulfate standards also gave almost no response. In the field, only the ammonium sulfate standards were run, which provided a double check of our blank and a lack of response to the ammonium ion.

### 4.5 Field Blanks

Dynamic blanks were determined by sampling filtered ambient air using a Teflon filter mounted inside a Teflon filter holder at the sample inlet. The blank was analyzed on-line exactly as if it had been a normal ambient air sample. Results for Riverside and Mira Loma are shown in Figure 8. Also shown is the response to ammonium sulfate standards, which provides a blank for the analytical step. The blank values from sampling filtered air are consistently higher than that for the analysis alone. The lower field blanks at Mira Loma are attributed to the change to the activated carbon denuder.

### 4.6 Data Reduction Procedures

At the end of each 8-minute collection period the nitrate collected is measured by rapidly heating the collection strip and measuring the integral of the evolved nitrogen oxides. For simplicity, we refer to each heating of the strip as a "flash". Each nitrate determination includes a 10-s reading of the NOx baseline reading before the first flash, followed by the two integrals of the output from the NOx analyzer during the 20 s period following each of two flashes of the strip. These values are converted to nitrate mass on the basis of the response to known standards, described above, and the response to field blanks.
Figure 8a. System response to filtered air (filtered) and ammonium sulfate standards (AmSO4) with KOH denuder, at Riverside.

Figure 8b. System response to filtered air (FILTERED) and ammonium sulfate standards (AmSO4) for carbon denuder at Mira Loma.
Slightly different procedures were used to reduce the Riverside and Mira Loma data sets. First, during the first few days in Riverside, the data acquisition computer was inadvertently running in a turbo mode in which the system clock operated at 8 MHz instead of the 4.77 MHz for which the data acquisition timing had been programmed. The resulting shorter integration periods produce erroneous but predictably larger integral values for the nitrate. To account for this effect, system standards run at both clock speeds were used to reduce the data accordingly. The second difference was in the handling of the field blanks. Different types of denuders were used for Riverside and for Mira Loma, as described above. Field blanks measured for the Riverside data were scaled to the indicated NOx concentration, whereas for Mira Loma a constant average value was used throughout.

For both data sets, the second flash yielded results insignificantly different from zero, such that the data were reduced using the integral from the first flash alone. Standards were run every few days, and apart from the clock speed difference, there was no apparent change in the system response throughout the two-week measurement period at Riverside, or the 4-week period at Mira Loma. The calibration data from each site and clock speed were reduced using a least-squares fit to the ammonium nitrate standards of the form:

\[ (F_1 - B_s - Bl_{Std}) = \frac{m}{k} \]

where \( F_1 \) is the integral in volt-s for the first flash, \( B_s \) is the 20s equivalent baseline reading, \( Bl_{Std} \) is the blank for standards and \( m \) is the nitrate mass for the applied ammonium nitrate standard. The blank for standards is taken as the average response to the ammonium sulfate standards. Three sets of calibration constants were derived, one each corresponding to the two clock speeds at Riverside, and one for all of the Mira Loma data. Figures 9 and 10 show the blank-subtracted calibration standards and the non-linear fits used according to Eq. (2).

The data were also corrected for the field blank, evaluated from measurements of filtered ambient air. For the Riverside data, for which a glass KOH coated denuder was used, the blank tended to be higher at higher NOx concentrations, such that the field blank was calculated based on a linear regression against the NOx reading. For the Mira Loma data set, for which an activated carbon impregnated ceramic denuder was used, the blank values were generally lower, and did not correlate with NOx. Thus, an average value of the filtered air readings was used. Blank values were calculated in volt-sec, and subtracted from the flash reading when applying the conversion to nitrate mass.
Figure 9. Responses to ammonium nitrate standards (AmNO3) at the two different computer speeds used for data acquisition at Riverside with resulting non-linear fits according to Eq. (3).

Figure 10. Response to ammonium nitrate standards (AmNO3) at Mira Loma with resulting non-linear fit.
Finally, the data were also corrected for the losses in the inlet, as measured in the laboratory. Laboratory measurements with monodisperse particles at 0.4 µm, 0.6 µm and 0.8 µm showed losses of 9%, 11% and 8%, respectively. Correspondingly, the data were multiplied by 1.108 to correct for the average measured loss.

The formula used to calculate fine particle nitrate concentration, in µg/m³, is of the form:

$$[\text{NO}_3^-] = f \cdot k \cdot \frac{(F_1 - B_s - B_{\text{field}})n}{V},$$  \hspace{0.5cm} (3)

where $F_1 - B_s$ is the baseline corrected integral for the first flash, $B_{\text{field}}$ is the field blank in Volt-seconds, $n$ and $k$ are defined by equation (2), $f=1.108$ is the correction for particle inlet losses and $V$ is the sample volume (liters). Values used in the data reduction are shown in Table 5.

Uncertainties for each data point were estimated by calculating the effect of subtracting one standard deviation from the predicted blank correction prior to applying the calibration Eq. (3). The error was taken to be the difference between this recalculated NO$_3$ value and the original. For cases in which this calculation gave ‘negative’ NO$_3$ values, the estimated detection limit was used instead. For Riverside, the detection limit was taken to be 1.2 µg/m³, which corresponds to the mean calculated uncertainty for values of predicted NO$_3$ between 0 and 1 µg/m³. This method takes into account the NOx dependence. For Mira Loma, where a NOx regression was not employed, the detection limit was taken to be 0.7 µg/m³, which corresponds to applying Eq. (3) to one standard deviation of the field blank correction.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Riverside (8 MHz)</th>
<th>Riverside (4.77 MHz)</th>
<th>Mira Loma</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>1.159</td>
<td>1.196</td>
<td>1.025</td>
</tr>
<tr>
<td>$k$</td>
<td>9.108</td>
<td>13.572</td>
<td>18.014</td>
</tr>
<tr>
<td>$B_{\text{field}}$ (Vs)</td>
<td>0.007829×[NOx]+0.5370</td>
<td>0.005436×[NOx]+0.3729</td>
<td>0.422</td>
</tr>
</tbody>
</table>
Data Format and Flags

The data are contained in two files, one for data from Riverside and one for data from Mira Loma. The file format is the same for each, as described in the pair of accompanying text “readme” files. The standard distribution format is comma-delimited text with seven fields per line. The first line contains field descriptors followed by the data in subsequent lines with the following format:

<table>
<thead>
<tr>
<th>Field</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sample start time</td>
</tr>
<tr>
<td>2</td>
<td>Sample date</td>
</tr>
<tr>
<td>3</td>
<td>Flag</td>
</tr>
<tr>
<td>4</td>
<td>Sample period (sec)</td>
</tr>
<tr>
<td>5</td>
<td>Sample temperature (°C)</td>
</tr>
<tr>
<td>6</td>
<td>Blank corrected NO$_3^-$ (µg/m$^3$)</td>
</tr>
<tr>
<td>7</td>
<td>Estimated uncertainty in NO$_3^-$ (µg/m$^3$)</td>
</tr>
</tbody>
</table>

The flag column indicates whether the reported nitrate values are above or below detection limits, at what clock speed the computer operated, and if a shorter sample period with filtering was used. The specific codes used are as follows:

<table>
<thead>
<tr>
<th>Flag</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>000</td>
<td>NO$_3$ equal to or above detection limit (4.77 MHz).</td>
</tr>
<tr>
<td>001</td>
<td>NO$_3$ equal to or above detection limit (8.0 MHz).</td>
</tr>
<tr>
<td>010</td>
<td>NO$_3$ below detection limit (4.77 MHz).</td>
</tr>
<tr>
<td>011</td>
<td>NO$_3$ below detection limit (8.0 MHz).</td>
</tr>
<tr>
<td>100</td>
<td>NO$_3$ equal to or above limit (4.77 MHz), short sample time</td>
</tr>
<tr>
<td>110</td>
<td>NO$_3$ below detection limit (4.77 MHz), short sample time</td>
</tr>
<tr>
<td>200</td>
<td>NO$_3$ equal to or above detection limit (4.77 MHz), partially filtered sample resulting in shorter sample time.</td>
</tr>
</tbody>
</table>

The detection limits are estimated to be 1.2 µg/m$^3$ for Riverside and 0.7 µg/m$^3$ for Mira Loma.
Section 5. FRM PM2.5 Measurements

5.1 Overview

As part of the SCOS'97 Particle Trajectory Study, Federal Reference Method samplers for PM2.5 were fielded alongside the Caltech samplers on the selected study days. Samplers were provided by Andersen Instruments and by South Coast Air Quality Management District (SCAQMD). The samplers were fielded by Caltech and ADI personnel, and all samples were analyzed by the SCAQMD.

Objectives were:
(1) to compare the FRM sampler to other measurements and
(2) to evaluate the extent of nitrate loss from the FRM sampler.

5.2 Protocol

Two FRM samplers were operated side-by-side at each of the three Trajectory Study sites. One FRM was operated with a single Teflon filter, exactly as prescribed in the FRM procedure. The second, collocated FRM was operated with Teflon and nylon filters in series. Special, dual filter holders were supplied by Andersen for all of these samplers. Sample collection started at midnight standard time (0100 PDT), and continued for 23.5 hours.

All inlets for the FRM samplers were cleaned by washing with water just prior to the study. These inlets were identical in design to that of the dichotomous sampler, which have been shown to denude nitric acid when clean (John et al., 1988). Thus the Teflon-nylon filter pair was expected to provide a reasonable estimate of particulate nitrate.

Prior to sampling, SCAQMD inspected, conditioned and preweighed all Teflon filters and loaded the filter cassettes. After each sampling episode the filter samples were hand-delivered to the District. SCAQMD postweighed all Teflon filters for gravimetric mass, and analyzed both nylon and Teflon filters by ion chromatography.

The sampling sites were the roof of Pierce Hall on the UC Riverside Campus, the Union Pacific transfer site in Mira Loma (next to the Jurupa High School), the SCAQMD headquarters in Diamond Bar, and the Azusa and downtown Los Angeles SCAQMD monitoring stations. At Riverside, LA, Diamond Bar and Mira Loma the FRM sampler was collocated immediately beside the Caltech sampler. At Azusa the FRM samples were collected at the SCAQMD monitoring site on Loren Ave, about one block away from the site of the Caltech and Riverside measurements.

Samplers at the different sites were operated cooperatively among the collaborating groups, as shown in Table 6. ADI operated FRM samplers at Riverside,
and SCAQMD operated samplers at the other two sites. These sites were downtown Los Angeles and Azusa in August, and Diamond Bar and Mira Loma in September. They were assisted by Caltech and ADI for the midnight sample changes.

### Table 6 Sites and Operators

<table>
<thead>
<tr>
<th>Date</th>
<th>Site</th>
<th>Operator</th>
<th>Midnight Change†</th>
</tr>
</thead>
<tbody>
<tr>
<td>August</td>
<td>LA N. Main</td>
<td>SCAQMD</td>
<td>CIT, Paul Mayo</td>
</tr>
<tr>
<td></td>
<td>Azusa (Loren Ave)</td>
<td>SCAQMD</td>
<td>ADI, Toni Miguel</td>
</tr>
<tr>
<td></td>
<td>Riverside-Pierce Hall</td>
<td>ADI</td>
<td></td>
</tr>
<tr>
<td>September</td>
<td>Diamond Bar</td>
<td>SCAQMD</td>
<td>CIT, Paul Mayo</td>
</tr>
<tr>
<td></td>
<td>Mira Loma</td>
<td>SCAQMD</td>
<td>ADI, S. Hering</td>
</tr>
<tr>
<td></td>
<td>Riverside-Pierce</td>
<td>ADI</td>
<td></td>
</tr>
</tbody>
</table>

† with logistical support from SCAQMD.

A standard operating procedure, and NCR logsheets were prepared and distributed in advance of the study, and are attached in Appendix B. Details are, as follows:

- All samplers inlets were cleaned prior to the study period. SCAQMD cleaned all samplers except those at Riverside, which were cleaned by ADI.

- Impactor oiled substrates were replaced each week, prior to the 2-day sampling period, according to SOP procedure.

- Filters were preweighed by the SCAQMD and loaded into labeled cassettes and placed into labeled transport tins.

- Samplers were operated according to SOP, with sampling beginning at 0100 PDT and a sample period of 23.5 hours. Logsheets completed in triplicate using NCR forms. One copy was shipped with samples, one copy was sent to ADI.

- Samples were returned to SCAQMD Diamond Bar lab the day following 2-day episode. Teflon filters equilibrated and post weighed. Then Teflon and nylon filters were submitted for ion chromatography analysis.

- Lab results were reported to ADI for processing and submission.

### 5.3 Summary of Measurements

Table 7 summarizes the samples collected. Although 4 episode periods were planned, only three were conducted due to unexpectedly low pollutant levels. Measurements during the fourth episode were conducted at Mira Loma only, to provide comparison with the automated nitrate system.
Table 7. Summary of FRM Samples Collected

<table>
<thead>
<tr>
<th>Day</th>
<th>Start Date</th>
<th>Start PDT</th>
<th>Dur (hrs)</th>
<th>Site</th>
<th>FRM#1</th>
<th>FRM#2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 1</td>
<td>Aug 21</td>
<td>0100</td>
<td>23.0</td>
<td>Azusa</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 1</td>
<td>Aug 21</td>
<td>0100</td>
<td>23.0</td>
<td>Los Angeles</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 1</td>
<td>Aug 21</td>
<td>0100</td>
<td>23.5</td>
<td>Riverside</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 2</td>
<td>Aug 22</td>
<td>0000</td>
<td>24.0</td>
<td>Azusa</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 2</td>
<td>Aug 22</td>
<td>0100</td>
<td>24.0</td>
<td>Los Angeles</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 2</td>
<td>Aug 22</td>
<td>0100</td>
<td>24.0</td>
<td>Riverside</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 3</td>
<td>Aug 27</td>
<td>0100</td>
<td>23.0</td>
<td>Azusa</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 3</td>
<td>Aug 27</td>
<td>0100</td>
<td>23.8</td>
<td>Los Angeles</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 3</td>
<td>Aug 27</td>
<td>0100</td>
<td>23.5</td>
<td>Riverside</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 4</td>
<td>Aug 28</td>
<td>0100</td>
<td>24.0</td>
<td>Azusa</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 4</td>
<td>Aug 28</td>
<td>0100</td>
<td>24.0</td>
<td>Los Angeles</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 4</td>
<td>Aug 28</td>
<td>0100</td>
<td>24.0</td>
<td>Riverside</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 5</td>
<td>Sep 04</td>
<td>0200</td>
<td>22.7</td>
<td>Diamond Bar</td>
<td>T</td>
<td></td>
</tr>
<tr>
<td>Day 5</td>
<td>Sep 04</td>
<td>0100</td>
<td>23.5</td>
<td>Mira Loma</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 6</td>
<td>Sep 05</td>
<td>0100</td>
<td>24.0</td>
<td>Diamond Bar</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 6</td>
<td>Sep 05</td>
<td>0100</td>
<td>24.0</td>
<td>Mira Loma</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 6</td>
<td>Sep 05</td>
<td>0100</td>
<td>24.0</td>
<td>Riverside</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 7</td>
<td>Sep 27</td>
<td>0600</td>
<td>19.6</td>
<td>Mira Loma</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 8</td>
<td>Sep 28</td>
<td>0135</td>
<td>23.0</td>
<td>Mira Loma</td>
<td>T</td>
<td>T/N</td>
</tr>
<tr>
<td>Day 9</td>
<td>Sep 29</td>
<td>0120</td>
<td>23.7</td>
<td>Mira Loma</td>
<td>T</td>
<td>T/N</td>
</tr>
</tbody>
</table>

5.4 Results

Precision

To date the analyses are restricted to internal comparisons between the FRM collocated samplers. As seen by Figures 11 and 12, the concentration of inorganic ions on the Teflon filters from the two collocated samplers were in excellent agreement. The correlation coefficient for these constituents is greater than 0.99, and the measurement precision ranges from 0.1 to 0.3 µg/m³ (Table 8.). There is no apparent bias between the FRM sampler operated with a Teflon-nylon filter pack (FRM #2 in the figures), and the one operated with a Teflon filter alone (FRM #1).

Table 8. Precision of Side-by-Side FRM Samples

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Standard Error (µg/m³)</th>
<th>Coefficient of Variation (%)</th>
<th>Correlation Coefficient R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric Mass</td>
<td>4.3</td>
<td>17.2</td>
<td>0.78</td>
</tr>
<tr>
<td>Mass, outliers removed</td>
<td>1.8</td>
<td>7.5</td>
<td>0.95</td>
</tr>
<tr>
<td>Nitrate</td>
<td>0.28</td>
<td>8.1</td>
<td>0.999</td>
</tr>
<tr>
<td>Sulfate</td>
<td>0.08</td>
<td>2.5</td>
<td>0.986</td>
</tr>
<tr>
<td>Ammonium Ion</td>
<td>0.13</td>
<td>5.9</td>
<td>0.997</td>
</tr>
</tbody>
</table>
For gravimetric mass, the precision is not as good as for ions. As shown in Figure 13 there are two obvious outliers in the data set, corresponding to samples collected on different days in Riverside and Azusa. The corresponding ion data for these two samples agree within 0.2 µg/m³. Even excluding the outliers, the precision of 2 µg/m³ is not as good as for ion analysis. As with other studies, the measurement precision for gravimetric mass is not as good for mass as for ions.

**Nitrate Loss**

Comparison between the Teflon filter nitrate values and that from the sum of Teflon and nylon filters places an upper limit on the nitrate loss from the Teflon filters. As a measure of particulate nitrate, the Teflon – nylon filter sum may be biased high if the inlet has not removed all of the vapor nitric acid and other gaseous compounds that are analyzed as nitrate on the nylon backup filter. Figure 14 shows the comparison between the Teflon-nylon filter sum, and the nitrate on the individual Teflon filters. The absolute magnitude of the nitrate collected by the nylon backup filter varied from 1 to 9 µg/m³. As shown in Figure 15, the fraction of nitrate on the nylon backup filter is less at higher nitrate concentrations. It will be interesting to compare these values with those of the Caltech sampler.

*Figure 11. Comparison of sulfate from the two FRM samplers at Azusa (AZ), Diamond Bar (DB), Los Angeles N. Main (LA), Mira Loma (ML) and UC Riverside (RV).*
Figure 12a. Comparison of nitrate from the two FRM samplers at Azusa (AZ), Diamond Bar (DB), Los Angeles N. Main (LA), Mira Loma (ML) and UC Riverside (RV).

Figure 12b. Comparison of nitrate concentrations from Fig 12a for 0-2.5 $\mu$g/m$^3$. 
Figure 13. Comparison of mass from the two FRM samplers at Azusa (AZ), Diamond Bar (DB), Los Angeles N. Main (LA), Mira Loma (ML) and UC Riverside (RV).

Figure 14. Nitrate concentrations from an FRM sampler operated with a Teflon filter (“Teflon-1”) and nitrate from a collocated FRM with a Teflon-Nylon filter pack. Points labeled “Teflon-2” are nitrate values from the Teflon filter in the collocated sampler; “Teflon2+Nylon” are nitrate values from the sum of the Teflon and nylon filters.
Figure 15. Comparison of vaporized nitrate measured by nylon backup filter on the FRM sampler to the particulate nitrate measured by teflon-nylon filter sum. Results are shown for measurements at Azusa (AZ), Diamond Bar (DB), Los Angeles N. Main (LA), Mira Loma (ML) and UC Riverside (RV).
Section 6.
Results from the Automated Nitrate Field Measurements

6.1 Comparison with Filter-Based Measurements

During the SCOS’97 study, three types of filter-based measurements were made in parallel to the automated nitrate system. At Riverside, Harvard University operated two Harvard-EPA Annular Denuder Samplers (HEADS). The “Full HEADS” employs a carbonate coated glass denuder to remove nitric acid, followed by a Teflon filter for particle collection, and two sodium carbonate filters to collect the volatilized particle nitrate and to correct for positive artifacts from nitrogen dioxide. A second, “Nylon HEADS”, was operated in parallel to the “Full HEADS”. The “Nylon HEADS” used a nylon backup filter in place of the carbonate impregnated filters. Samples were collected daily, with 23.5 hr collection commencing at 1000 am PDT. These measurements were made with EPRI sponsorship as part of the Methods Evaluation Study.

On days selected for the Trajectory Study, measurements were made with the FRM sampler and with the Caltech Sampler. As described in Section 5, one of the two FRM samplers at each site was operated with a Teflon-nylon filter pair, with 24hr samples commencing at midnight PST. No explicit denuder was used, although the cleaned aluminum surfaces in the inlet are expected to provide a fairly effective denuding of vapor nitric acid (John et al., 1988). The nylon filter in this sampler will collect particulate nitrate vaporized during sampling plus any vapor nitrate species not removed by the inlet. As such, the sum of nitrate from the Teflon and nylon filters in the FRM is expected to provide an upper limit for PM$_{2.5}$ nitrate.

Averages of the automated nitrate data were calculated corresponding to the filter samples for all periods for which data recovery was 80% or greater. The only day not meeting this criterion is the 23.5-hr period starting 1000 on August 24. Apart from interruptions for calibration, the data from the Nitrate Monitor are continuous except for the period from 1600 August 24 until 1500 August 25 (when a pressure sensor line became disconnected.) and from 1030 to 1700 September 28 (when the orifice became clogged).

Figures 16 and 17 compare data from the 23.5-hr average nitrate from the Automated Nitrate Monitor and the two Harvard Samplers at Riverside (Van Loy et al, 1999). Data from both samplers were obtained on 12 of the 15 sampling days. The time series plot indicates that the values from the Automated Nitrate system tended to be slightly lower than from the HEADS at the beginning, and intermediate between the two HEADS during the latter half of the study period. Regression of the Automated Nitrate values against the Full HEADS gives a correlation coefficient of $R^2=0.94$, and a slope 1.06±.05. Nitrate values measured by the Nylon HEADS are higher than from the full HEADS. Correspondingly, regression of the Automated Nitrate against the Nylon HEADS yields a lower slope, 0.88±.03, with an $R^2=0.96$. 
Figure 16. Daily averaged nitrate concentration measured by the Automated nitrate monitor, and the two HEADS systems at Riverside. The Full HEADS was operated with carbonate backup filters and the nylon HEADS used a nylon backup filter (HEADS data courtesy of EPRI).

Figure 17. Daily average nitrate concentrations from the automated nitrate monitor compared to that measured by the HEADS operated by Harvard. (courtesy of EPRI).
Figure 18. Nitrate measured by automated monitor compared to nitrate from Teflon filters (T1 and T2) and from the sum of Teflon and nylon filters (T+N) from the FRM sampler.

Figure 19. Comparison of nitrate from ADI automated monitor to the nitrate from the sum of Teflon and nylon filters (T+N) from the FRM sampler.
Comparison to the Teflon–nylon filter sums from the FRM sampler are displayed in Figures 18 and 19. This data set includes 4 days of measurements in Riverside in August, and 5 days at Mira Loma in September. Figure 18 also shows nitrate concentrations derived from the Teflon filter alone. The least squares fit of the automated nitrate data against the Teflon-nylon filter sum, shown in Figure 19, yields a slope of 0.96±0.02, an intercept of −1.2±0.3 and a correlation coefficient of $R^2 = 0.996$.

These comparisons indicate that the 24-hr averaged nitrate values obtained from the Automated Nitrate Monitor are comparable to values obtained by denuder filter sampling. For comparison to each of three types of filter collectors, the square of the correlation coefficient is greater than 0.94. Regression slopes range from 0.88 to 1.06, depending upon the comparison. These data indicate that on average the automated nitrate system yields values that are in agreement with the denuded filter data to the extent to which the filter systems agree with one another.

6.2 Comparison to Nephelometer Data.

At the Riverside site an Optec open-air nephelometer was used to measure the light scattering ($B_{scat}$) and ambient relative humidity. From this data we approximated the dry particle scattering $B_{sp,dry}$ using a heuristic correction of the form:

$$B_{sp,dry} = (B_{scat} - B_r) \left[ 1 + a \left( \frac{RH}{100 - RH} \right)^b \right]^{-1}$$

with $a = 0.518$, $b = 0.709$, and $B_r = 12 \text{ Mm}^{-1}$. The constants $a$ and $b$ were derived from a comparison of dry particle scattering to ambient relative humidity scattering from the Dallas Fort Worth Winter Haze Study (Kreisberg, personal communication). $B_r$ is Rayleigh scattering.

Comparison of the nitrate concentration and the RH-adjusted scattering is shown in the time series plots of Figure 20. Scaling of the graphs has been held constant so that the differences among days is more readily apparent. The ratio of the nitrate concentration to the estimated dry particle scattering varied from day to day, and varied slowly within a day. However, small details in the changes in nitrate and in particle scattering track quite nicely. For example, both show a drop in particle concentration near 12 o’clock noon on many days (e.g. August 18, 23, 24, 26, 28, 29, 30). The small fluctuations in nitrate concentration, such as on the afternoons of August 18, or August 27-29, are mirrored in the changes in the particle scattering.

The similarity in these signals indicates that (1) the short term fluctuations observed in the nitrate data are real, and (2) that the origins of these fluctuations is the same as for particle scattering. Changes in the overall particle concentration at the site appear to occur more rapidly than do changes in the fraction of the particle mass that is nitrate. This is a reasonable scenario for a downwind site such as Riverside, that is influenced by transport from the Los Angeles Basin.
Figure 20a. Comparison of nitrate concentration profiles to the particle light scattering adjusted for relative humidity.
Figure 20b. Comparison of nitrate concentration profiles to the particle light scattering adjusted for relative humidity.
Figure 20c. Comparison of nitrate concentration profiles to the particle light scattering adjusted for relative humidity.
Figure 20d. Comparison of nitrate concentration profiles to the particle light scattering adjusted for relative humidity.
Figure 20e. Comparison of nitrate concentration profiles to the particle light scattering adjusted for relative humidity.
Figure 20f. Comparison of nitrate concentration profiles to the particle light scattering adjusted for relative humidity.
Figure 20g. Comparison of nitrate concentration profiles to the particle light scattering adjusted for relative humidity.
Figure 20h. Comparison of nitrate concentration profiles to the particle light scattering adjusted for relative humidity.
Figure 21. Comparison of the nitrate concentration from the automated monitor (APNM) to the number counts of nitrate containing particles measured by the Aerosol Time of Flight Mass Spectrometer (ATOFMS). Graph courtesy of Liu et al, 1999

6.3 Comparison to the Aerosol Time of Flight Mass Spectrometer.

The University of California Riverside, under the direction of Prof. Kimberly Prather, operated an Aerosol Time of Flight Mass Spectrometer at their laboratories, located approximately 1 km from our Riverside sampling site. They compared their data to the Automated Nitrate Monitor on several days of the study, as shown in Figure 21. The ATOFMS data showing the number of particles containing nitrate over time are plotted alongside the nitrate mass concentration data obtained with the nitrate monitor. It is displayed over a 53 hour time period between 8/22/97 12:00 PDT to 8/24/97 16:50 PDT in Riverside, CA with 10-minute temporal resolution. One can see the trends in the data track each other quite well. Sharp rises and falls are evident in both data sets. On 8/23/97, both data sets show midmorning and afternoon maxima, with much lower concentrations at noon. A similar pattern is repeated on 8/24/97, with a midmorning maximum at 10:00 PDT with a local minimum at noon, and another afternoon maximum centered around 13:00 PDT. This comparison is discussed in more detail by Liu et al (1999)
6.4 Nitrate Profiles.

The data in Figure 20 show considerable time variation in the nitrate concentrations throughout the day. Often a factor of 10 difference between the daily minimum and maximum 10-minute averaged concentrations was observed.

Many of the study days showed two daily maxima in the nitrate concentration at Riverside. The first peak occurring in the midmorning, with a sharp drop in concentrations near noon, followed by a second peak in the afternoon. The relative magnitude of the morning and afternoon concentration peaks varied from day to day. Similar time-variation was observed in total fine particle concentrations, as indicated by nephelometry.

The time series plots in Figure 22 compare the nitrate concentration profiles to the ozone and nitrogen oxide concentrations measured by the South Coast Air Quality Management District. Inspection of these graphs shows that the morning nitrate maxima occurs after the input of NO from the morning rush hour, but prior to the increase in ozone. On several days, it was coincident with a slight increase in the indicated NO2. The afternoon increase in nitrate generally coincided with the rise in ozone concentrations, with a nitrate maxima occurring near the time of the maximum daily temperature. On most days the elevated ozone levels persisted longer than the nitrate.

For the period from August 28 – August 31, the relative magnitude of the morning nitrate concentration peak increased with each successive day. On August 28-29 the highest nitrate concentrations are observed in the afternoon. On August 30 the two peaks are comparable. The highest nitrate concentration period observed the morning of August 31, with 10-min concentrations in excess of 30µg/m³ between the hours of 10 and 11 in the morning. On this day the afternoon nitrate concentration peak is negligible by comparison. The morning nitrate peak was smaller, yet still dominant on September 1. This peak nitrate day occurred on Labor Day weekend, in the aftermath of a hurricane in Mexico that brought moisture into the Los Angeles Basin.

The pattern of nitrate concentration profiles observed in Mira Loma is somewhat different. As with Riverside, there are strong diurnal fluctuations in nitrate levels, but the pattern is more variable. As seen in Figure 23, often there was one dominant nitrate concentration peak near noon. This concentration maximum followed the morning NO peak, but generally preceded the ozone maximum by 1 to 2 hours. The days of highest nitrate concentrations, September 27-30, were characterized by moist conditions with higher than average nighttime nitrate concentrations. On these days the initial increase in nitrate occurred during the morning hours, before the increase in ozone.
Figure 22. Time series of particulate nitrate, ozone, and nitrogen oxide concentrations at Riverside.
Figure 23a. Time series of particulate nitrate, ozone, and nitrogen oxide concentrations at Mira Loma.
Figure 23b. Time series of particulate nitrate, ozone, and nitrogen oxide concentrations at Mira Loma.
Figure 23c. Time series of particulate nitrate, ozone, and nitrogen oxide concentrations at Mira Loma.
At Mira Loma the nitrate maximum occurred at noon to early afternoon on most days. However, on the days with the highest nitrate concentrations, the increased concentrations appear in early to mid-morning. A quantitative understanding of the nitrate profiles will require modeling that includes profiles of nitric acid and ammonia. The cooler, more humid morning conditions are more favorable for partitioning of NO$_3^-$ to the particle phase. This nitrate may be derived from nighttime formation mechanisms, heterogeneous formation processes, or carry-over from the previous day. The midday nitrate is likely associated with transport from the upwind portions of the Los Angeles Basin, and from the ammonia-rich regions immediately upwind of these sites.

It is possible that the morning and afternoon nitrate peaks are derived from different mechanisms. The afternoon peak concentrations of fine particle nitrate may be attributed to the photochemical formation of nitric acid, followed by mixing with the ammonia and condensation of the resulting ammonium nitrate on fine particles. On the other hand, the morning peak concentrations could be due to fog chemistry. Nitrate radical and N$_2$O$_5$ are reactive in the aqueous phase during nighttime, and are a potential source of nitrate (Seinfeld and Pandis, 1998).

Evaluation of the extent of heterogeneous nitrate formation for selected study days would require detailed air quality modeling, together with input of other high-time resolution gaseous and meteorological data, and emissions data. Such as will become available for this study. It would then be possible to calculate back trajectories with a detailed treatment of nitrate chemistry such as described by Joos and Seigneur (1994). Then through process analysis one could attribute the particle nitrate to its various chemical formation pathways.

6.5 Comparison of Performance to Data Quality Goals

Data quality goals for the field performance of the automated nitrate measurements were set prior to deployment, as described in Section 4. These goals specified values for accuracy, precision, lower quantifiable limit and data completeness. In each case the stated goals were met, as described below.

**Accuracy:** Comparison to three types of filter-based measurements gave regression slopes of 0.88, 0.96 and 1.06, with $R^2$ values of 0.96, 0.99 and 0.94 respectively. The corresponding systematic bias in the automated nitrate measurement varied from -12%, to -4% to +6%, depending on the comparison. The stated goal was to be within 25%. The differences between the automated nitrate and the filter based measurements was no more than among the filter based measurements themselves.

**Precision:** The pooled standard deviation of replicate ammonium nitrate standards run on the same day was 3%. The overall deviation in standards throughout the entire study period was 10%. The stated goal was 10% precision.
**Lower Quantifiable Limit:** The largest source of uncertainty in the data was the variability of the field blank. For measurements at Riverside using the KOH denuder one-sigma uncertainty arising from the field blanks was 0.8 µg/m³. For measurements at Mira Loma using the activated carbon denuder the one-sigma uncertainty was 0.4 µg/m³. Corresponding lower quantifiable limits, based on 3-sigma uncertainties, are 2.4 and 1.2 µg/m³. The stated goal was 2 µg/m³.

**Data Completeness:** Only two instrument failures occurred, one due to a disconnected vacuum gage, and one due to a dirty orifice, resulting in a down time of 30 hours over the 45 days of sampling. Apart from power outages and periods of calibration, the data recovery was 97%. On average, instrument calibrations took the instrument offline another 4% of the time. Validated data were reported for 93% of the 10-min periods over the 45 day study period. Our stated goal was 88% data recovery.

### 6.6 Summary

The performance of a new, automated method for high-time resolution measurement of fine particle nitrate has been tested in the laboratory and in the field. Specific components of the system were tested in the laboratory and through field performance tests. The overall performance was evaluated through field comparison to filter-based methods operated by others.

Laboratory tests showed less than 2% loss due to particle deposition in the humidifier, greater than 98% particle collection efficiency, and less than 2% evaporative losses. Similar results for particle collection efficiency and evaporative losses were obtained in field tests.

The system operated reliably in the field, without operator attention. A nearly continuous data base was obtained for the 45-day study. Field comparisons to denuder-filter methods, and to an FRM sampler operated with a Teflon-nylon filter pair showed no observable bias. The precision was 3% based on replicate standards and the three-sigma lower detectable limit was 1.2 µg/m³. Positive artifact from the sampling of filtered ambient air was the determining factor in the lower quantifiable limit.

On most days the nitrate concentrations were largest during daytime hours. Often two nitrate peaks were observed, one midmorning and a second in the afternoon. The largest nitrate concentration events were associated with the morning nitrate peak, when ozone concentrations were low and relative humidity was high. The data are suggestive of a heterogeneous formation of nitrate under some conditions.


Kreisberg, N. private communication


Appendix A.

Standard Operating Procedures for Automated Nitrate Monitor and FRM Sampler
Automated Nitrate

Standard Operating Procedure
July 22, 1997

Susanne Hering
Aerosol Dynamics Inc., Berkeley California

Measurement Objectives:

The objective of the nitrate flasher measurements is to determine the time variation in fine particle nitrate concentrations with at least 5 measurements per hour.

Quality Assurance Objectives:

Quality assurance objectives for the nitrate flasher system are as follow:

Accuracy: Four-hour average of 10 minute nitrate concentrations from the nitrate flasher to agree within 25% of denuded nylon filter values from the sequential sampler at the same site.

Precision: at least ±10% (= 1 sigma) as determined by replicate standards.

Lower Quantifiable Limit: at least 20 ng, or 2µg/m3 for a 10 min sample.

Completeness: At least 88% data completeness during designated intensive.

Method Description:

Ambient samples are pulled through a pre-impactor to remove particles above 3 µm, denuders to remove potential gaseous interferents, and a humidifier to facilitate collection. Sampled particles are impacted onto a stainless steel strip mounted in an integrated collection and vaporization cell (patent pending). After 10 min of sample collection the system switches from this collection mode to the analysis mode. The analysis mode takes just under 2 minutes. In analysis mode the pumping is switched to a bypass line, the cell is flushed with nitrogen gas which then passes into a TECO 42C analyzer operating in manual NOx mode. After flushing the strip is rapidly heated by a capacitor discharge, and the evolved nitrogen oxides are quantitated by the TECO. The output is integrated to yield the nitrate concentration. Starting January 16, the system is operated automatically under the control of a XT-type computer. The entire pre-impactor, denuder, humidifier and collection-analysis cell are housed in a 3ft³ box which is ventilated with outside air to try to maintain sampling temperatures close to ambient.

Because this is a prototype system, a Particle Measuring Systems LPS optical counter is operated downstream of the impaction cell during collection so that the impaction efficiencies can be determined. These data are collected manually by a separate 286 computer equipped
with a Nucleus pulse height analysis card. The PMS optical counter has been modified to operate a low pressure.

Quality Assurance Plan

This is a prototype method which has never before been deployed in Southern California. Several tests will be done in the field to evaluate the system performance. These include: (1) analysis of nitrate and ammonium sulfate standards applied directly to the particle collection strip; (2) measurement of particle collection efficiencies on-line by the optical counter; (3) collection and analysis of filtered air samples to check for positive interferences; and (4) variation of sample duration to check for consistency and volatilization.

The running of standards (item 1) will be done twice weekly, preceding and following each of the two-day Trajectory intensives. Additional standards testing may be added if deemed necessary, but this would inherently be at the sacrifice of some of the data. The checks for positive artifacts, with sampling of filtered air, will be done at least once per week. On-line particle collection efficiency data will be recorded automatically with each sample. The checks of variation with sample duration will be done during setup. All of these tests will all be conducted by Susanne Hering.

Similarly, the initial system set-up and testing will be done by Susanne Hering, and will include all of the above quality assurance tests. Daily operations follow the attached "SOP for Daily Operation Checks", including completion of the attached log sheet.
Nitrate Flasher: SOP for Daily Operation Checks

1) **Nitrogen Tank:** Note nitrogen cylinder pressure on log sheet and arrange for replacement cylinder if under 1000 psi. Change out if below 500 psi, as described below.

2) **Humidifier and Fill System:** Check that water bottle on top of box is not leaking by checking that there is no water in aluminum pan under bottle. Check that humidifier is full by visual inspection - there should be no large bubbles visible. If not full, refill following instructions below.

3) **System Readings:** Check and record system readings per log sheet. Nitrogen flows may be adjusted with valve on the N2 cylinder as necessary. If pressure readings are not within specifications, then call Susanne Hering at (510) 649-9360-office or (510) 524-6141-home. Both have phone machines.

4) **Download Data:**
   Data is stored on the hard disk of the XT computer, which has the amber monitor. There is not enough space to store more than 15 days of data.
   - Exit program by typing "Ctrl-e" during sample collection
     - then wait for final analysis and return to main menu- about 2 min,
     - "Cntr-x" to exit
   You will be in C:\FLASH>. Files are in subdirectory C:\FLASH\DATA>
   - Copy to floppy, load onto IBM AT into directory C:\FLASHDAT>
   - Delete data files as necessary from XT (check available space)
   - Restart program by typing at C:\FLASH> prompt
     - "flash1" to enter main menu,
     - "Ctrl-c" for cycle,
     - "Return" to accept default of 600 sec sample duration.
   On startup, the system will clean strip as in analysis cycle, and then will start sample collection on the next even 12 min after the hour.

**To Change Nitrogen Cylinder:**
   This may be done anytime during the 10 min collection period, but it is critical that N2 be flowing during the analysis step as flashing in air will damage the strip. You can put the system in standby mode by pressing "Cntr-e" and waiting for analysis cycle. "Cntr-e" restarts automatic operations ("c" for cycle), hit return when queried for sample duration which defaults to 600 sec.
   After exchanging cylinder regulator pressure should be adjusted to 5 psi. Wait for analysis mode and check that left hand Dwyer (#1) reads 0.15-0.3 lpm and middle Dwyer (#2) reads 0.45-0.50 lpm.

**To Refill Humidifier:**
   Put system in standby mode by pressing "Cntr-E" on amber monitor computer to the left of TECO. Remove the plexiglas front of the box at joint with black tape. Disconnect black hose at inlet of humidifier. Using two 9/16 in wrenches (in tool box) loosen swage nut between
humidifier tee and RH probe tee. Be very careful not to loosen the hex fitting into the lower humidifier tee. There should be no leakage of water out of the humidifier from this step because the annular space that contains the water should still be sealed.

Being careful not to disconnect the tygon water line at the top of the humidifier, rotate the humidifier so that it is upside down from its normal position. Raise it so that the swage cap on the lower tee is above the water level in the bottle. Loosen this cap. Slowly lower humidifier so that water from bottle refills humidifier (there will be a small amount of water spilled, and be careful not to get on electronics - there are paper towels near tool box.) Once full replace and tighten cap, and reinstall humidifier. Restart cycle operation by pressing "Cntr-C" on computer.

**About Data Acquisition Program**

The program is in basic, running on an XT computer with Kiethly AD. Program name is "Flash1", and resides in the directory C:\FLASH>. Data is stored in subdirectory of Flash1 directory called "Data" [C:\FLASH>DATA>]. To start the program type "flash1" from the C:FLASH> prompt.

The program has two levels of menus. You enter onto the first level or "Main Menu". Apart from exiting the program there are three choices:

From Main:  
ctrl-s: sample -- manual sample collection  
ctrl-f: flash -- manual analysis by flashing  
ctrl-c: cycle -- automated collection and analysis.

You will always want ctrl-c for automated operation. It will ask for sample duration showing default value of [600] - hit return to take this default value unless instructed to use a different sample duration. The manual modes are only for special testing.

Defaults for the program are stored in a configuration file called "flash1.cfg". You should not change this.
Automated Nitrate - Daily Log Sheet

Date:__________ Time__________ Operator:__________

1) **Nitrogen cylinder**
   Cylinder pressure_________
   Arrange for replacement cylinder if under 1000 psi. Change out if below 500 psi.

2) **System Readings:**

   In sample mode - amber highlight on screen says "Collecting Sample"

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Acceptable Range</th>
<th>Reading in Sample Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔPTECO</td>
<td>6±1 inches water</td>
<td></td>
</tr>
<tr>
<td>Gilmont #1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Gilmont #2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Smpl Vac.</td>
<td>18 in Hg</td>
<td></td>
</tr>
</tbody>
</table>

   In analysis mode - amber highlight "flushing" or "charging" or "flashing" or "integrating"

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Acceptable Range</th>
<th>Reading in Analysis Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔPTECO</td>
<td>8±1 inches water *</td>
<td></td>
</tr>
<tr>
<td>Gilmont #1</td>
<td>150-250</td>
<td></td>
</tr>
<tr>
<td>Gilmont #2</td>
<td>65±2 **</td>
<td></td>
</tr>
<tr>
<td>Smpl Vac.</td>
<td>18 in Hg ***</td>
<td></td>
</tr>
</tbody>
</table>

   * ΔPTECO depends on the Gilmont #2 reading.
   ** Note initial and final readings if nitrogen flows adjusted.
   *** Do not adjust sample vacuum if OK in sample mode.

3) **Humidifier and Fill System:**
   Is aluminum pan under humidifier water bottle dry?_______
   Does humidifier appear full (no large bubbles visible)?_______

4) **Download Data**
   This need only be done every 3 to 4 days. "LL3"
   Files Transferred:_________________________________________

Comments
SOP FOR FRM TESTING

SCOS '97 Nitrate Volatilization Study

1. General

Equipment and Supplies

- Preweighed filters in cassettes
- Cassette tins
- Ice chest with blue ice
- Plastic bags
- Logsheets (NCR forms in Triplicate)
- PM2.5 Reference Samplers
- Impactor 37 mm filters
- Impactor oil in squeeze bottle
- Spare impactor wells
- Kim-wipes
- Squirt bottle with distilled water

Data recording

- All times should be recorded as Pacific Daylight Time
- Note any unusual observations on log sheets.

Sample Handling

- Be careful not to touch sample filter.
- Store samples in ice chest on blue ice or in refrigerator.

Contacts

- Solomon Teffara, SCAQMD 909-396-2199
- Susanne Hering, ADI 510-646-9360/ fld: 909-787-5141
- Jonathan Allen, CIT 818-395-6891

- Paul Mayo, CIT 818-395-3717  night operator at Los Angeles and Diamond Bar (CIT)
- Toni Miguel, ADI 818-792-7891  night op. at Azusa (ADI)
Before Study Start

2. **Inlet Cleaning**
   - To be done before start of study and after moving samplers in place.
   - Clean PM10 (dichot) inlet and other parts of sampler by washing down with water, and wiping with paper towels.

Weekly Sampler Checks

3. **Impactor Cleaning**
   - Note condition of impactor well (clean, light loading, heavy loading, evidence of particle bounce in chamber) on data sheet, comments section.
   - After the sample filter has been removed, lower the screw-jack to its lowest point. Pull the impactor assembly from the sample tube. Unscrew the impactor assembly and pull off the top.
   - Replace the well with clean well with new, 37 mm filter with 1 mL of oil to center of filter. Filter should appear transparent from oil. Thread the impactor together until it fits firmly. Wipe all oil from exposed surfaces, if any, especially those that might come into contact with the sample filter. Re-install in sampler. -Note on log sheet.

4. **Flow Verification and Leak Test**
   - Remove water from dichot inlet bottle and reinstall as needed. Remove dichot inlet, set upside down, and install flow adapter.
   - Install dummy cassette and assure it is sealed properly.
   - From main menu go to "leak test", close valve. Timer comes on at flow of <0.08 L/min. Wait until 1 min on timer. Record approx. time.
   - Open valve slowly so as not to aspirate oil from impactor. Can watch pressure from "monitor - module 1" menu.
   - Verify flow by installing flow meter such as differential orifice on inlet and going to "verify flow". Record sampler and flow meter flows simultaneously.
Sampler Set-up and Check

5. Dynamic Blank

- Run one dynamic blank at beginning of 2-day episode. Rotate between the samplers for this test.

- Enter filter number under DYNAMIC BLANK on log sheet, and place cassette into sampler metal grid toward the bottom. Raise the screw jack by rotating the knurled knob until a solid seal is felt.

- Start the sampler by going to "verify flow", and run for approximately 30 seconds.

- Remove filter, return to transport tin, and store in the compartment adjacent to the filter block assembly. Retrieve upon retrieval of the filter from the next sample to be run.

6. Filter Installation

- If not already completed, enter planned start date on Log Sheet (triplicate NCR form). Also record your name and date and start time of sample handling.

- Record filter cassette ID and sampler S/N.

- On the sampler, lower the filter holder, if not already done so, by rotating the knurled knob on the screw jack stand receptacle. Place the filter cassette into the receptacle with the metal grid toward the bottom. Be careful not to touch the filter.

- Raise the screw jack by rotating the knurled knob in a clockwise direction. Hand tighten until a solid seal is felt, but be careful not to over compress, as you will push the extension tube to inlet out of its clamp.

6. Programing Samplers to Start

- From the sampler screen, select "Setup Run---> Sample Start ", enter start date & time.
  ---> Sample For " and enter duration (23.5 h)
  ---> Filter ID and enter number (3 digits)

- Go to "review settings". Record programmed start and duration on data sheet. Verify filter number. "Interval" is always 0.

- From sampler screen select "Sample", and check that the time until start is correct. Note on log sheet that sampler set to sample.
7. **Final Check**

- Caps secure on com ports
- Filter assemblies tight
- Time until sample start run is correct on all samplers.

**Sample Retrieval**

8. **Record Information on Log Sheet**

- Enter retrieval date, your name, your starting time on next line. All times should be given as Pacific Daylight Time.
- Sampler should say "Sample Complete".
- Go to "Review Sample" and press "up" arrow. Enter sampling times in PST. Push "down" arrow, and enter elapsed time in hours, sample volume (m³), average flow (Q avg in L/min) and variability in flow rate (Q cv in %).
- Go to "Maintenance" and press "enter" for monitor, and "enter" again for modual 1. Noting the current time, record the current temperatures as indicated. TC1=ambient temperature, TC2=sample temperature.

9. **Remove and Store Filter**

- Remove filter from the sampler by moving the knurled wheel on the screwjack in a counterclockwise direction.
- Grasp the filter ring around its edges and place it into transport tin labeled with Sampler S/N. Replace lid and place in plastic ziplock bag in ice chest with blue ice.
- Record final time for completion of shut-down operations at the top of the log sheet.
- Store samples in refrigerator or ice chest on site, ready for pickup by SCAQMD personnel.
10. **Sample Numbering System**

Examples for third day of sampling at Azusa, two samplers in parallel:

- AZ1-03T
- AZ2-03T
- AZ2-03N

where:
- AZ1 = first sampler at Azusa
- AZ2 = second sampler at Azusa

- 03T = third day of testing, Teflo filter
- 03N = third day of testing, Nylasorb filter

Site-sampler designators are:
- LA1 & LA2 for North Main
- AZ2 & AZ2 for Azusa, Loren Ave.
- RV1 & RV2 for Riverside, Pierce Hall
- DB1 & DB2 for Diamond Bar
- ML1 & ML2 for Mira Loma

Sample days will be 01 through 08.
WEEKLY SAMPLER CHECKS:

Operator _________ Date ________ Time PDT _________ Site: _________

Sampler S/N ___________ ___________ ___________. Comments
Impactor Clean? ___________ ___________.
Leak Test? ___________.
Verify flow: ΔP ___________.
sampler flow ___________.

SAMPLE START:

Operator _________ Date ________ Time PDT _________ Site: _________

Dynamic Blank: Filter No._______, Sampler No._______, Run Time _________

Filter ID Number ___________ ___________. Comments.
Setup Start Date ___________.
Setup Start -PDT ___________.
Setup For (hrs) ___________.
Sample Selected? ___________.

CHECK AFTER SETUP

Time -PDT ___________.
Time till Start (h) ___________.

SAMPLE STOP:

Operator _________ Date ________ Time PDT _________ Site: _________

Sampler S/N ___________ ___________. Comments:
Sample Start-PDT ___________.
Sample Stop-PDT ___________.
Elapsed Time (h) ___________.
Q avg (L/min) ___________.
Q cv (%) ___________.
Volume (m³) ___________.
Amb. Temp.(°C) ___________.
Smpl Temp.(°C) ___________.

Yellow - with filters; Pink - to Susanne Hering, Aerosol Dynamics Inc. 2329 Fourth St., Berkeley, CA 94710