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Study to Evaluate the CADMP Sampler

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

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STUDY TO EVALUATE THE CADMP SAMPLER

Final Report
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ABSTRACT

The California Acid Deposition Monitoring Program (CADMP) sampler was evaluated for nitric acid measurement accuracy under both laboratory and field conditions. The key issues of this denuder difference-based sampling method were nitric acid penetration through the perfluoroalkoxy (PFA) Teflon-coated cyclone assembly and sampling plenum, and the efficiency of the denuder in removing nitric acid.

One aspect of the field evaluation involved sampling particle-free ambient air containing nitric acid, and monitoring concentrations before and after the major components. This was done for the Azusa sampler that had been used for over one year in the field after reconditioning (5 years of total use). Nitric acid penetration was approximately 85%, while the denuder efficiency was over 90%. These values are similar with those determined by the developers of the sampler. Another aspect was to compare ambient nitric acid measurements with a tunable diode laser absorption spectrometer (TDLAS). For this comparison, the Azusa sampler (now with two years of use since reconditioning) was employed in a one-month field study in Claremont, California. The correlation of concentrations between these two methods was less than 0.36 and the CADMP was, on the average, four to eight times lower. These results indicated that the denuders had failed during the second year of sampling after reconditioning. A third aspect of the field evaluation involved operating two nylon filters in series in both Riverside and Claremont, California. In Riverside (unlike Claremont) a mean of 25% of the nitrate was found on the back filter, indicating either collection inefficiency for nitric acid under these conditions or adsorption of an interfering nitrogenous species such as nitrous acid. Laboratory testing showed that peroxyacetyl nitrate (PAN) was not such an interferent.

The laboratory study of nitric acid penetration was conducted by introducing synthetically generated nitric acid into the sampler and monitoring the concentrations at various points of the sampler using either a commercial NO-NO$_X$ analyzer or the nylon filters normally used for nitric acid collection. The NO-NO$_X$ analyzer allowed real-time concentration measurement. This feature led to the discovery of temporally changing sorptive properties of nitric acid to the PFA Teflon-coated aluminum surfaces as a function of temperature, relative humidity, and previous nitric acid sampling history. The penetration of nitric acid through the sampler was evaluated by allowing the nitric acid concentration to stabilize prior to filter sampling. The results, under these conditions, were the same as those for filtered ambient air.

The cyclone inlet assembly from the sampler used in the TDLAS comparison study was evaluated in the laboratory using nylon filters to quantify the nitric acid concentrations, but without using a continuous analyzer to determine whether concentrations had stabilized. Under these conditions, the cyclone inlet assembly was found to be both a source and sink of nitric acid. After cleaning the cyclone, conditioning was necessary to achieve quantitative penetration of nitric acid under warm, dry conditions. For humid conditions the maximum penetration was 80%. A similar test using the denuders from this sampler showed them to be sources of nitric acid. It was concluded that aluminum-based denuders have a finite capacity for nitric acid.

The cyclones, both in greased and ungreased condition, were evaluated for cutpoint using laboratory-generated aerosol and were found to be close to the 2.5 µm expected. Continued exposure to aerosol indicated that the ungreased cyclone would shed previously collected particles under loadings far less than normally encountered when sampling ambient air.

The results of the study show that regular (at least annual) cleaning and reconditioning of the sampler is needed, as is an evaluation of nitric acid penetration using filtered ambient air. Nitric acid denuders should be tested in the laboratory before and after field use to validate the data obtained. Nighttime measurements of nitric acid should be discontinued, as concentrations are near the detection limit and measurements are subject to interferences. Nylon filters for sampling nitric acid are susceptible to collection artifacts and should be replaced by a more selective adsorbent substrate. The cyclone should be replaced with a size-selective device less subject to particle shedding.

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EXECUTIVE SUMMARY

The objective of this study was to perform a comprehensive evaluation of nitric acid losses in the $PM_{2.5}$ portion of a CADMP sampler, and to quantify denuder and cyclone efficiency so that the accuracy of the nitrate and nitric acid measurements could be assessed for a monitoring network. Nitric acid penetration was studied in the field by using filtered ambient air as a nitric acid source, and in the laboratory by using synthetically generated nitric acid. Nylon filters were used to sample nitric acid for both field and laboratory evaluations; a continuous $NO\text{-}NO_x$ analyzer was used for selected laboratory measurements. The sampler was also operated in ambient air with a collocated TDLAS. Penetration of particles through the cyclone was determined using a laboratory generated aerosol.

The CADMP sampler was specifically designed by the Desert Research Institute (DRI) for a ten-site network established as a part of the California Acid Deposition Monitoring Program. The sampler measures airborne concentrations of particles and gases that contribute to acidic dry deposition. The CADMP collects particle samples in both $PM_{2.5}$ (fine) and PM_{10} size fractions, which are analyzed for mass, calcium, chloride, magnesium, nitrate, potassium, sodium, sulfate, and ammonium. Gases are collected on specialized filters that trap the gases as ions for later analysis. These gases include nitric acid, sulfur dioxide, nitrogen dioxide, and ammonia. To avoid sampling artifacts due to the volatility of ammonium nitrate (which readily equilibrates to ammonia and nitric acid), fine particulate nitrate is sampled with a nylon filter downstream of a diffusion denuder, a device that removes all of the gaseous nitric acid but allows particles to pass through. Nylon filters have been shown to quantitatively retain nitric acid; therefore, any collected ammonium nitrate that volatilizes will be immediately trapped. Total nitrate is sampled from the fine airstream without a denuder by using a filter pack which consists of a Teflon front filter and a nylon back filter. This filter pack collects any nitric acid volatilized from the Teflon filter. Nitric acid is measured as the difference between the total nitrate and the fine particulate nitrate.

While DRI tested the CADMP sampler for nitric acid penetration (this species has a tendency to adsorb on surfaces) and denuder efficiency, a review of the CADMP network data suggested that after several years denuders at some of the sites may have lost efficiency, causing nitric acid concentrations to be biased low. During a previous comparison with nitric acid measured by a tunable diode laser spectrometer (TDLAS), both used and reconditioned CADMP samplers were found to be consistently lower than the TDLAS. This finding could be a result of losses of nitric acid in the sampler, loss of denuder efficiency, or a bias of the TDLAS.

In addition to the evaluation of the CADMP sampler, the collection efficiency of the nylon filters used to remove nitric acid was evaluated by sampling particle-free air (Teflon filters were used) with two nylon filters in series. This sampling was done at Riverside in the fall of 1994 and at Claremont in the summer of 1995. For samples collected in Riverside, about 25% of the nitrate was found on the back filter, indicating either collection inefficiency for nitric acid or partial adsorption of an interfering nitrogenous species. Collocated sodium chloride-coated filters collected less nitrate than the nylon filter (with very little nitrate on the second filter or third backup filter; this indicated high collection efficiency), therefore an interferent was suspected. Peroxyacetyl nitrate (PAN) was later shown not to collect on nylon filters, so nitrous acid was the likely interferent. For the Claremont samples, the nitrate on the second nylon filter was less than 10% of that on the first, suggesting a mix of pollutants different from that of the Riverside sampling. The reason for this is not known, but may be due to heterogeneous reactions facilitated by greater humidity.

Filtered ambient air as a source of nitric acid (particulate nitrate must be removed since this would interfere with nitric acid measurements using a sorptive filter technique) is a useful approach to evaluate sampler performance since the temperature, humidity, and copollutant environment represents actual sampling conditions. In order to do this a PFA Teflon-coated aluminum test inlet housing was fabricated to fit around the CADMP cyclone inlet assembly. Four open face filter holders were installed in this housing. Teflon filters were installed in these holders to filter the air entering the cyclone of the CADMP. Nitric acid was sampled using nylon filters at four locations: (1) within the test inlet housing, (2) between the cyclone and the CADMP sampling plenum, (3) at the exit of the CADMP sampling plenum, and (4) at the outlet of the denuder. The sampler evaluated was the CADMP used for collocated sampling at Azusa. This sampler had been used for a year since being refurbished. A series of 12-hour samples was collected for both daytime (6 am-6 pm) and nighttime (6 pm-6 am) intervals during periods of moderate air pollution (peak ozone of approximately 0.10 ppm). While the nighttime results were inconclusive due to low nitric acid concentrations, the daytime samples showed nitric acid losses of approximately 15% through the cyclone and plenum, (losses of nitric acid through the cyclone and plenum separately were within the experimental uncertainty) while the denuder efficiency was over 90%. These values are comparable to the limited measurements by DRI (which were not published). The Azusa collocated CADMP sampler was then evaluated in the laboratory for nitric acid and PAN penetration using synthetically generated sources under controlled conditions of temperature, relative humidity, and concentration. Nylon filters were used to collect samples at the same positions used for the ambient filtered air study. In addition, concentrations at various points of the sampler were measured using a commercial NO-NO_x analyzer with a molybdenum converter. The NO-NO_x analyzer allowed real-time concentration measurement. This feature led to the discovery of significant temporally changing sorptive properties of nitric acid to the PFA Teflon-coated aluminum surfaces of the sampler as a function of temperature, relative humidity, and previous nitric acid sampling history. The penetration of nitric acid through the sampler was evaluated by allowing the nitric acid concentration to stabilize prior to filter sampling; a process that would often require from many hours to days. The filtration results, under these conditions, were indistinguishable from those for filtered ambient air. PAN did not exhibit the surface losses observed for nitric acid using the NO-NO_x analyzer, nor was it retained by nylon filters. During the course of stabilizing the CADMP with nitric acid, the denuder lost efficiency for removing this species.

The Azusa primary sampler, which had been refurbished about two years ago, was installed at a site in Claremont collocated with a TDLAS and a long pathlength Fourier transform infrared spectrometer (FTIR). While we had not originally proposed to compare the CADMP results with collocated ambient measurements from other instruments, this special study provided a unique and cost-effective opportunity to do so. The primary CADMP sampler was used because the collocated Azusa sampler's denuders had lost efficiency during the laboratory evaluation. The TDLAS was used to measure nitric acid in real time. The advantages of this instrument are that it has high sensitivity (less than a ppb) and measurements can be obtained without constant supervision. One disadvantage is that a Teflon filter is required at the inlet to protect the mirrors in the optical system, and volatilization of ammonium nitrate collected on this filter may cause a positive nitric acid artifact. In addition, the sample must be transported through a cell to maintain the 20 torr pressure necessary to measure the absorption feature; wall losses are therefore possible. The FTIR by comparison measures nitric acid directly in ambient air using a multiple-pass optical system with a 25 meter base path. Its main disadvantages are that the detection limit is approximately four ppb and that the instrument requires constant operator attention. Daytime and nighttime samples were collected with the CADMP for a 28-day period starting in late August using the same filter substrate combination as the network operations. The nominal collection periods were from 11am to 5pm for the daytime sample (in order to sample concentrations of nitric acid high enough to be detected by the FTIR) and 5pm to 11am for the nighttime sample. The correlation of nitric acid concentrations between the CADMP and the TDLAS was less than 0.36 and the CADMP was, on the average, four to eight time lower. In addition, many values, even in the daytime sampling period, were at or below zero. This is evidence that the denuders had lost significant efficiency, further supported by the laboratory evaluation. The TDLAS nitric acid concentrations were lower than the FTIR in the morning and higher in the afternoon during the eight filter collection periods, for which FTIR data were available, with the TDLAS an average of 11% higher. This pattern suggests adsorption and desorption of nitric acid from the inlet system of the TDLAS.

The cyclone inlet assembly and denuders from the primary Azusa CADMP were then evaluated in the laboratory for nitric acid penetration using synthetically prepared nitric acid. Sampling was done before and after each component with nylon filters; the analytical precision was approximately 10%. These components were tested as is; no attempt was made to monitor the concentration until stabilized. Under warm, dry conditions the cyclone inlet assembly behaved as a source of nitric acid, with the concentration at the outlet more than twice that of the laboratory source. When tested under cool, moist conditions the nitric acid penetration ranged from 31% to 74%. These tests were re-run after cleaning the cyclone inlet assembly. The results showed that after a conditioning run, the penetration of nitric acid ranged from 67% to 115%. Similar tests were performed on the three denuders used with the CADMP (one for daytime, one for nighttime, and one for field blank collection). While the denuder used to collect field blanks operated with approximately 90% efficiency, the two others were, under all temperature, humidity, and concentration conditions, sources of nitric acid (the outlet concentration was often an order of magnitude higher than the inlet concentration). The denuder as a source of nitric acid would explain the field measurements where the nitric acid concentrations were reported to be negative (more nitrate collected after the denuder compared to without the denuder).

The particle collection efficiency of the cyclone was also tested in the laboratory using synthetically generated aerosol. There were only slight differences in cut-points between greased and ungreased cyclones. When sampling particles greater than the cut-point, the greased cyclone maintained high removal efficiency, while the removal efficiency of the ungreased cyclone became significantly lower after 30 minutes of sampling, which is indicative of particle shedding. If this shedding occurs while sampling ambient air, it is likely to cause a positive artifact in the measurement of fine particulate nitrate and possibly a positive artifact for nitric acid measurements (large particles are more likely to settle within the denuder and contribute to 'apparent' nitric acid).

This study resulted in a number of conclusions concerning the CADMP sampler:

- Regular maintenance of the sampler is necessary. In addition to cleaning the cyclone (at least quarterly) and the sampler's interior surfaces (at least annually), the denuders should be replaced at regular intervals (one to two years depending on the exposure to nitric acid).

- We have shown that it is possible to saturate aluminum-based nitric acid denuders under both laboratory and field conditions.

- While overall penetration of nitric acid under field conditions was adequate (approximately 85%), we have shown that nitric acid adsorption to the sampler's walls is reversible and dependent on temperature and humidity. The CADMP 6 am to 6 pm sampling schedule may have resulted in little net nitric acid measurement artifact since acid desorbed from the sampler's surfaces in the morning while warming, may be compensated for in the late afternoon by adsorption while cooling.

- The measurement of nitric acid penetration should be conducted over typical ambient diurnal changes of temperature, relative humidity, and concentration rather than under controlled laboratory conditions. This should be done on a regular basis to confirm performance.

- The potential sampling artifact for nylon filters should be examined more thoroughly. This artifact may bias the nitric acid results high (although this may be compensated by losses within the sampler). We have shown that PAN is not an interferent.

- Since nitric acid concentrations are low at night (shown by spectroscopic methods) and the sampler is likely to adsorb that which is present, nighttime sampling could be discontinued without affecting the completeness of the data set.

- A particle size-resolution device that is less prone to particle shedding should be considered.

1.0 INTRODUCTION AND STATEMENT OF THE PROBLEM

1.1 CADMP Sampler

As part of the California Acid Deposition Monitoring Program (CADMP), a 10-site monitoring network was established to measure the airborne concentrations of particles and gases that contribute to acidic dry deposition. Monitoring is done with the CADMP sampler, which was specifically designed to meet the needs of the program (Watson and Chow, 1991). The CADMP sampler collects acidic gases and two size fractions of particles: those below 10 µm in diameter (PM_{10}) and those below 2.5 µm ($PM_{2.5}$). Sampling is done using denuder and filter-based methods, with Teflon, nylon, and impregnated filters for the collection of particles and gases. Gases measured include nitric acid, sulfur dioxide, nitrogen dioxide, and ammonia. Particle mass is measured in addition to calcium, chloride, magnesium, nitrate, potassium, sodium, sulfate, and ammonium ions. The sampler provides both daytime and nighttime samples.

Figure 1-1 is a schematic of the sampling arrangement for the $PM_{2.5}$ sampling unit of the CADMP sampler. The Teflon filter (without pre-treatment from the denuder) is extracted and analyzed for mass and ions, while the nylon filters are analyzed for nitrate only. The nitrate on the nylon filter below the Teflon filter provides a measure of nitric acid by the 'filter pack' approach. In this approach the Teflon filter removes particulate matter (including nitrate-containing particulate matter) and nitric acid penetrating the Teflon filter is adsorbed by the nylon filter as nitrate. The sum of nitrate on both filters is referred to as 'fine total nitrate'. The nitrate on the nylon filter with the denuder pre-treatment is a measure of 'fine particulate nitrate'. Volatilization of fine particulate nitrate is prevented by the nylon filter immediately adsorbing the nitric acid produced from volatilization. The difference between the fine total nitrate and fine particulate nitrate is a measure of gaseous nitric acid by the 'denuder difference' approach.

A review of data by Ashbaugh et al. (1991) indicated satisfactory performance of the CADMP sampler during its first year of operation. Linear regression data from collocated samplers operated in Sacramento yielded regression coefficients greater than 0.92 for $PM_{2.5}$ gravimetric mass, sulfate, nitrate, sulfur dioxide, nitrogen dioxide, and ammonium. The correlation coefficient for nitric acid determined by the denuder difference, on the other hand, was only 0.78. Comparison of daytime values of nitric acid by the denuder difference and filter pack methods, both of which are measured by the CADMP sampler, showed that filter pack nitric

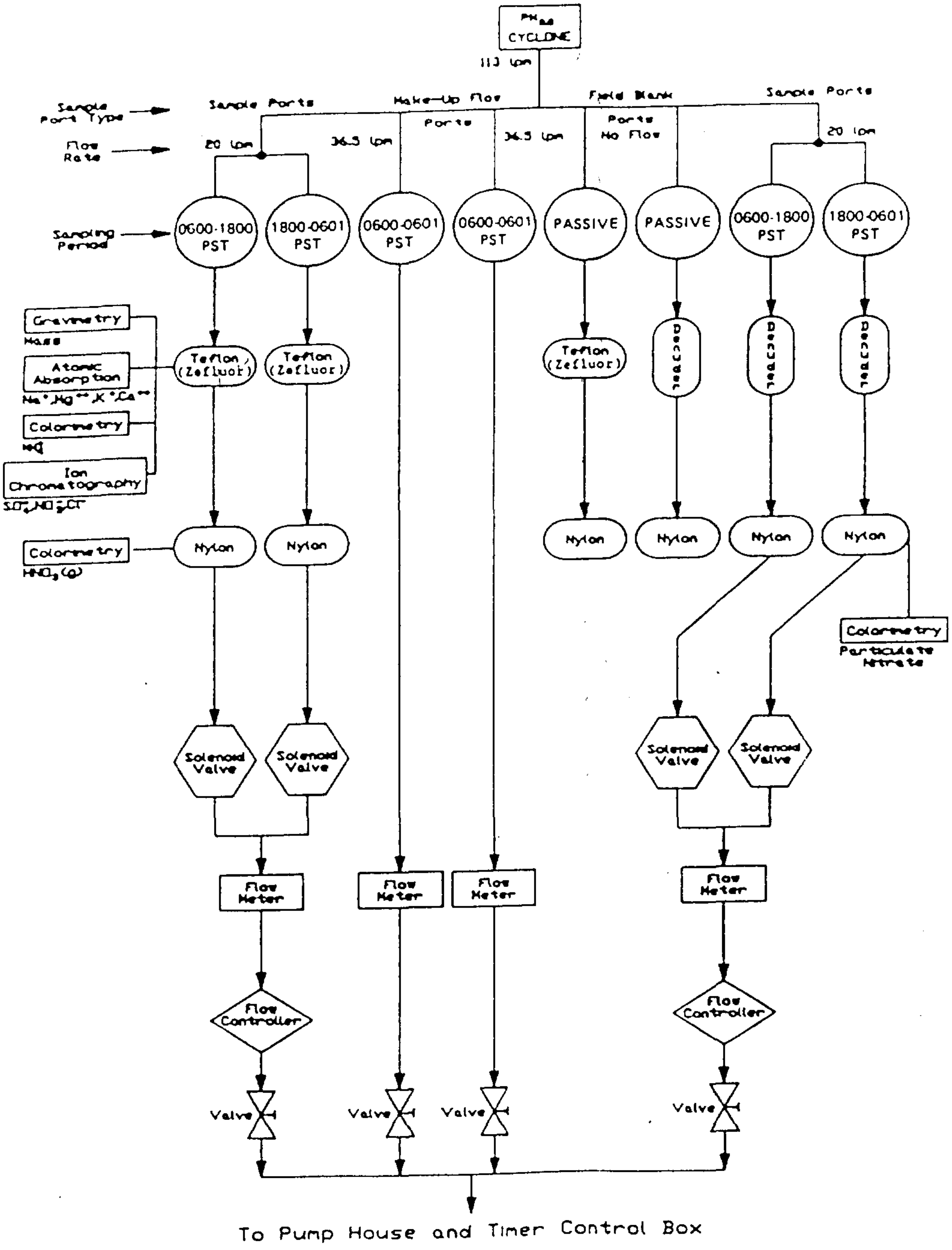


Figure 1-1. Sampling and measurement flow diagram for the CADMP $PM_{2.5}$ unit.

acid values were higher than those obtained by denuder difference. This could be due to the volatilization of ammonium nitrate from the Teflon filter during sampling and subsequent trapping of the nitric acid produced by the volatilization, a well-known phenomenon (Appel et al., 1980). At the sites with the high nitric acid concentrations (Bakersfield, Long Beach, Los Angeles, and Azusa) the average filter pack measurements of the acid were approximately twice those from the denuder difference approach.

Subsequent data analyzed by Blanchard (1993a,b) raised questions regarding the performance of the sampler for nitric acid measurements. In the three-and-a-half years of data analyzed, Blanchard found a gradual divergence in the ratio between denuder difference nitric acid and filter pack nitric acid measurements. The filter pack nitric acid showed seasonal trends following expectations, and correlated with ozone concentration. Denuder difference nitric acid showed the same seasonal trend in the first year's data, but in subsequent years the seasonal trend gradually diminished. The ratio of denuder difference nitric acid to ozone concentrations also decreased. At the Azusa and Los Angeles sites, Blanchard found that particulate nitrate concentrations below the denuder increased relative to PM_{10} nitrate, at the same time as denuder difference nitric acid decreased. Discrepancies were greatest on summer daytime samples when one expects the highest nitric acid concentrations. Comparisons between CADMP and collocated Graseby Andersen hivol PM_{10} samplers with SA-321 inlets showed, on the other hand, good agreement for mass, sulfate, nitrate and ammonium ion concentrations, even though the CADMP sampling period was offset six hours later than the hivol monitoring period. Blanchard concluded that there were no significant errors due to leaks or flow rate instabilities. He also concluded that the denuders may have become less effective after several years of use at Azusa and Los Angeles. No evidence of denuder degradation was observed at the other eight sites in the network.

In fall of 1993, a side-by-side nitric acid comparison test was conducted at the Azusa site between the CADMP sampler and a Tunable Diode Laser Absorption Spectrometer (TDLAS) operated by Unisearch, Inc. Overall, the CADMP nitric acid concentrations were approximately a factor of two lower than the TDLAS. Differences between the collocated CADMP samplers were small by comparison (Ashbaugh, 1994a). Tuazon et al., 1995 has reviewed this data and concluded that the TDLAS nitric acid measurements were higher than expected when using ratios of nitric acid to ozone in order to compare with previous nitric acid measurements in the area.

1.2 Objectives

The primary objectives of this study were to evaluate sources of bias in the measurement of nitric acid by the CADMP and to recommend changes to improve the accuracy and precision of these measurements. Potential sources of bias include:

- Nitric acid losses in the cyclone assembly.
- Nitric acid losses in the sampling plenum.
- Decreased nitric acid removal efficiency by the denuder.
- Re-emission of nitric acid from the denuder.

Although the cyclone assembly (which includes a cyclone, weather shelter, and insect screen) and the plenum of the CADMP sampler are coated with PFA Teflon, using the method applied and tested by Watson and Chow (1991), they could still act as a sink for nitric acid. Appel et al., (1987) found significant nitric acid losses within PFA Teflon-coated cyclones, which were linearly dependent on residence time within the cyclone. Fitz and Zwicker (1988) found more than a 75% loss of nitric acid in a PFA Teflon-coated plenum in the first prototype configuration of the South Coast Air Quality Study (SCAQS) sampler. This plenum was subsequently eliminated from the SCAQS sampler design. Tests conducted on the CADMP sampler when it was new indicated that washing of the surfaces with nitric acid minimized nitric acid loss. The effectiveness of this treatment after several years of sampling has not been tested. It is quite possible that deposition of dusts (which are alkaline) or neutralization by atmospheric ammonia could contribute to a significant increase in the rate of nitric acid loss.

In extremely dusty environments, the Bendix 240 cyclone used in the CADMP sampler might allow the penetration of coarse particulate matter unless it is greased (Watson, 1993). For CADMP, the cyclone is operated ungreased since nitric acid would probably be partially adsorbed by the grease. If coarse particles penetrate the cyclone, the size cut resolution would be compromised, potentially causing a positive bias for all fine particulate parameters measured. In addition, larger particles are more readily deposited to surfaces by gravitational settling than smaller ones, due to their higher terminal settling velocity. Since the denuder line provides additional surfaces, compared to the non-denuder line, more of these larger particles might be removed. If these larger particles contain nitrate, the 'fine particulate nitrate' will be biased low compared to the 'total fine nitrate'. This would cause the nitric acid determined by the difference method to be biased high. It should be noted, however, that in comparison with the TDLAS, the nitric acid measured by the CADMP denuder difference approach was always lower.

Collection and retention efficiencies are important parameters for denuder difference nitric acid measurements. While substrates must have high collection efficiencies for accurate nitric acid measurement, it is equally important that they retain the collected nitric acid under changing atmospheric conditions. For the nylon filters and the anodized aluminum denuders, the mechanism for binding of nitric acid is not entirely understood but may involve surface adsorption. During sampling these substrates may behave as chromatographic columns with a long retention time; thus, it is possible that collected nitric acid retained under one atmospheric condition (i.e., cool and humid) could be released by subsequent exposure to less favorable conditions for retention (i.e., hot and dry). In fact, desorption of nitric acid from nylon filters has been observed for multiday exposures to hot (41°C), dry air (Luhrmann et al., 1994). In this report, two types of nylon filters were exposed to high concentrations of nitric acid and then subsequently exposed to clean, hot, dry air. Under these conditions, nitric acid losses of 0.3 to 0.8% per hour were observed.

Motivation for this study was to evaluate discrepancies between the sampler and the TDLAS during the October 1993 comparison study and to identify the mechanisms which account for the lower than expected nitric acid values from CADMP. Specific objectives were:

- Assess the integrity of samplers as they are now operating in the field (assessments included leak tests and flow calibrations).
- Quantify nitric acid transmission through the CADMP sampler (cyclone inlet assembly and plenum) for a variety of concentrations, temperatures, and relative humidities.
- Quantify nitric acid collection efficiency of the denuder and filter substrates at different operating temperatures and relative humidities.
- Assess the cyclone performance, including penetration of large particles as well as nitric acid.
- Assess the potential for interferences from PAN.
- Assess the capacity of the denuder and filter substrates to retain collected nitric acid upon exposure to hot, dry conditions.
- Assess the need for routine maintenance of the CADMP sampler.

2.0 APPROACH

2.1 System and Performance Audits

2.1.1 System Audit

A system audit was performed on the two CADMP samplers used for collocated sampling in Azusa. The audit involved an examination of the samplers and questioning the site operator to determine whether the design parameters were met during field operation. The criteria used were based from the DRI CADMP Operations Manual (Bowen et al., 1990) and EPA QA Handbook (U.S. EPA, 1984). Parameters evaluated included:

- Overall cleanliness of the visible portions of the sampler.
- Frequency of calibration.
- Traceability of calibration standards.
- Filter handling, storage, and shipping procedures.
- Frequency and procedures for routine cleaning.

The suitability of the sampling location with respect to the measurements made was evaluated based on EPA guidelines for ambient monitoring of ozone, nitrogen dioxide, and PM_{10} for prevention of significant deterioration (U.S. EPA 1987). These guidelines specify methods for quality control for the data collected and provide probe siting criteria such as spacing from obstructions, roads, and other sources.

2.1.2 Performance Audits

In addition to the systems audit, the primary and collocated Azusa CADMP samplers were given a performance audit. This audit involved leak evaluation and an independent determination of the samplers' flow rate, two of the most likely sources of error in sample collection. To measure flow rates, a dry test meter was used which is traceable to the National Institute of Standards and Testing (NIST). Inlet and outlet flows were compared to determine whether the sampler leaked under usual operating conditions.

2.2 Field Evaluation

2.2.1 Filtered Ambient Air

The objective of this evaluation was to determine the penetration of nitric acid through the sampler components (cyclone assembly, sampling plenum, and nitric acid denuders). This evaluation was conducted using ambient air as a source of nitric acid, and sampling at various positions using nylon filters, which quantitatively adsorb nitric acid. The advantage of using ambient air is that it contains typical concentrations of other gas-phase nitrogenous species which may interfere with the nitric acid measurements (an interference would result if a gas were completely or partially retained by the denuder <u>and</u> completely or partially adsorbed by the nylon filter as soluble nitrate). The nylon filters were then extracted in an aqueous solution and analyzed for nitrate. Since the filters will also collect particulate nitrate, the air was passed through a Teflon membrane filter that removes particles but transmits nitric acid (Appel et al., 1980). While particulate ammonium nitrate collected on these filters may volatilize, generating additional nitric acid, the origin of the nitric acid should not bias the results. The air passing into the sampler then contained only gas-phase nitrogenous species such as nitric and nitrous acid and PAN. Figure 2-1 shows the testing arrangement and the various sampling points where nitric acid was measured. Note that the CADMP's three denuders (one normally used for daytime sampling, position 4A, one normally used for nighttime sampling, position 4B, and one normally used for the collection of field blanks, position 4C) were all evaluated simultaneously.

The nitrate concentrations determined by filter sampling were used to determine nitric acid losses through the sampler by comparing the nitric acid concentrations at the various sampling positions shown in Figure 2-1:

[1] - [2] Losses through the cyclone assembly (bug screen, cyclone housing and cyclone)
[2] - [3] Losses through the CADMP sampling plenum
[3] - [4] Losses through the denuder (denuder efficiency)

Note that position 1 in Figure 2-1 was placed as close to the inlet of the cyclone assembly as possible (within 1 cm) so that any losses of nitric acid in the test inlet housing would not bias the results.

The test inlet housing was constructed from aluminum and coated with PFA Teflon to cover the cyclone chamber sampler inlet and provide a leak-tight seal at that point. Figure 2-2 shows a

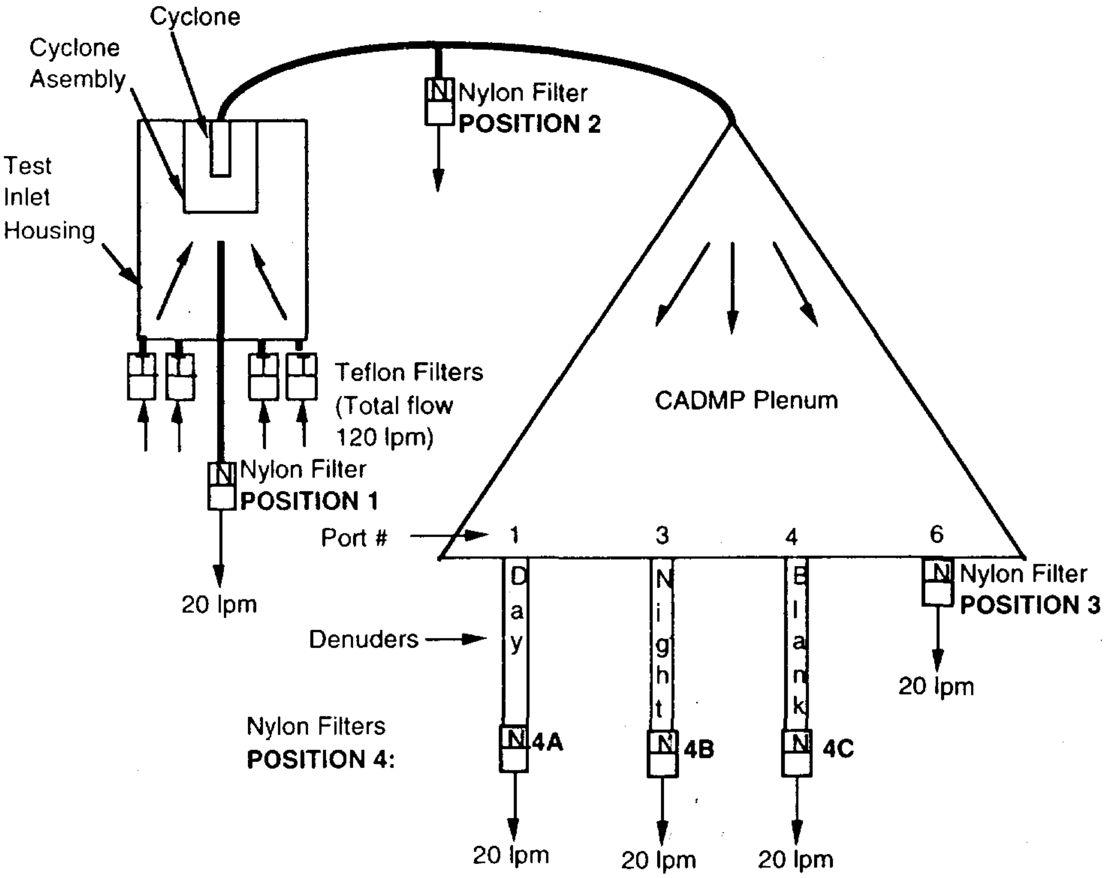
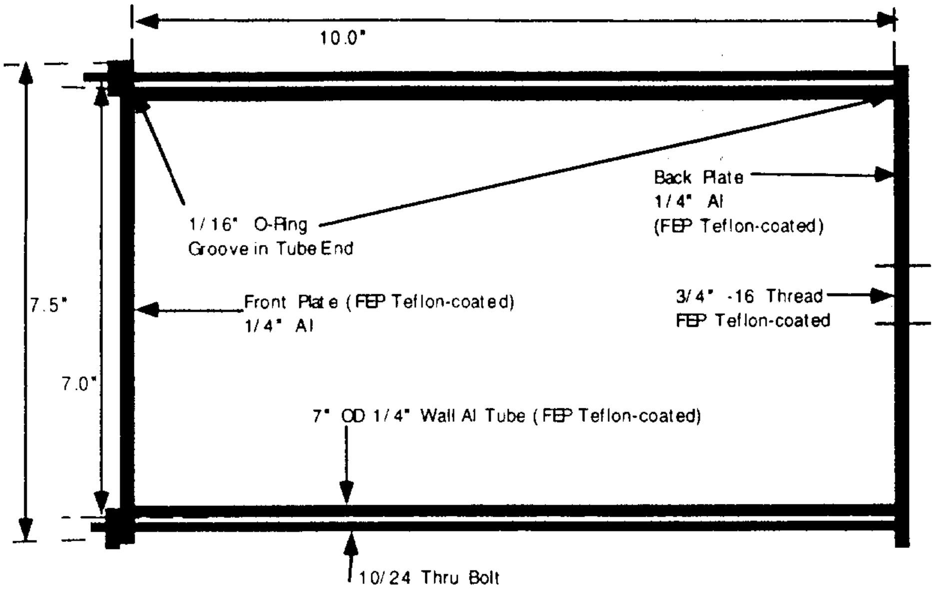


Figure 2-1 Schematic diagram for the field evaluation of the CADMP Sampler



FRONT PLATE(note-back plate has 1/8" holes and center hole only)

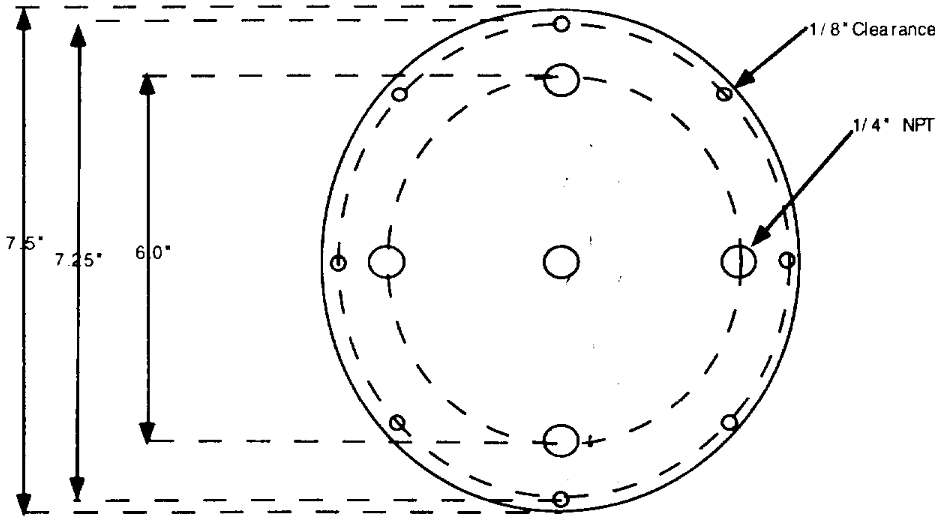


Figure 2-2 Side and top views of the inlet design to encase the cyclone assembly

drawing of the design of this inlet assembly. The particle filtration system consisted of four open face Savillex filter holders using 47 mm Gelman Zefluor'Teflon filters with an effective pore size of 2µm. These filters have a stated efficiency of greater than 99.9% for 0.3 µm dioctyl phthalate (DOP) particles at a face velocity of 5 cm/sec. The efficiency for field use was probably even greater, since 0.3 µm is the diameter of maximum filter penetration and the operation was at a face velocity of approximately 35 cm/sec. The sampler was thoroughly tested to ensure that the additional pressure drop due to the Teflon filter did not cause leaks.

Savillex in-line PFA Teflon filter holders were used to collect nitric acid at the various positions shown in Figure 2-1. Since all surfaces remove nitric acid to some degree (even the Teflon filter holders), the concentration of nitric acid reaching the CADMP was quantified by sampling as close to its inlet as possible (position 1). A 1/2 inch PFA Teflon tee was installed at sample position 2 in order to attach the filter holder. Separate pumps, needle valves, and rotameters were used to measure and control the sampling flow at positions 1 and 2. The flow calibration was the same as previously described for the initial audit. The filter holders at positions 3 and 4 were those of the CADMP sampler. In order to collect samples at two additional denuder positions (the CADMP normally samples from only one), the CADMP sampler was re-plumbed using the flow bypass lines. Nylon filters were provided by the ARB Monitoring and Laboratory Division and analyzed by them in the same manner as CADMP samples.

Experiments were conducted at the Azusa air monitoring station operated by the South Coast Air Quality Management District. The collocated sampler was used so that the primary sampler collected the scheduled samples. During these evaluations, samples were collected using four CADMP filter holders (day denuder, night denuder, field blank denuder, and total nitrate positions) in addition to the two added filter holders. One sample set (of six substrates) was collected per day for twelve-hour day or night periods identical to the CADMP schedule. Sets of field blanks were collected by leaving loaded filter cassettes in the sampler for a similar period but without operating the pumps. Filter substrates were removed within 2 hours of sampling, placed in extraction vials, and stored below 4°C in a refrigerator on site. These filters were sent to the ARB laboratory in batches, packed in an ice chest to minimize exposure to excessive heat.

Sampling was conducted when there was at least moderate air pollution, the criteria being a prediction of 0.10 ppm ozone or higher. Samples were collected during two intervals in the fall of 1994. In the first interval, four sets of daytime (6 am to 6 pm PST) and two sets of nighttime samples (6 pm to 6 am PST) were collected. After analyzing the results from the first interval, it was determined that additional night sample sets would not be useful due to low nitric acid concentrations. Therefore, during the second interval only daytime sample sets were collected.

2.2.2 1995 Claremont Comparison Study

As part of another ARB-sponsored contract, a special nitric acid measurement study was conducted in Claremont, California from August 29 to September 26, 1995. While it had not been originally proposed to compare the CADMP results with collocated ambient measurements from other instruments, this special study provided a unique and cost-effective opportunity to do so.

The study was conducted in the parking lot of a vacant industrial building located at 613 W. First Street in the city of Claremont, located in the San Gabriel Valley approximately thirty miles east of Los Angeles. Claremont is a receptor for photochemical air pollutants, and since it is not downwind of ammonia sources relatively high concentrations of nitric acid were expected to be observed in the pollutant mix. The Claremont Colleges have also been the site of previous nitric acid measurement studies. In the study reported here, spectroscopic methods were used to measure nitric acid, as these methods were expected to be more selective and interference free than filter/denuder approaches. The CADMP primary Azusa sampler was installed at the site and two samples per day were collected. The daytime sample was collected when nitric acid was expected to be significant, nominally from 11am to 5pm, while a nighttime sample was collected during the remainder of the time.

Two other collection-based samplers were also operated at this site. The South Coast Air Quality Management District's sampler used for the Enhanced Fine Particulate Monitoring Program and the CE-CERT acid species evaluation sampler were operated on the same schedule as the CADMP sampler.

Two spectroscopic instruments were used to monitor nitric acid vapor. The first was a tunable diode laser absorption spectrometer (TDLAS), which uses a single absorption line of nitric acid for quantification. Reference spectra are used to confirm identification and secondary lines are monitored to determine interferences. The detection limit of this instrument is less than one ppb and it can operate without constant operator attendance. The primary limitation of the instrument is that ambient air must be filtered and then sampled into a cell maintained at 20 torr pressure, and sampling artifacts may occur during this air handling. The second instrument was a long pathlength Fourier transform infrared spectrometer (FTIR). The absorption is measured directly in ambient air using a multiple pass optical system with a 25m base path.

While no sampling artifacts are possible, the detection limit of this instrument is about 4 ppb; therefore nitric acid can only be quantified during episodes of high concentration. This instrument also required constant operator attendance. The FTIR was considered the reference instrument and it was used to assess the accuracy of the TDLAS during periods of high nitric acid.

The TDLAS was considered the reference for nitric acid for comparisons with the CADMP sampler since it could, unlike the FTIR, provide around the clock measurements. The 15-minute data periods from the TDLAS was composited to match the CADMP sampler intervals so that a direct comparison could be made.

2.3 Laboratory Evaluation

The laboratory evaluation of the CADMP sampler was conducted in two phases. In the first phase the whole sampler was studied, while in the second phase individual components were tested. The first phase was conducted by CE-CERT while the second was done at ADI.

2.3.1 Whole Sampler Evaluation

The collocated CADMP sampler which had been used at the SCAQMD Azusa air monitoring station since October 1993 was the sampler to be evaluated. This sampler had been cleaned and reconditioned prior to installation and was used every sixth day until October 1994, after which it was used for a limited number of collection intervals as a part of the ambient evaluation reported here. The sampler was brought to the CE-CERT laboratory in early 1995 and evaluated in 'as found' condition.

2.3.1.1 Penetration of Nitric Acid

Synthetically generated nitric acid at typical ambient concentrations was used to evaluate losses of nitric acid through the sampler. The concentrations used were in the range from 25 to 100 $\mu g/m^3$ (concentrations will be reported in these units for consistency based on an average molar volume of 24.6 ℓ at Riverside and 24.5 ℓ at Berkeley). The same arrangement was used as in the field evaluation (see Figure 2-1) except that the inlet was attached to a source of nitric acid vapor. While nylon filters were used to collect samples for nitric acid determination, the initial screening of penetration was done with a Thermoenvironmental Model 42 NO-NO_x analyzer. The NO_x converters in these instruments effectively convert all HNO_3, NO_2, and PAN to NO (Winer et al., 1974), which is quantified by chemiluminescence detection.

Figure 2-3 is a schematic diagram of the sampling system. Another schematic showing the flow control and measurement system is presented in Appendix A. All tubing and fittings exposed to nitric acid were made of PFA Teflon. Nitric acid vapor was generated by flowing 1 ℓpm of dry, purified air (Aadco model 737 air generator) past a diffusion tube (VICI Metronics diffusion vial with a 2 mm bore) containing liquid nitric acid (68% aqueous solution). This air containing nitric acid vapor was then mixed with 130 ℓpm of purified air. Prior to mixing with nitric acid, the purified air was humidified by splitting the stream into two lines, bubbling one line through doubly distilled water (maintained at constant temperature by means of a heater and thermostat), and then recombining. All air flows were measured with rotameters and controlled with needle valves. Nominal concentrations of nitric acid were calculated based on flow and diffusion rates (supplied by VICI Metronics). The nitric acid-containing air was introduced into the sampler by means of the PFA Teflon-coated aluminum test inlet housing described in the previous section. The housing had four 1/2 inch PFA Teflon bulkhead tube fittings; two connected to the nitric acid source (two were used to provide uniformity of mixing inside the test inlet housing), another attached to a filter holder for sampling, and the last was a vent for excess nitric acid. The NO-NO_x analyzer sampled the vented air by attaching it to the line with a PFA Teflon tubing 'T'. The inlet line leading to the sample filter was placed as close to the CADMP cyclone assembly inlet as possible (within 1 cm) so that any losses of nitric acid in the test inlet housing would not bias the results. The laboratory space used for this evaluation has an independent thermostat, and could be heated to approximately 40°C and cooled to approximately 13°C.

A single Thermoenvironmental Model 42 NO-NO_x analyzer was used to determine nitric acid concentrations at the various sample points by sequentially inserting the inlet through the filter sampling ports. The instrument was calibrated and maintained in accordance with EPA PSD guidelines (U.S. EPA 1987). At a minimum, zero and span checks were made before and after each day of measurements. To zero the instrument, the humidified and purified air stream was sampled prior to the addition of nitric acid vapor. A Columbia Model 1800 calibrator was used to prepare a nominal concentration of 0.30 ppm NO by blending purified air with a certified gas standard of NO in nitrogen. The NO-NO_x analyzer was operated in the NO_x manual mode with an additional NO_x converter placed as close to the sample point as possible to minimize

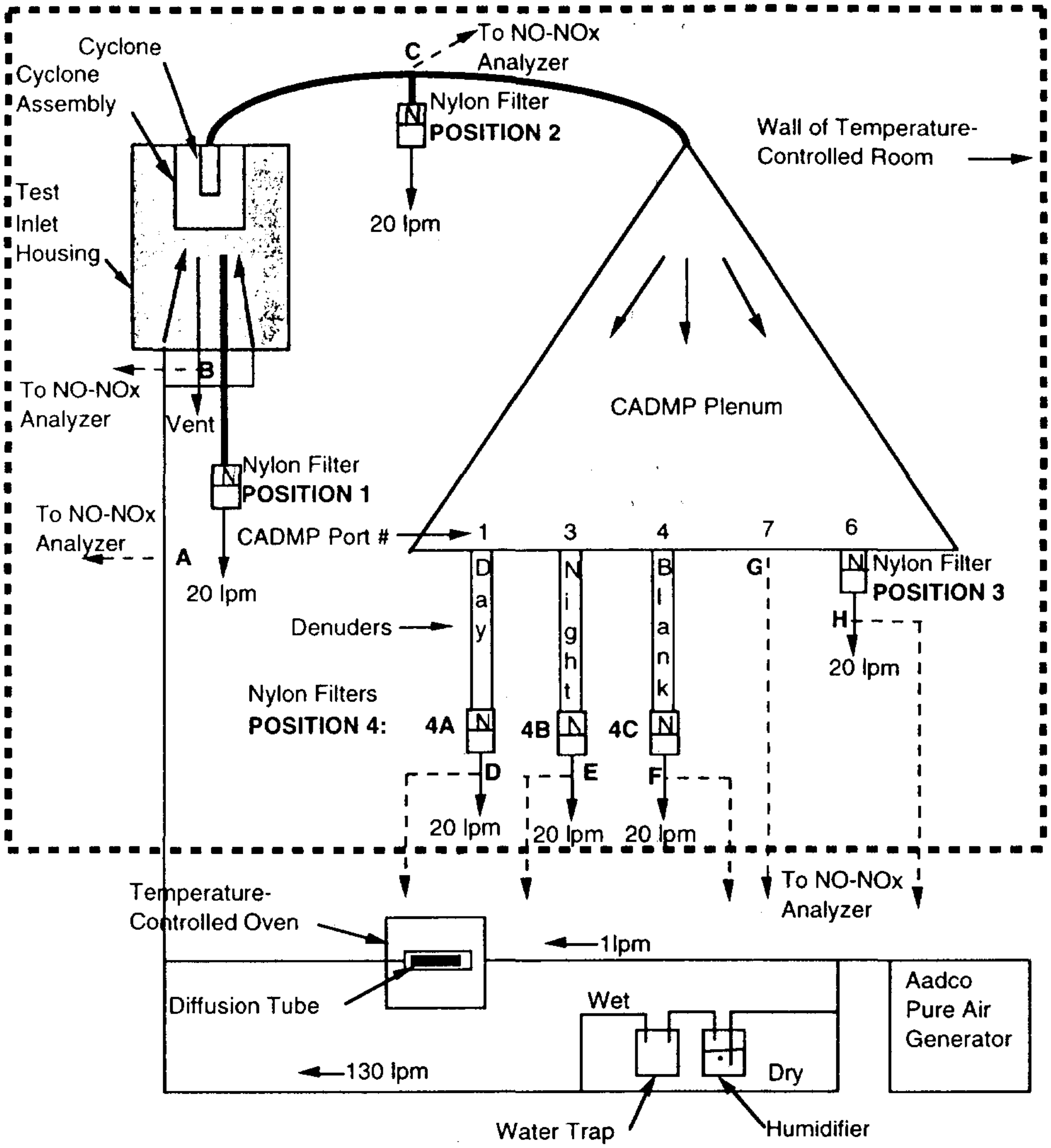


Figure 2-3 Schematic diagram for the laboratory evaluation of the CADMP Sampler

nitric acid losses through the sampling inlet. After passing through the converter, the nitric acid was converted to the much more stable nitric oxide.

Table 2-1 shows the experimental matrix proposed for evaluating the sampler. The concentrations, temperatures, and relative humidities were nominal in the table but quantified during the experiment. The concentrations of nitric acid were measured to the nearest 0.1 ppb with the NO-NO_x analyzer (the readout of the instrument was ppb). This was converted to µg/m^3 nitric acid by multiplying by 2.56. With the NO-NO_x analyzer it was possible to assess concentrations rapidly at different points of the sampler and to monitor the equilibration time required after making changes in concentration, temperature, and humidity. The NO-NO_x analyzer also provided data which could be used to compare with those of the filter collections and analyses.

Zero nitric acid concentration experiments were used to determine dynamic zero or blank levels. Over ten per cent of the experiments were replicated to evaluate overall precision. For the filter evaluation, approximately 50-100 µg of nitrate was collected. Sampling time was therefore adjusted to an interval between one and twelve hours depending on the concentration of nitric acid used. Filters were used in 'as received' condition from the MLD laboratory and were stored at CE-CERT in a refrigerator, both before and after sampling. After sampling they were immediately placed in extraction vials provided by the MLD laboratory and batches were shipped to the laboratory using an ice chest.

Table 2-1. Matrix of Penetration Experiments using Synthetically Generated Nitric Acid.

	50% RH			37°C
HNO_3 (µg/m^3)	13°C	20°C	37°C	10% RH
0	F	F	A,F	F
25	F	F	A,F	F
130	A,F	F	A,F	A,F

F= Filter Collection   A= NO-NO_x Analyzer

Based on the experimental results, the need for cleaning and reconditioning the denuder was evaluated.

2.3.1.2 Penetration of PAN

Peroxyacetyl nitrate (PAN) and other nitrogenous species may interfere with nitric acid measurements using the CADMP sampler's denuder difference technique, provided that they are adsorbed by the nylon filters <u>and</u> removed by the aluminum-based denuder. Previous studies have shown this does not occur to any significant degree with nylon filters (Joseph and Spicer, 1978), but we are unaware of any studies that evaluated aluminum-based denuders. Nylon filters have been reported to have variable chemical and physical properties between batches and manufacturers. Aluminum-based nitric acid denuders require an anodizing process that may not be consistent between plating shops. For these reasons, the properties of the filters and denuders actually used in the CADMP sampler were evaluated with respect to the penetration of PAN.

The laboratory study for PAN was similar to that described in the previous section for nitric acid. In this case PAN concentrations typical of ambient air were artificially generated and blended into the sample stream for evaluation of the entire sampler. The filter sampling approach was used to determine the amount of nitrite (or nitrate) retained on the filters.

PAN was prepared in the gas phase by photolyzing ethyl nitrite in a mixture of air followed by chromatographic purification and concentration (Stephens et al., 1965). Gas phase PAN was introduced into a 30 liter stainless steel cylinder and the pressure was increased to 50 psi with nitrogen. The amount and purity of the PAN was determined with a Fourier transform infrared spectrometer equipped with a 10 cm gas absorption cell. The pressurized PAN was then metered into the purified air stream with a needle valve to achieve the concentrations needed. PAN concentrations were measured at the sampling points in Figure 2-3 using a NO-NO_x analyzer.

PAN was generated at two nominal concentrations, 40 and 200 $\mu g/m^3$ (representing average and maximum ambient concentrations). Measurements were made at high and low humidity and high and low temperature. Table 2-2 summarizes the experimental matrix.

Table 2-2 Matrix of Penetration Experiments using synthetically generated PAN.

	10% RH		50% RH	
PAN ($\mu g/m^3$)	13°C	37°C	13°C	37°C
50	A,F	A,F	A,F	A,F
200	A,F		A,F	A,F

F= Filter Collection A=NO-NO_x Analyzer

2.3.2 Component Evaluation

2.3.2.1 Nitric Acid Collection Efficiency and Retention Measurements

The collection and retention of nitric acid in the cyclone inlet, in the nitric acid denuders, and on the nylon filters, were tested in the laboratory for both clean and used cyclones and denuders. Of interest is whether nitric acid is efficiently transmitted through the cyclone used to remove coarse particles, and whether nitric acid is efficiently trapped and retained by the denuders and nylon filters. Measurements were made under two conditions: at high temperatures with low relative humidity, and at room temperature with high relative humidity. For the denuders and nylon filters, experiments were conducted to determine whether nitric acid collected under high humidity conditions was retained when the denuders were exposed to warmer temperatures and low humidity.

The cyclone tested was a Bendix 240 cyclone and housing from the CADMP network site at Azusa. The sampler had been used at that site from the inception of the network in 1989 until it was refurbished and cleaned in October 1993. It was used again as the primary Azusa sampler from October 1993 until August 1995. The sampler was also used for the August - September 1995 sampling study at Claremont. The cyclone was contained in a 155 mm x 105 mm x 105 mm metal housing with a coarse screen inlet. All parts except the red plastic dust cup of the cyclone were PFA Teflon coated. A 50 cm length of 0.5 inch diameter PFA Teflon tube connected the cyclone outlet to the plenum. Testing was done for as-received condition (labeled 'dirty') and after cleaning (labeled 'clean'), as described in Table 2-3. Note that the 'dirty' cyclone contained a heavy particle loading in the cyclone body, exit tube, dust cup, and housing.

Table 2-3. Designations of CADMP Sampler Components Tested

Dirty Cyclone	*Dirty cyclone* testing was done on the CADMP cyclone in 'as-received' condition. It had been used for approximately 2 years on the primary sampler at the Azusa site since cleaning in October 1993, and contained a heavy loading of particles within the cyclone body, exit tube, dust cup, and housing.
Cleaned Cyclone	*Clean cyclone* testing was done on the same cyclone described above after it had been cleaned. The cleaning was done by washing in water in an ultrasonic bath for thirty minutes, and rinsing with distilled water and isopropanol. No visible particle deposits remained. It was not conditioned by rinsing in acid.
Denuder #1	*Denuder #1* was taken from port 1 of the primary CADMP sampler at Azusa, and had been used for daytime sampling for approximately 2 years since it was refurbished in October 1993.
Denuder #3	*Denuder #3* was taken from port 3 of the primary CADMP sampler at Azusa, and had been used for nighttime sampling at the Azusa, CA site for approximately 2 years since it was refurbished in October 1993.
Denuder #4	*Denuder #4* was taken from port 4 of the primary CADMP sampler at Azusa, and had been used for blanks only since it was refurbished in October 1993. Ambient air was not pulled through this denuder.
Nylon Filters	*Nylon filters* were Gelman Sciences (Ann Arbor, MI) 1 µm pore size Nylasorb, prepared by the ARB labs by soaking in a 0.16% sodium carbonate solution for 4 hours, rinsing in nanopure water, then soaking again overnight in nanopure water, and dried in a preheated 45°C vacuum oven.

The denuders tested were anodized aluminum annular denuders from the nitric acid channels of the CADMP. They were approximately 360 mm in length, with an inner diameter of 46.6 mm and an annular gap of 1.1 mm. The denuders are blunt at the inlet with a tapered 30° cone at the base to homogenize the particle concentration across the filter placed at the denuder exit. Three denuders were tested, all from the primary CADMP sampler at the Azusa site. Denuder #1 had been used for daytime sampling, Denuder #3 for nighttime sampling, and Denuder #4 for collecting field blanks (this denuder had never had ambient air pulled through it). Denuder designations are summarized in Table 2-3.

All nylon filters tested and used for these experiments were Gelman Sciences Nylasorb, 1 μm pore size, provided by Charles P. Cowell of the California Air Resources Board Monitoring and Laboratory Division. The ARB laboratories had prepared these filters following standard CADMP operating procedures (Bowen et al., 1990), which included washing in sodium carbonate and water. The sequence of experiments for the cyclone testing is summarized in Table 2-4. First, the dirty cyclone was tested under hot, dry conditions (T=30-40°C; RH=30-40%), then under room temperature damp conditions (T=20-22°C; RH=60-99%). The cyclone was cleaned and the testing repeated. For the clean cyclone, testing was also done after exposing the cyclone to 30 ppb of ammonia.

Table 2-4. Test Sequence for the Cyclone Nitric Acid Penetration Experiments (nitric acid concentrations varied from 11-153 μg/m3).

Sequence (Run No.)	No. of Runs	Cyclone	Experimental Condition
1 - 3	3	Dirty cyclone	Hot and dry
4 - 6	3	Dirty cyclone	Room temp and wet
8 - 9	2	Clean cyclone	Hot and dry
10-12	3	Clean cyclone	Room temp and wet
13-14	2	Clean cyclone	After NH_3 conditioning†

† Exposed to 30 ppb of NH_3 for 2 hours at room temperature prior to measurement.

The denuders and filters were tested separately from the cyclones. All three denuders and a nylon filter were tested in each experiment. Collection efficiencies were determined by measuring the nitric acid concentrations before and after the nitric acid-laden air passed through the denuder or filter. As outlined in Table 2-5, efficiencies were measured for nitric acid concentrations of 20 to 40 μg/m^3. Additionally, retention efficiencies were determined by measuring nitric acid downstream of the denuders when sampling hot, dry air with no addition of nitric acid; measured nitric acid concentrations for these exposure experiments was 0 to 4 μg/m^3. The initial experimental plan called for only two sets of retention measurements, but based on chromatographic effects observed in whole sampler testing, exposure testing was added after each collection efficiency measurement.

Table 2-5. Test Sequence for the Denuder and Filter Nitric Acid Collection and Retention Efficiency Measurements

Sequence (Run No.)	Experimental Condition†,T,RH	HNO_3	Type of Measurement
15	Hot and dry	high	Collection efficiency
16	Hot and dry	~0	Retention
19	Hot and dry	high	Collection efficiency
20	Hot and dry	~0	Retention
21	Humid	high	Collection efficiency
22	Hot and dry	~0	Retention
23	Humid	high	Collection efficiency
24	Hot and dry	~0	Retention
25	Hot and dry	~0	Retention

†Hot and dry was typically 30-40°C and 30%-40% RH
Humid was 60-99% RH at room temperature
High [HNO_3] was 20-40 μg/m^3, ~0 [HNO_3] was <4 μg/m^3

The experimental configuration used for the cyclone nitric acid penetration is shown in Figure 2-4, and that for testing nitric acid collection and retention efficiencies of the denuders and nylon filters is shown in Figure 2-5. For both configurations nitric acid was generated using 7 cm, Teflon-walled, high emission rate permeation tubes containing 68% HNO_3 (VICI Metronics, Santa Clara, CA), with a quoted emission rate at 90°C of 5 ± 0.7 μg/min. The permeation tube was housed in a glass U-tube through which clean, dry air flows at 9 ± 1 ℓpm. The clean air source was compressed laboratory air which was passed through silica gel to remove water, an oxidizing bed (Purafil) and activated charcoal to remove hydrocarbons, an oxalic acid impregnated filter to remove ammonia, and a filter to remove particles. The 9 ℓpm flow exiting the nitric acid permeation cell was mixed with approximately 110 ℓpm of filtered make-up air which was humidified as needed. For the low relative humidity experiments, the make-up air was room air passed through five parallel 47 mm glass fiber filters impregnated with oxalic acid to remove ammonia, and then through a high efficiency particulate filter to remove particles.

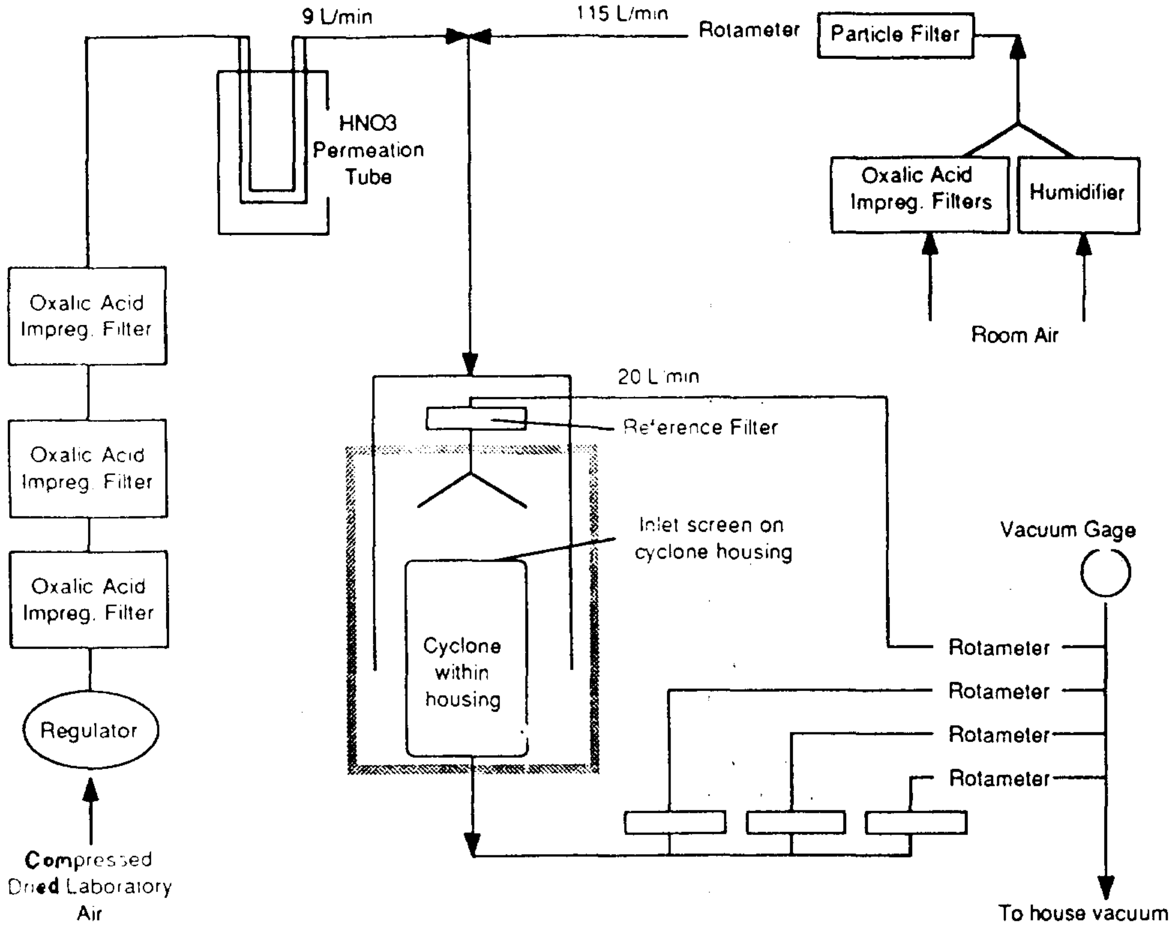


Figure 2-4 Experimental configuration for testing nitric acid penetration through cyclones

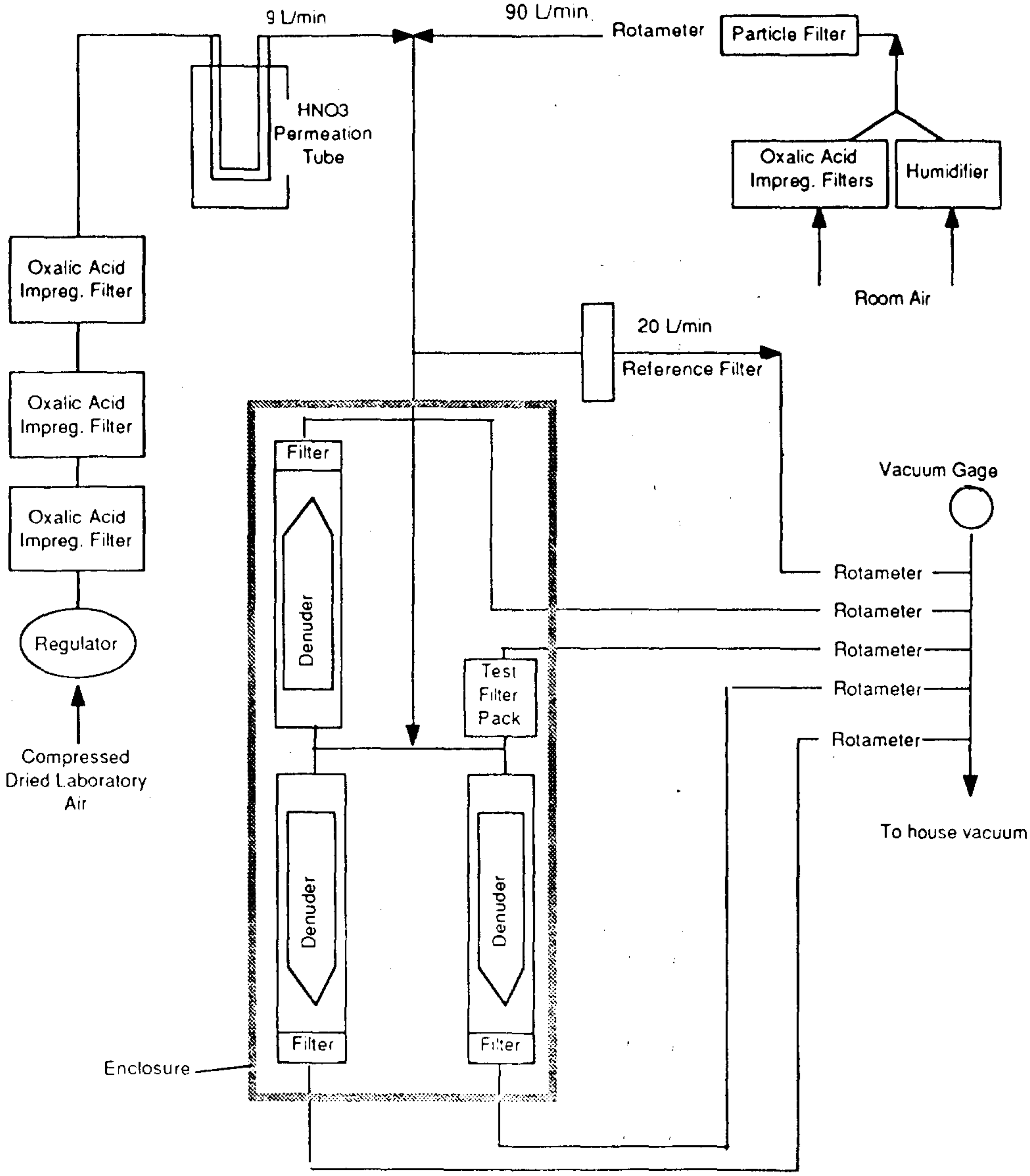


Figure 2-5 Experimental configuration for testing nitric acid penetration through denuders and filters

For the high relative humidity experiments, room air was bubbled through a 3.5 ℓ container of oxalic acid dissolved in water and then through a filter to remove particles. In both cases the make-up air flow was metered by a rotameter.

Once the nitric acid was introduced into the airflow, the flow was split between a reference filter and the test components. Penetration of nitric acid through the test components was assessed by comparing the collection of nitrate on filters placed downstream of the test component with that on the reference filter. Temperature and relative humidity were monitored using a Vaisalla Humitter (Woburn, MA). Individual flows on each line were monitored downstream of the collection filters using rotameters noting their operating pressure. The rotameters were individually calibrated at their operating pressures, which were 9" Hg vacuum for the cyclone experiments and 5" Hg vacuum for the denuder experiments, using a Gilmont rotameter operated at atmospheric pressure.

For the cyclone testing a Teflon-coated aluminum plenum was used to enclose the cyclone and its housing (Figure 2-4). Nitric acid was measured downstream of the cyclone using three 47 mm nylon filters in parallel, each sampling at approximately 35 ℓpm. Filters were mounted in all-Teflon filter holders and connected at the end of the 50 cm length of Teflon tubing provided with the cyclone. The reference value was provided by a fourth nylon filter which sampled directly from the Teflon-coated plenum. All plumbing connections were Teflon. The relative humidity and temperature probe was mounted immediately outside the plenum in a 1/4" diameter line aspirated at 5 ℓpm. A nylon filter, at the head of the probe was used to protect it from corrosion by the nitric acid.

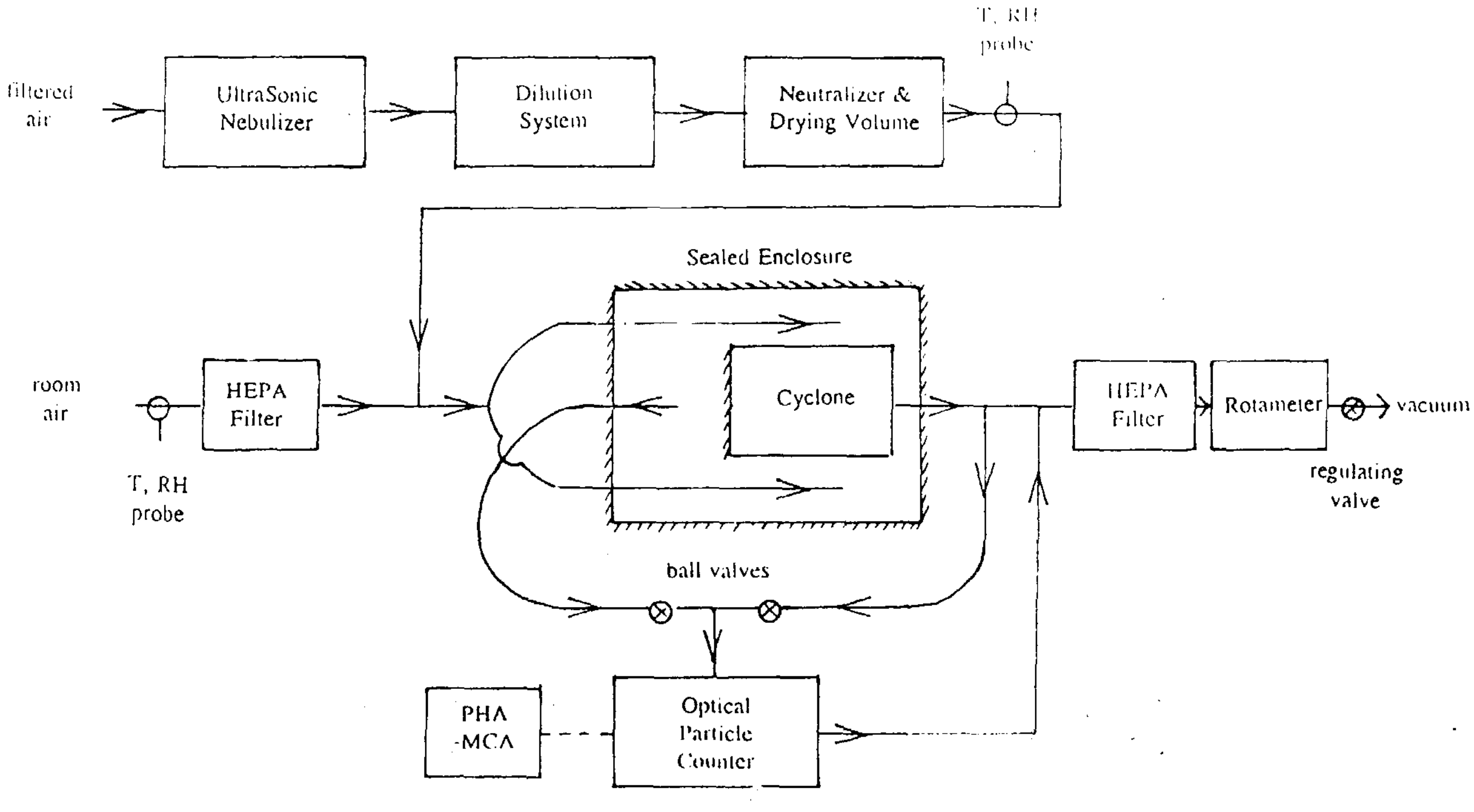
The same nitric acid generation and make-up air dilution and humidification system was used for the denuder and filter testing as for the cyclone testing, but the flow splitting system was somewhat different, as shown in Figure 2-5. Instead of using a plenum chamber, all sampling was done from the main 1/2" Teflon lines. Soon after the nitric acid was mixed with the dilution air, a reference filter was used to sample the nitric acid concentration in the main Teflon line which then lead to a thermally insulated box containing the three denuders and the test nylon filter pack. These sampled simultaneously from the Teflon line with symmetric flow splits. A single nylon backup filter was operated downstream of each denuder, and the test nylon filter pack consisted of two nylon filters in series. Flows were monitored downstream by rotameters specifically calibrated for the operating pressure in this experiment. For collection efficiency measurements, nitric acid penetration was measured on filters behind each denuder and on the backup filter in the test nylon filter pack. Results were compared to the reference filter. For retention experiments, all backup filters and the reference filter were changed, and the amount of nitric acid collected on these substrates was measured for exposure to clean air. Each set of collection efficiency and retention experiments generated 11 nylon filters, 2 reference filters, 8 backup filters, and 1 front nylon test filter.

As a quality control check, the measured inlet flow was compared to the sum of the atmospheric-pressure adjusted flow through the reference and test legs for each experiment. Experiments which did not agree within 10% were discarded. For the denuder-filter testing system, the sum of the two reference nitric acid filters from the sequential collection efficiency and retention experiments was compared to the sum of the three filters (one front and two backup) from the test nylon filter pack.

2.3.2.2 Particle Collection Characteristics of $PM_{2.5}$ Cyclone

The Bendix 240 cyclone used in the CADMP sampler is used as a size-selective inlet for many specialized samplers, including the SCAQS sampler (Fitz and Zwicker, 1988), the Western Regional Air Quality Sampler (Tombach et al., 1987) and the Size Classifying Isokinetic Sequential Air Sampler (SCISAS) (Rogers et al., 1989). For the CADMP sampler, the cyclone is operated ungreased, but for some networks the inside of the cyclone body is greased to prevent particle bounce and re-entrainment. In the experiments described here, the cyclone collection efficiency for large, dry bouncy particles was measured to determine the degree of large particle penetration by bounce or re-entrainment. Particle-size dependent collection of solid particles was measured in the laboratory for clean and greased cyclones. Results were compared to assess whether grease, which reduces particle bounce, improved the collection of large, solid particles.

Aerosol penetration as a function of particle size was measured for a clean cyclone and a greased cyclone using the experimental setup shown in Figure 2-6. Aerosol was generated from a saturated solution of ammonium sulfate using a DeVilbiss Ultra-Neb 99 ultrasonic nebulizer. It was diluted with clean dry air to a relative humidity of less than 10% to ensure complete drying and crystallization of the particles which were then passed through a radioactive charge neutralizer. Additional filtered room air at 45% RH was then added to give the total cyclone flow rate of 4 ft^3/min. The clean and greased cyclone measurements were made on the same cyclone using a Climet Model CI-208 optical particle counter (OPC) with detector pulses accumulated by a Nucleus PCA-1000 pulse height analysis card installed in an IBM PC-compatible computer. Each measurement set consisted of OPC particle size distributions measured upstream and downstream of the cyclone.



Cyclone flow: 4 cfm

OPC flow: ~6 L/min

OPC inlet pressures: ~14 in H_20 below atmospheric (matched for up and downstream sampling)

RH at aerosol generator exit: <10%

Room RH: ~45%

Figure 2-6 Experimental configuration for testing particle collection characteristics of cyclones

One-minute upstream measurements were alternated with one-minute downstream measurements for accumulated total sampling times of 15 minutes each. This was done to reduce the effects of varying aerosol concentrations. The OPC sample flow rate of 5.8 ℓpm was the same for all measurements (upstream/downstream) within a measurement set.

The approximate aerodynamic particle diameter was derived from the MCA channel number in the following manner. Channel number was converted to pulse peak height in volts using the nominal MCA calibration. This in turn was converted to PSL (polystyrene latex) equivalent light scattering diameter using the Climet factory calibration curve. The index of refraction of PSL is 1.59 and that of ammonium sulfate is 1.53. Approximate modeling of Mie scattering in the Climet indicates that the equivalent light scattering diameter for ammonium sulfate is within 6% of that for PSL for particles within the size range of interest here. This difference was therefore neglected so that the physical diameter of the ammonium sulfate particle was assumed to be equal to the PSL equivalent light scattering diameter derived earlier. Physical diameter D_p was converted to aerodynamic diameter D_a via the formula

$$C_s(D_a)\cdot D_a^2 = C_s(D_p)\cdot r_p D_p^2 \qquad (1)$$

where C_s is the Cunningham slip correction factor and $r_p=1.769$ is the density of ammonium sulfate.

Each accumulated MCA number distribution was divided by the corresponding total live sample time to obtain a count rate frequency distribution, N. (PHA-MCA dead times were less than 2% of real time.) Cyclone penetration, P, as a function of MCA channel number was calculated as:

$$P = N_d/N_u \qquad (2)$$

where the subscripts u and d are for upstream and downstream, respectively. Owing to the small number of counts per channel for the larger particles and the resulting Poisson statistical fluctuations, the N vs. channel number curves were first smoothed using a modified LOWESS routine with a smoothing window width of 25 channels. These smoothed N values were then used to calculate P.

3.0 SAMPLER EVALUATION AND DISCUSSION

3.1 System and Performance Audit

A performance and systems audit of both the Azusa primary and collocated CADMP samplers was conducted on August 16, 1994. Appendix B contains the complete audit report. The primary sampler was last cleaned and calibrated in October, 1993 while the collocated sampler was cleaned in late 1992 and installed at Azusa in the summer of 1993. The operator was not aware of the recommended cleaning or maintenance schedule (Bowen et al., 1990), although flow rates were checked monthly with a rotameter as a quality control check. There was no indication that the recommended maintenance was being performed; a lack of maintenance has the potential to compromise the data in an unquantifiable manner.

The Azusa monitoring site had potential sources of contamination from both the water heater vent on the roof and from the light industrial operations in the surrounding area. The sample flow rates determined by the auditor for both CADMP samplers compared to within a few percent of that provided by the sampler operator. The bug screens of the cyclone assembly were noticeably dirty as were the 1/2" Teflon sample lines connecting the cyclone to the CADMP plenum. These conditions could lead to nitric acid loss. Samples were not removed immediately after the collection period, but sometimes remained in the sampler for several days. Sample substrates were shipped to the ARB MLD laboratory without packing in a refrigerant which would have minimized exposure to high temperatures. Both of these practices could also result in nitric acid losses or additional passive adsorption.

3.2 Field Evaluations

3.2.1 Azusa Filtered Air

Objective and Approach

The objective of this study was to measure the penetration of nitric acid through various components of the CADMP using filtered ambient air as a source of nitric acid vapor as described in Section 2. Ambient collections were conducted, during daytime (6 am - 6 pm PST) and nighttime (6 pm - 6 am PST) schedules, on days of predicted moderate air pollution (forecast of 0.10 ppm ozone or higher) from September to November, 1994. The collocated Azusa sampler was used in 'as found' condition. Figure 3-1 presents the schematic diagram for this sampling.

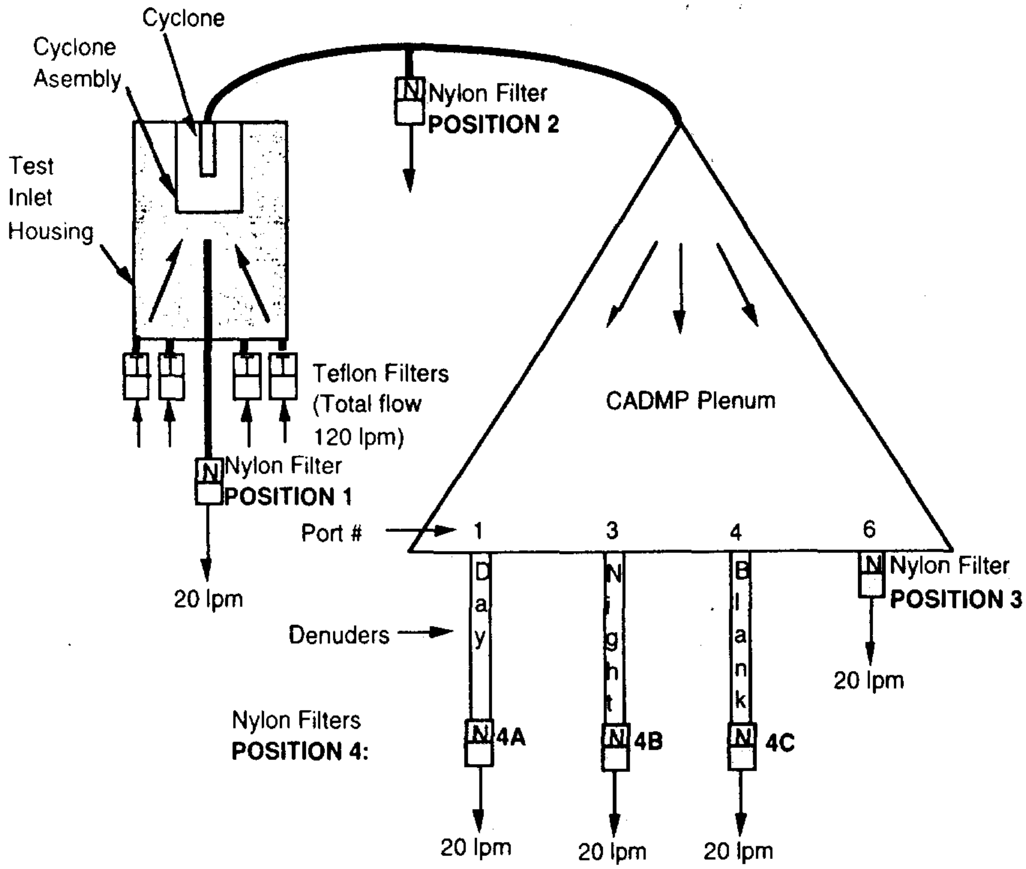


Figure 3-1 Schematic diagram for the field evaluation of the CADMP Sampler

Measurement Uncertainty

A set of six field blanks were collected, one for each sample channel (positions 1-3 and 4A-4C). The three blank samples below the denuders (positions 4A-4C) showed similar nitrate concentrations, with a mean of 1.3 μg/filter (equivalent to 0.09 μg/m^3). The three other samples also showed similar nitrate concentrations but averaged 6.3 μg/filter (equivalent to 0.43 μg/m^3). It is likely that the denuders prevented the exposure of nitric acid to the nylon filters, and therefore these concentrations were significantly lower than those without a denuder in place. These blank values are low relative to nitric acid concentrations in the daytime even during periods of low photochemical air pollution. For nighttime samples however, the blank levels, and more importantly the blank variability, are likely to cause significant measurement error since the nitric acid concentrations are typically 1 μg/m^3.

Since the six measurements of nitrate blanks depended on whether or not the filter was preceded by a denuder, two different sets of three measurements each were available to estimate variability; this was not considered sufficient. However, the blank concentrations can be compared with those obtained from the routine network, for which a good deal of data are available. In doing so, it must be noted that the sample' handling conditions were quite different. During the routine sampling, loaded filter cassettes are sent to the field days before being used, allowed to stay in the sampler for up to several days, and shipped back to the laboratory without refrigeration. In contrast, our filters were loaded immediately before sampling, recovered within a few hours of the end of the sampling interval, immediately placed in extraction vials, and returned to the laboratory in chilled ice chests. In addition, a Teflon filter was not used in front of the nylon filter used to collect samples without a denuder. Blank variability for the network operation is therefore expected to be an upper limit for our samples. The mean field blank (blanks were collected monthly) from the network sampling at Azusa between May and December was 7.2 ± 3.2 μg for the filters without a denuder and 4.5 ± 3.2 μg for the filters placed below the denuder. The estimated uncertainty of the nitrate measurements due to blank variability was therefore estimated to be 0.2 μg/m^3.

The two main sources of analytical error for the nitrate concentration measurements were due to uncertainties in the flow rate and extract analysis. We estimated the precision of the flow rate determination to be approximately 5% based on our ability to read the dial of the vacuum gauge used to calculate flow rate and the results of the performance audit. The precision of the laboratory analysis based on duplicate determination was reported to be 3% for duplicate analyses, with a control limit of 10%. Thus the combined precision of the measurement was estimated to be 6% (the square root of the sum of the squares of the precision). Allowing for additional measurement variability such as that in filter extraction and handling, the precision of the measurement was estimated to be 8% when blank variability was not accounted for (this uncertainty is not a percentage and cannot be factored in to the precision determination above). The overall measurement uncertainty was therefore 8% plus the blank variability.

Results

Table 3-1 summarizes the results of the nine sample collections conducted. These values were all blank subtracted using one of the two values discussed above, as appropriate.

Table 3-1 Summary of Nitrate on Nylon Filters Sampling Filtered Air at Azusa (blank corrected)

Date - day or night	**Test Inlet Housing (Position 1)**	**Cyclone Assembly (Position 2)**		**CADMP Plenum (Position 3)**		**Day Denuder (Position 4A)**		**Night Denuder (Position 4B)**		**Blank Denuder (Position 4C)**	
	µg/m³	µg/m³	Ratio to Inlet	µg/m³	Ratio to Cyclone	µg/m³	Ratio to Plenum	µg/m³	Ratio to Plenum	µg/m³	Ratio to Plenum
9/20/94-night	1.00	0.80	0.80	2.16	2.70	1.18	0.55	1.23	0.57	0.58	0.27
9/21/94-night	1.90	1.10	0.58	1.22	1.11	0.79	0.65	0.87	0.71	1.08	0.89
9/23/94-day	10.55	7.56	0.72	9.53	1.26	0.71	0.07	0.95	0.10	0.97	0.10
9/26/94-day	12.78	10.27	0.80	9.60	0.93	0.92	0.10	1.28	0.13	1.22	0.13
9/27/94-day	19.72	19.69	1.00	17.72	0.90	1.03	0.06	1.12	0.06	1.13	0.06
9/28/94-day	19.31	17.05	0.88	15.83	0.93	0.94	0.06	1.12	0.07	1.24	0.08
9/29/94-day	12.41	10.57	0.85	11.94	1.13	1.08	0.09	1.16	0.10	1.23	0.10
10/29/94-day	12.51	7.17	0.57	5.64	0.79	0.96	0.17	1.05	0.19	1.02	0.18
11/1/94-day	10.16	10.15	1.00	9.38	0.92	0.94	0.10	0.90	0.10	0.83	0.09
Means - day	**13.92**	**11.78**	**0.83**	**11.38**	**0.98**	**0.94**	**0.09**	**1.08**	**0.11**	**1.09**	**0.11**
Std. Dev. - day			0.15		0.16		0.04		0.04		0.04
Means - day w/o 9/23/94			0.85		0.93						
Std. Dev.			0.16		0.11						
Means - night	1.45	0.95	0.69	1.69	1.90	0.99	0.60	1.05	0.64	0.83	0.58

Ratios for positions (2)/(1), (3)/(2) and (4)/(3) were also calculated. For the daytime samples, the standard deviation for the mean ratio is also included (with only two nighttime samples, the calculation of standard deviation would not be meaningful). The uncertainty of the mean concentration of the daytime samples collected without a denuder (well above the blank variability) was expected to be approximately that of the estimated uncertainty of the measurement, 8%. The standard error of the mean ranged from 10.7 to 15.2% for these means. Another approximation of the uncertainty was from the square root of the mean square residual obtained from regression of data from position 1 vs. 2 and position 2 vs. 3. This approach factors out variability inherent with the parameter being measured. The first regression resulted in an uncertainty of 13% and the second of 14%. The measurement uncertainty therefore could range between 8 and 15%, so it was felt that 10% would be a reasonable value to use when analyzing the data.

Nighttime concentrations of nitrate before the denuder were much lower than daytime. The concentrations measured at position 2 were higher than position 3. This may be due in part to experimental uncertainty since the blank variability (from the routine sampling program blanks collected without a denuder) was from 8 to 36% of the values measured in this study. Another possibility was desorption of nitric acid from the plenum of the CADMP sampler, which will be discussed in the laboratory evaluation. Given the low values of nitric acid and the uncertainty of the nighttime concentrations, further nighttime sampling to evaluate the penetration of nitric acid through the CADMP sampler was not considered useful. The values obtained do, however, allow an estimate of the upper limit for the uncertainty of the nitric acid measurements obtained from the routine sampling.

The nighttime nitrate below the denuder was approximately the same as that of the daytime samples. This was not expected since the nitric acid concentrations in the plenum were much lower at night (resulting in a lower denuder efficiency). The filters below the denuder appear to collect a constant amount of nitrate whether the nitric acid concentrations are high or low which may be due, as mentioned previously, to desorption of nitric acid from the denuders. Another possibility is adsorption or partial adsorption by the nylon filters of a nitrogenous species which is not effectively removed by the denuders. Potential candidates include nitrous acid and PAN; the PAN adsorption characteristics were evaluated in the laboratory and found not to be significant (see section 3.1.1.3).

The denuders were generally all functioning at 90% efficiency in the daytime when nitric acid concentrations were significant. This is similar to the report for the sampler used in the

Southern California Air Quality Study (SCAQS) (Fitz and Zwicker, 1988) and typical of base-coated annular denuders. It has been our experience that denuder efficiency measured using ambient filtered air is always less than that obtained with synthetically generated nitric acid and is most likely due to other nitrogenous species. The denuders, even though subject to more than a year of every sixth day sampling, appeared to be functioning adequately to measure nitric acid by the denuder difference approach at mean concentrations up to 20 $\mu g/m^3$.

An average of 83% of the nitric acid penetrated the cyclone assembly with a standard deviation of 15 per cent. However, it is significant that all seven nitric acid measurements at the cyclone outlet were lower than at the inlet (position 2 compared to position 1). The Wilcoxan Ranked Sum Test was applied to analyze this statistically. The non-parametric statistical test, described in more detail in Appendix C, is particularly useful for small data sets and does not assume a normal distribution. The test determines at a given confidence level whether or not two data sets are equivalent. This is done by finding the difference and the absolute difference between each pair of data points. The absolute values of the differences are then ranked from smallest to largest, starting at one. The ranks of the positive and negative differences (R^+ and R^-) are then added separately and compared with a critical value (T_C). If one of the ranked sums is smaller than the critical value, the two data sets are not equivalent. When all seven differences are positive, the R^+ value is 28 and R^- is 0. For seven pairs of data, T_C is 4 at the 95% confidence level. Thus it is concluded that statistically significant losses occurred in the cyclone assembly.

The variability of the mean ratio of position 2 to position 1 was greater than the expected measurement precision [18% (0.15/0.83 x 100) compared to the 10% estimated], primarily due to two sample days, September 23 and October 29, which differed from the mean by nearly one and two standard deviations, respectively. These outliers are shown in Figure 3-2, which is a plot of the nitric acid measured at the cyclone assembly outlet (position 2 in Figure 3-1) versus that at the test inlet housing (position 1). This plot appears to show a linear relationship, which is supported by the square of the linear regression coefficient, r^2, which is 0.86. While excluding the data from September 23 and October 29 would increase the r^2 to 0.93, this cannot be done arbitrarily. The higher nitric acid losses in the cyclone assembly on these two days could be due to environmental conditions, such as temperature and relative humidity which promote the adsorption of nitric acid. While the laboratory evaluations, to be discussed later, give some support to this hypothesis, it does not explain why on September 23 there was a gain in nitrate from the cyclone assembly to the CADMP plenum. As it is unlikely that environmental conditions would work in opposite directions, it is more likely that the nitrate after the cyclone assembly was low due to a measurement anomaly. Excluding this day results

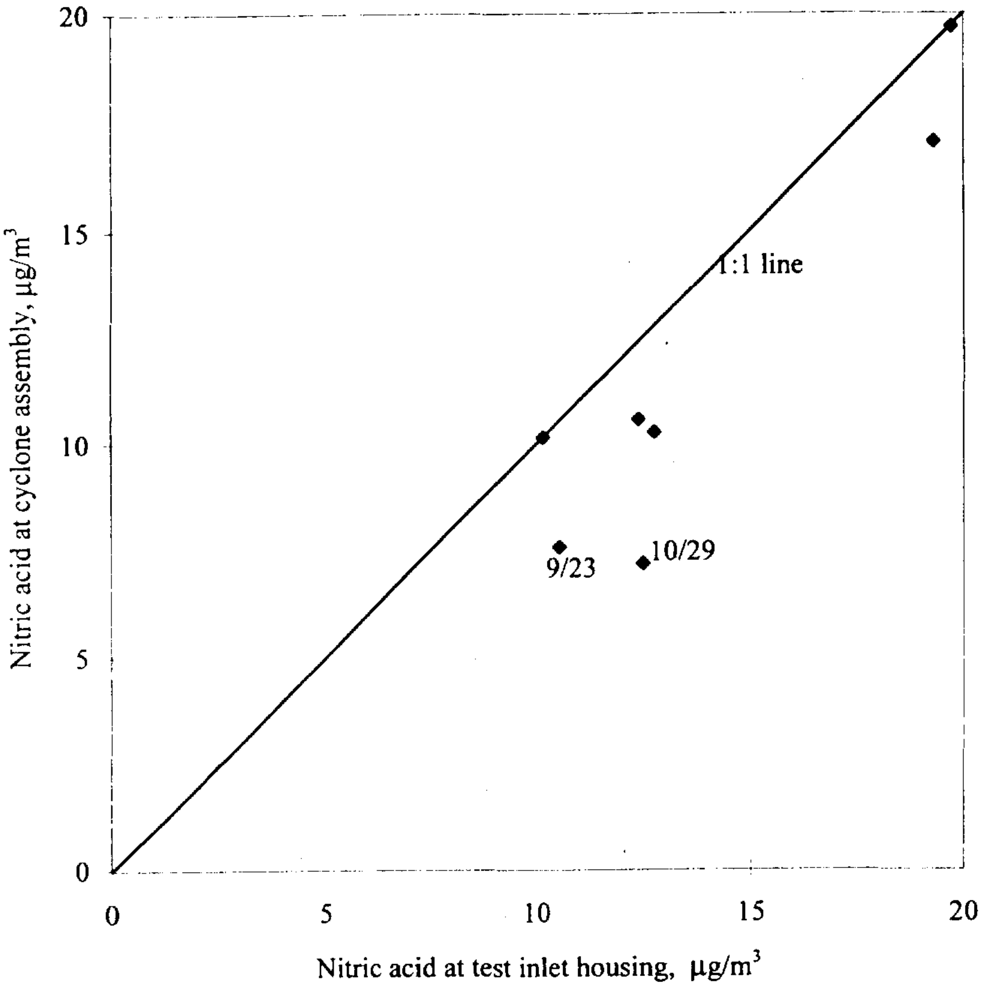


Figure 3-2. Azusa filtered air ambient nitric acid measurements: cyclone assembly vs. test inlet housing (position 2 vs. position 1)

in a mean penetration of 85%, and given the experimental uncertainty, it is concluded that losses through the cyclone averaged 15% with an uncertainty of ± 10%.

The mean daytime ratio of nitric acid measured after the CADMP plenum (position 3) to that before the plenum (position 2) was 0.98 with a standard deviation of 0.16. This indicated virtually no losses through the CADMP sampling plenum. Figure 3-3 is a plot of the nitric acid measured before and after the plenum. These data points again appear to be linearly related, with an r^2 of 0.91. September 23 and October 29 were again outliers, with September 23 over a standard deviation unit higher than the mean and October 29 over a standard deviation lower. It can again be justified to remove the data from September 23 since the nitric acid at position 2 appeared be anomalous as discussed previously. This resulted in an r^2 of 0.94 and a mean ratio of 0.93 with a standard deviation of 0.11. Application of the Wilcoxan test to this set of six pairs resulted in an R^+ of 17 and an R^- of 4. Since the critical value is 2, the test result was that the data sets are equivalent. It was concluded that no losses of nitric acid were observed through the plenum within the experimental uncertainty of ± 10%.

By looking at Figure 3-4, which compares the nitric acid measurements at the outlet of the CADMP plenum (position 3) to the test inlet housing (position 1), the total losses of nitric acid through both the cyclone assembly and the CADMP plenum can be evaluated. There was again a linear relationship ($r^2 = 0.81$). The data from October 29 is also an outlier, but the data point from September 23 is no longer one. Since position 2 data was not included in this plot (positions 1 and 3 are compared directly), this was the expected result if that data point for September 23 for position 2 was anomalous. All values at the CADMP plenum outlet were less than at the test inlet housing so the data sets were not equivalent, and there is no justification in excluding the outlier from October 29. The mean ratio of nitric acid concentrations of the CADMP plenum to test inlet housing was 0.81 with a standard deviation of 0.18, which indicated that approximately 19% of the nitric acid was lost through the sampler. This is supported quite well by the slope of the regression line, 0.87,

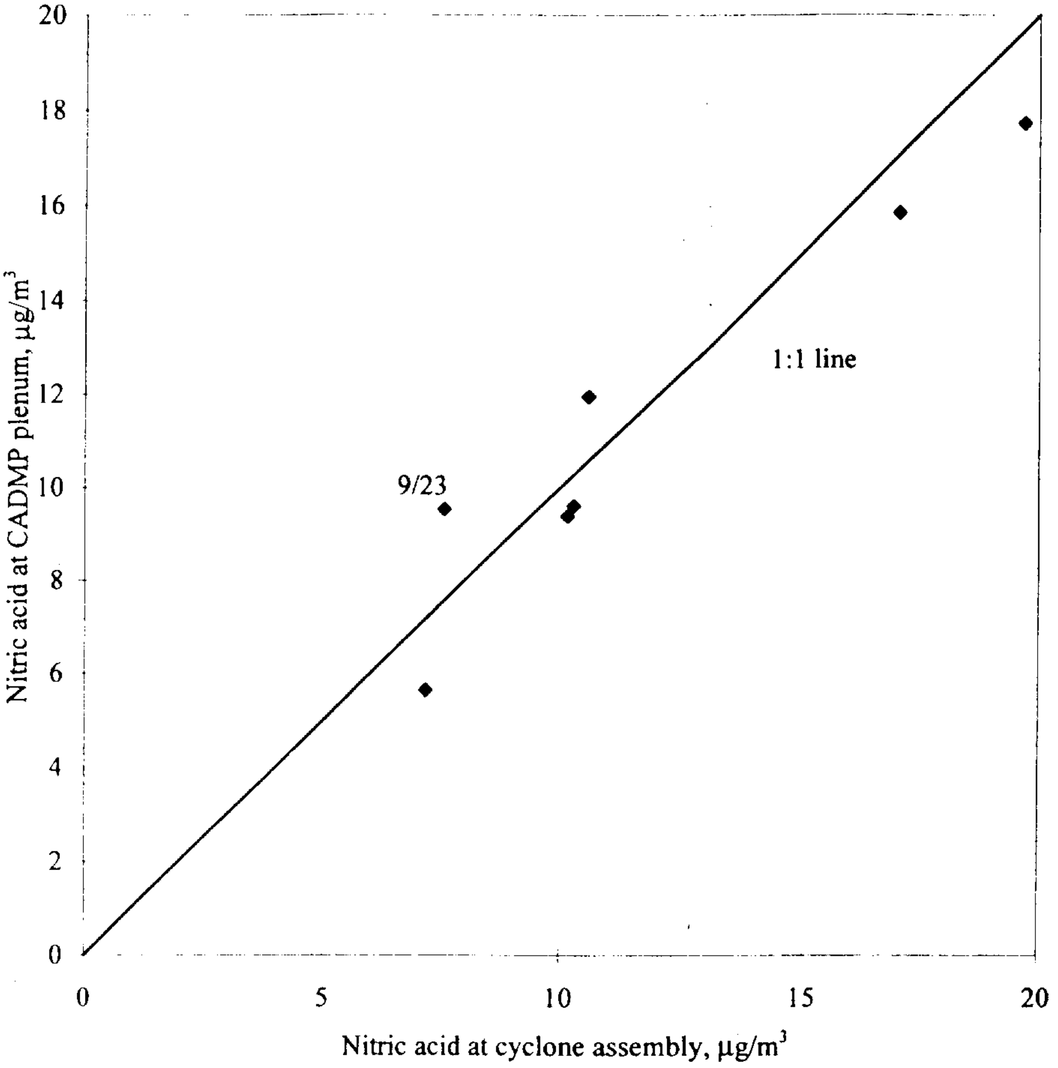


Figure 3-3. Azusa filtered air ambient nitric acid measurements: CADMP plenum vs. cyclone assembly (position 3 vs. position 2)

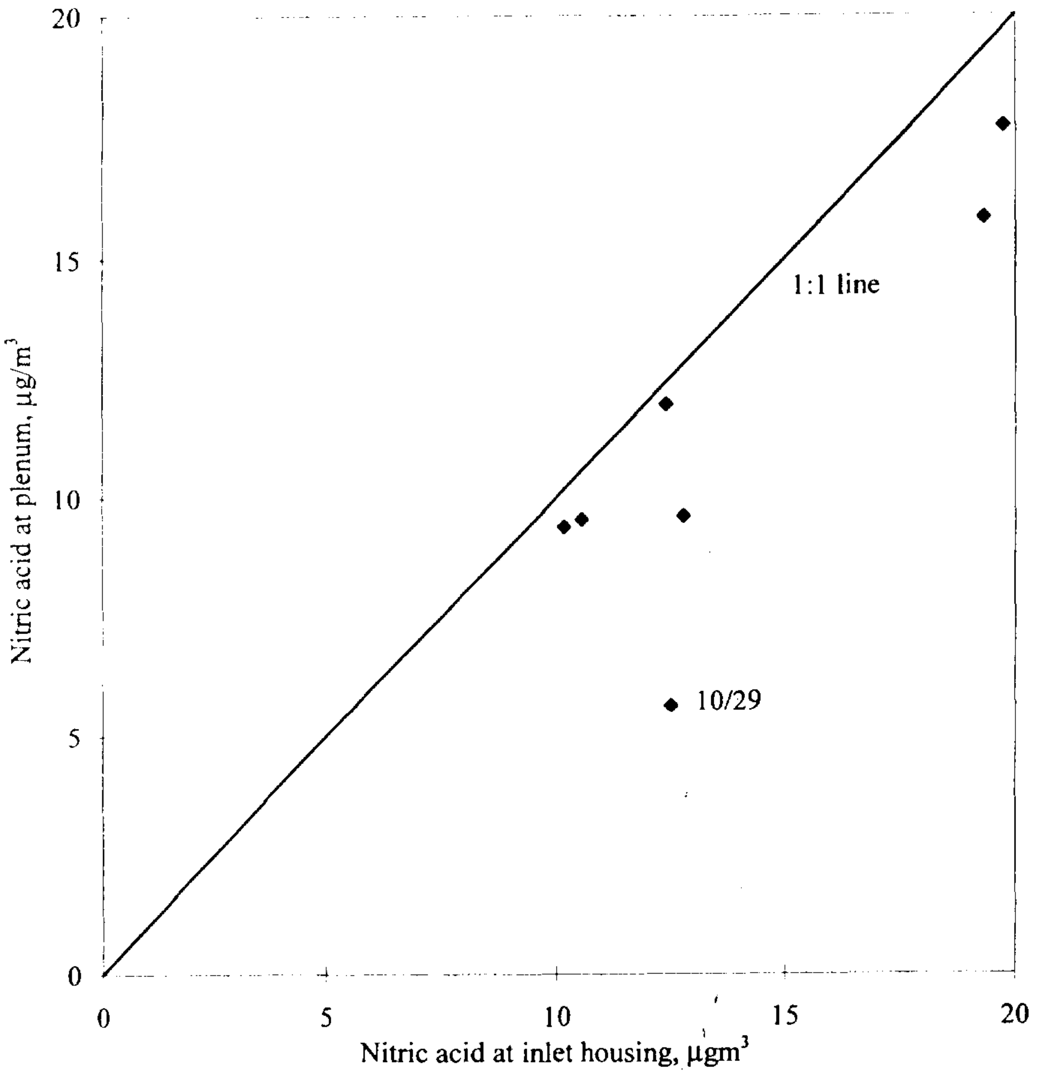


Figure 3-4. Azusa filtered air ambient nitric acid measurements: CADMP plenum vs. test inlet housing (position 3 vs. position 1)

Conclusions

Using filtered ambient air as a source of nitric acid and the samples collected at the Azusa CADMP site with the collocated sampler it was found that the mean loss of nitric acid in the daytime was 15%. The denuders were removing an average of 90% of the nitric acid. The low concentrations of nitric acid at night precluded meaningful measurements of nitric acid loss and denuder efficiency. The nitric acid penetration was similar to that obtained by the Desert Research Institute when they evaluated a new and cleaned sampler. This indicates that cleaning the interior surfaces may not be necessary to achieve high throughput of nitric acid.

3.2.2 Riverside and Claremont Nylon Filter Pack Experiments

Objective and Approach

The objective of this study was to determine the efficiency of nylon filters (Gelman Nylasorb) in collecting nitrogenous species. The approach was to sample ambient air with a pair of nylon filters in series behind a Teflon front filter (Gelman Zefluor, 2 µm pore) in order to determine the amount of nitrate, if any, collected by the second filter. The origin of this nitrate may either be due to the partial penetration of nitric acid or some other nitrogenous species, followed by collection and retention on the back filter. Daily nylon filter packs were collected using ambient filtered air as a part of this and another component of an ARB-sponsored project to evaluate the Two-Week Sampler (Fitz and Hering, 1996). Filter samples were collected at a nominal flow rate of 3.5 ℓpm for 24 hour periods. This was expected to provide a detection limit of approximately 0.2 µg/m^3. Although neither the sampling schedule nor the flow rates matched either sampler, this was not considered significant because this was a test of the filtration medium.

Riverside Results

A fourteen-day collection period was conducted starting mid-October in Riverside. Samples were extracted and analyzed for nitrate, nitrite, and sulfate by Global Geochemistry of Canoga Park. It was found that the average front filter (blank corrected) collected 2.67 µg/m^3 of nitrate while the back filter collected an average of 0.67 µg/m^3. The mean of three blanks was 0.05 µg/m^3 with a standard deviation of 16%. The measurement uncertainty was estimated as the standard deviation of the blank plus an 8% uncertainty derived from replicate analyses. Since nylon filters have been shown to be quantitative for synthetically generated nitric acid (Joseph and Spicer, 1979; Appel et al., 1980), which was verified during our laboratory evaluation for this project, penetration of this species through the filter for the ambient air collections would be unlikely. It was later determined in laboratory experiments that nylon filters have little affinity for collecting PAN, which suggests that the nitrate being collected on the back filter was due to another nitrogenous species, most likely nitrous acid, which is partially retained and oxidized to nitrate. Evidence of this nitrous acid collection by nylon filters has been reported (Sanheza et al., 1984) and oxidation of the collected nitrite on filters was shown in the laboratory evaluation of the Two-Week Sampler (Fitz and Hering, 1996) and by others (Perrino et al., 1988; Sickles and Hodson, 1989).

Claremont Results

A similar collection period in Claremont during September 1994 yielded results different from the Riverside sampling. For this study, the mean nitrate on the front nylon filter was 16.0 μg/m^3 while the back filter concentration was only 0.5 μg/m^3. The same type of filters were used in each study. While these results confirm that nitric acid is collected on nylon filters with high efficiency, the composition of the air pollutants during the hot summertime conditions in Claremont were clearly different from the fall conditions in Riverside.

Discussion

The results of the dual nylon filter experiments in Riverside may explain the results of the field evaluation of the CADMP sampler conducted during the same time of the year in Azusa. The nearly constant 1.0 μg/m^3 of nitrate on filters below the denuder may have originated from nitrous acid penetrating the denuder and then being partially retained on the following nylon filter and oxidized to nitrate. If this is the case, then the denuder actually may be more effective in removing nitric acid than the filtered-air experiments showed. Nitrous acid photolyzes rapidly in sunlight so low daytime concentrations would not present a significant interference. Nitrous acid concentrations may rapidly increase after sunset, achieving a concentration of 5-10 μg/m^3 (Harris et al., 1982). The daytime CADMP samples, collected from 6 am - 6 pm PST would therefore be subjected to some nitrous acid during the early morning and early evening hours in October, which may be partially adsorbed by the nylon filter.

Whether this nylon filter collection artifact has an effect on the nitric acid measurement depends on whether the nitrous acid (or whatever the source of the artifact is; previous studies have ruled out NO or NO_2) partially or completely penetrates the denuder. If it effectively penetrates the denuder, the nylon filters with and without a denuder will be subject to the same artifact collection, and subtracting one from the other to determine nitric acid would effectively cancel out the artifact. This cancellation of the artifact would occur only if the interfering species effectively passed through the denuder, and any oxidation from nitrite to nitrate on the filter was the same at the two collection points. Determining the penetration of ozone through the denuder would therefore be recommended before accepting this cancellation in data analysis. If nitrous acid were removed by the denuder, and retained by the nylon filter used without a denuder, it would contribute to a positive nitric acid bias (although it would be low since the collection efficiency of the nylon filter is not high).

In either case of denuder penetration, the nylon filter below the denuder is used to determine particulate nitrate and the artifact would remain. Particulate nitrate might be positively biased high, representing an upper limit of particulate nitrate. The amount of bias would depend on the nature and concentration of the interfering species and the opportunity for any adsorbed nitrite to be oxidized to nitrate. The amount of this oxidation would depend on the concentration of oxidizing species (such as PAN and ozone) that reach the nylon filter in addition to environmental factors such as temperature and relative humidity. Without multiple nylon back filters for the sampling day in question, the magnitude of this sampling error cannot be measured. The nylon filters below the denuder in the filtered-air experiments, assuming 100% denuder efficiency for nitric acid, could be used as the upper limit to this artifact when measuring particulate nitrate. For routine CADMP collections, multiple nylon back filters might be useful in quantifying the collection artifact and assessing particulate measurement error and denuder efficiency for nitric acid. Similar approaches are used for annular denuders.

Conclusions

A significant amount of nitrate was found on the second nylon back filter during a study in the fall at Riverside but not in the summer at Claremont. This was most likely due to a nitrogenous species which was not nitric acid or PAN that was only partially retained by the first nylon filter. If this is the case, then the front nylon filter nitrate contains a greater amount of this interferent than the second. This will lead to a positive bias in particulate nitrate, and a positive bias for nitric acid if this species is removed by the denuder. Multiple nylon back filters should be used to estimate the magnitude of this sampling artifact.

3.2.3 1995 Claremont Comparison Study

Objective and Approach

The objective of this study was to compare the measurement of nitric acid by the CADMP sampler with spectroscopic methods, which are expected to be more compound specific. As mentioned in section 2.2.2, the FTIR nitric acid data, when available, is expected to be less subject to measurement errors than that of the TDLAS. For this reason, the FTIR data will be considered the reference value. This collocated measurement study was conducted in Claremont for a 28-day period starting August 29, 1995.

The sampler used in this study was the primary sampler at Azusa. This was used instead of the collocated sampler from the laboratory evaluation because the extensive exposure to synthetically-generated nitric acid had caused the denuders to become inefficient. It was also not clear if cleaning the denuder surfaces exposed to such conditions would restore the denuder efficiency to its original level. The primary sampler was last reconditioned in October 1993 and had been used for every sixth day sampling until the start of this study. Thus, it had been used for nearly two summers. Since the denuders of the collocated sampler were found to be operating quite efficiently after one summer of sampling, using the primary sampler would give information on the effect of another summer of nitric acid sampling on denuder efficiency. Unlike the usual CADMP sampling schedule, the sampler was operated nominally from 11am to 5pm PDT for the daytime interval and the remainder of the time for the nighttime interval.

Results

Appendix D presents the entire data set of nitric acid measurements made at Claremont used to compare with the CADMP sampler. Figure 3-5 is a time series plot (with time on the abscissa) of 15-minute averages of nitric acid measured by the TDLAS during the 28-day study. The nitric acid typically peaked at about 20 ppb in the early afternoon and went to near zero at night. Several 15-minute peaks of greater than 30 ppb were recorded. Several days of data were missing due to instrument breakdowns. Figure 3-6 is a composite diurnal profile of nitric acid for eight days when data from both spectroscopic methods are available. It should be noted that the TDLAS is lower in late morning but higher for most of the afternoon. This may be caused by adsorption of nitric acid on the Teflon prefilter of the instrument until early afternoon, when the ammonium nitrate collected on this filter volatilizes.

Figure 3-7 and 3-8 are scatterplots, for the daytime and nighttime periods respectively, of the nitric acid determined by the CADMP sampler by both the denuder difference and the filter pack approach compared to corresponding averaged nitric acid concentrations measured by the TDLAS. Data were excluded in which TDLAS values were not available for at least 75% of the CADMP's sampling interval.

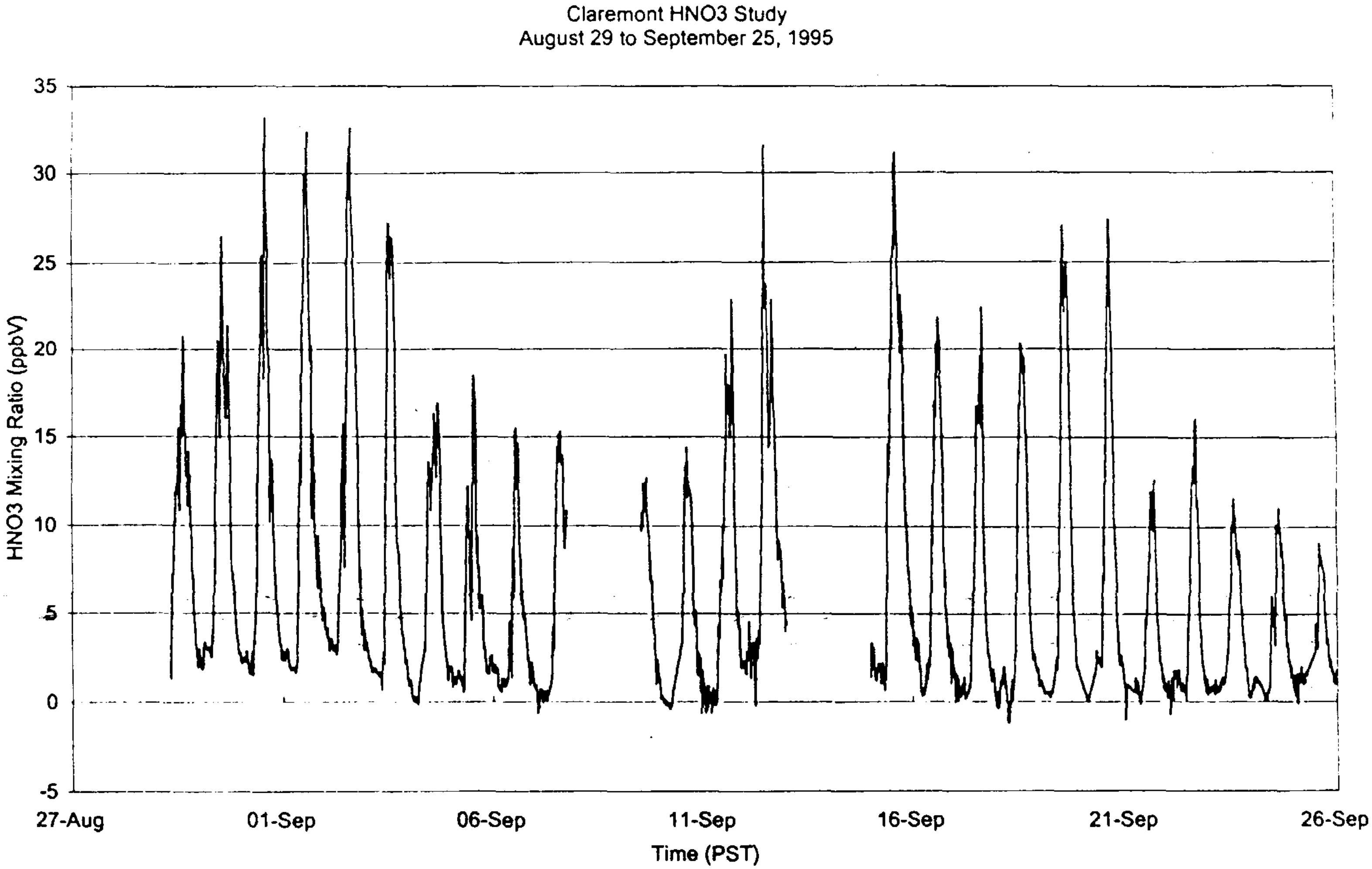


Figure 3-5
Time Series of 15 Minute Nitrate Acid Concentrations from the TDLAS at Claremont, CA

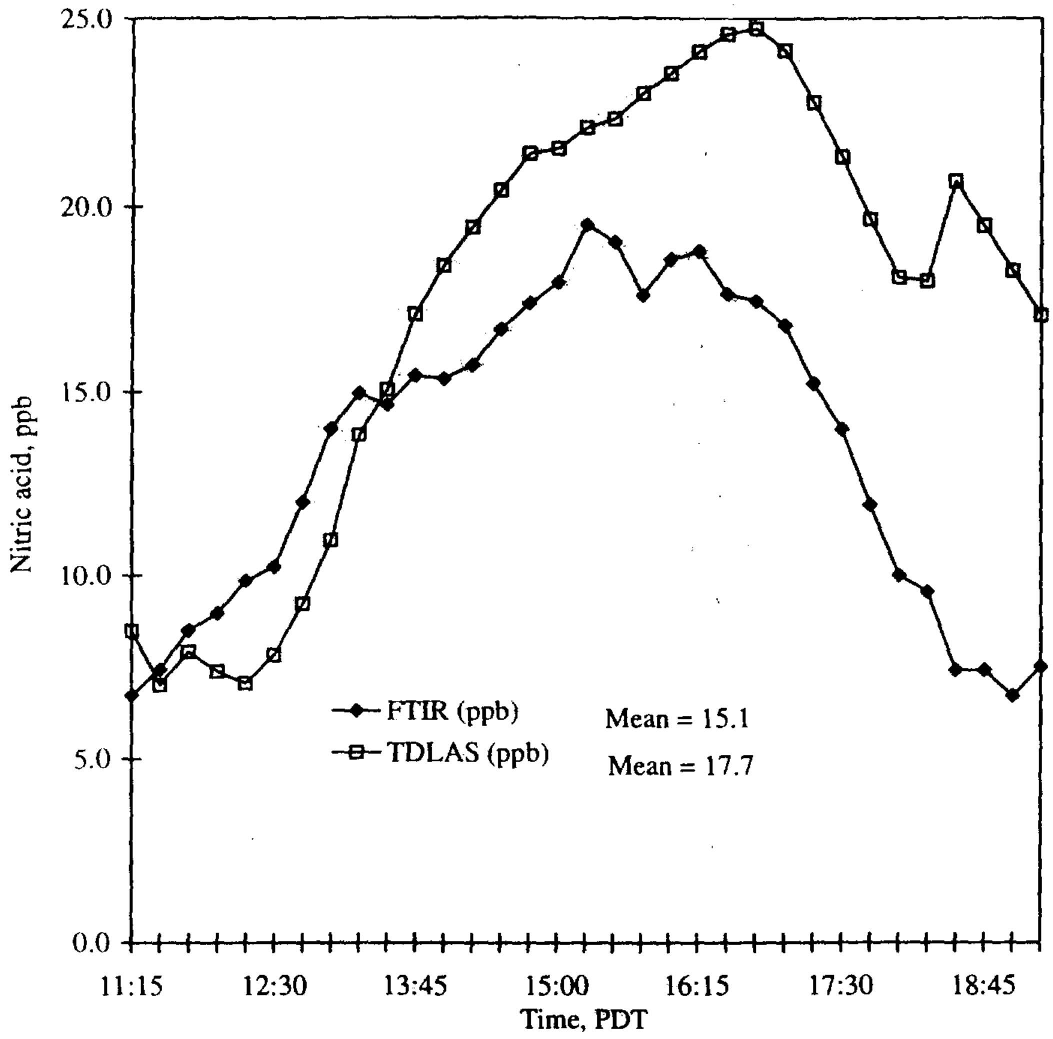


Figure 3-6 Comparison of nitric acid by TDLAS and FTIR at Claremont for eight composited days in September, 1995

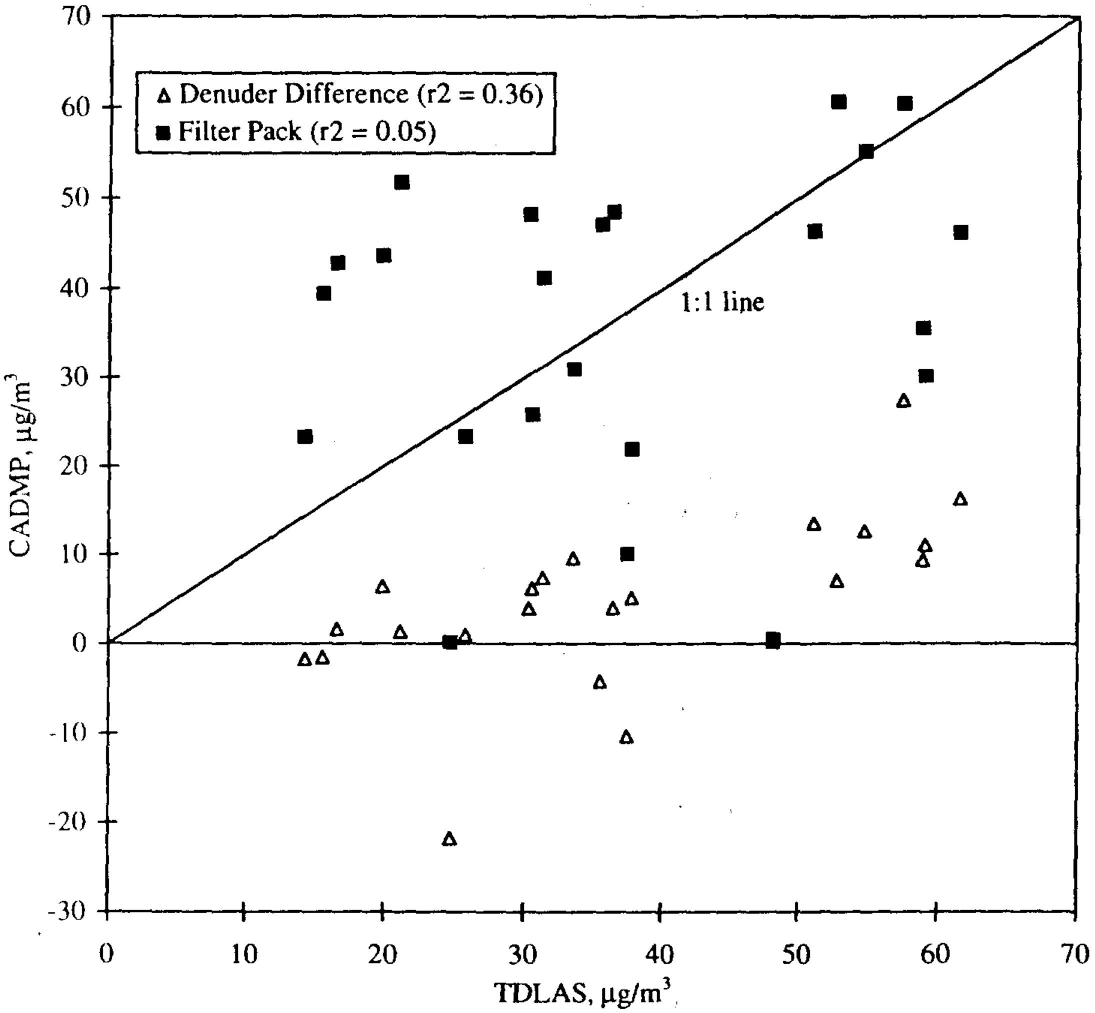


Figure 3-7. CADMP vs. TDLAS nitric acid measurements, daytime Claremont

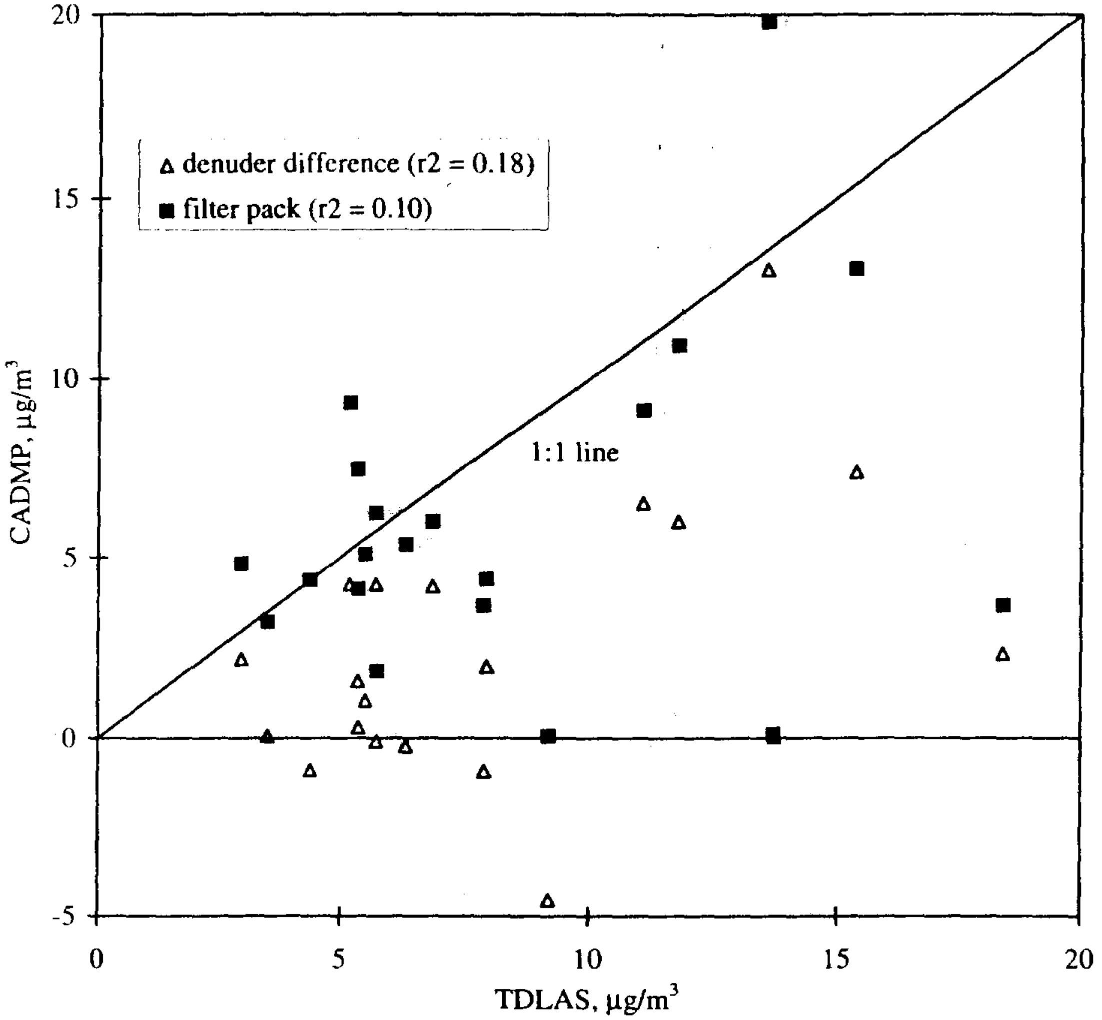


Figure 3-8. CADMP vs. TDLAS nitric acid measurements, nighttime Clarmont

It is clear from the figures that the CADMP concentrations by the denuder difference approach were much lower than those of the TDLAS and that there was a wide scatter.

The scatter was so great (r^2 values of 0.35 and 0.18 for day and night, respectively) that further statistical analyses were not warranted. The nitric acid from the filter pack (nitrate on a nylon filter downstream of a Teflon filter) was higher than that of the denuder difference method, as expected, since it also collects volatilized nitrate, but the correlation with nitric acid from the TDLAS was even lower.

Figures 3-9 and 3-10 are time series plots for daytime and nighttime periods, respectively, of the nitric acid concentrations determined by the CADMP compared with those of the TDLAS. Nitric acid measurements by both the denuder difference and filter pack vary in concert with the TDLAS measurements during the daytime, with the TDLAS generally higher until September, 1995 and lower after that date. This difference may be due to an artifact of the TDLAS, as the diode laser was replaced at this time. Alternatively, the CADMP's surfaces may be conditioning to nitric acid and allowing greater penetration during the later part of the period.

Figure 3-11 compares the nitric acid measured with the CADMP and that of the FTIR. The denuder difference method is much better correlated with the FTIR data, (r^2 = 0.71 compared to r^2 = 0.10) than the filter pack, but also much lower than the FTIR (mean = 8.0 $\mu g/m^3$ compared to 37.8 $\mu g/m^3$) and with a large intercept (- 20.9 $\mu g/m^3$) for the linear regression line. These data were from the last half of the study (after September 10, 1995) when the filter pack data showed that nitric acid was adequately penetrating the cyclone and plenum of the CADMP. The low values relative to the FTIR therefore indicate poor denuder performance.

Discussion

The scatter and generally low nitric acid measured by the CADMP compared to the TDLAS (mean of 4.6 ± 9.6 $\mu g/m^3$ versus 37.2 ± 15.4 $\mu g/m^3$) during the daytime indicated that this denuder (daytime denuder) had little removal efficiency, possibly due to saturation from previous sampling. This was further supported by the large number of CADMP data points near or below zero (which occurs when the sample collected by the nylon filter with the denuder is similar or less than that collected without the denuder). The nighttime measurements of nitric acid by the CADMP were not as low relative to the TDLAS (mean of 2.4 ± 3.8 $\mu g/m^3$ versus 8.4 ± 4.3 $\mu g/m^3$). This could be explained in part by the nighttime denuder being more

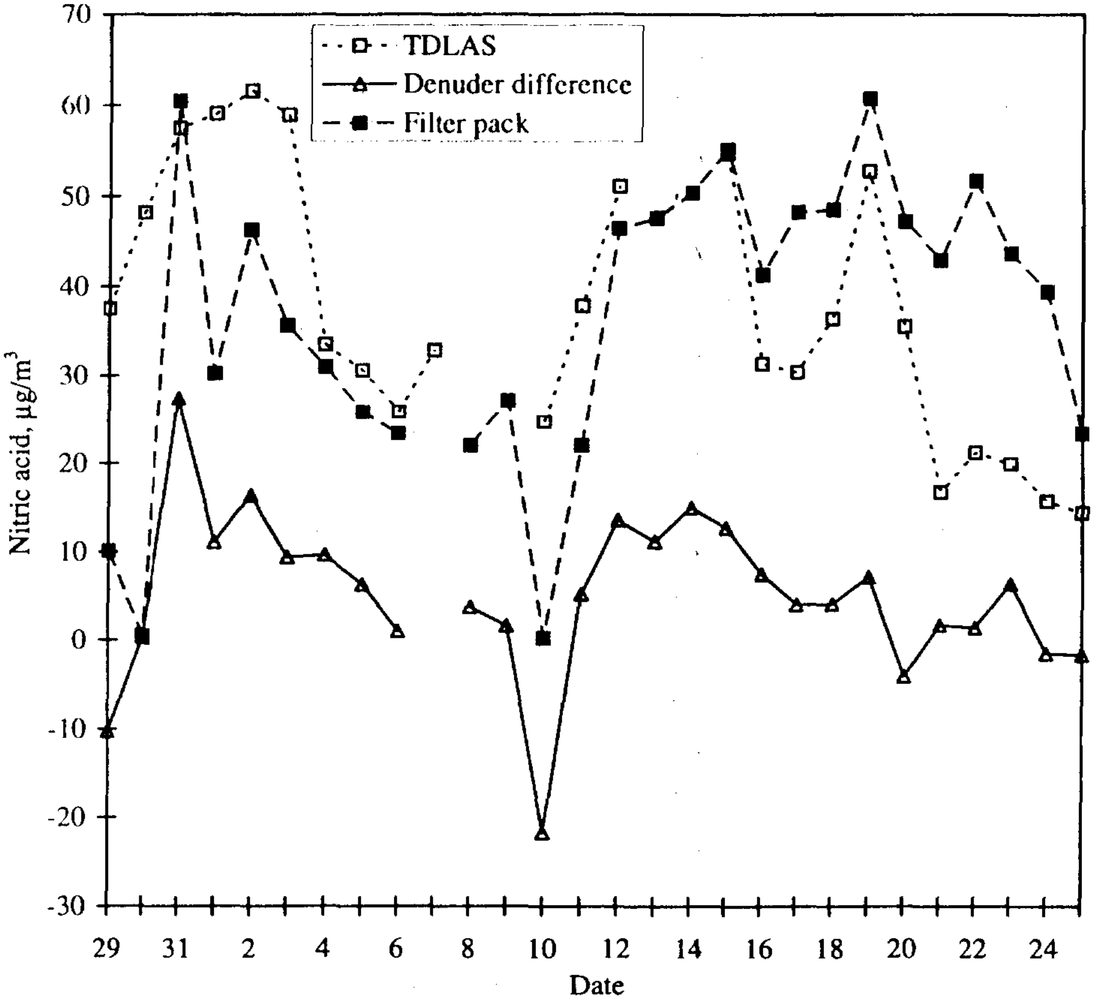


Figure 3-9 Time series plot of nitric acid by TDLAS, CADMP denuder difference and CADMP filter pack, Claremont daytime

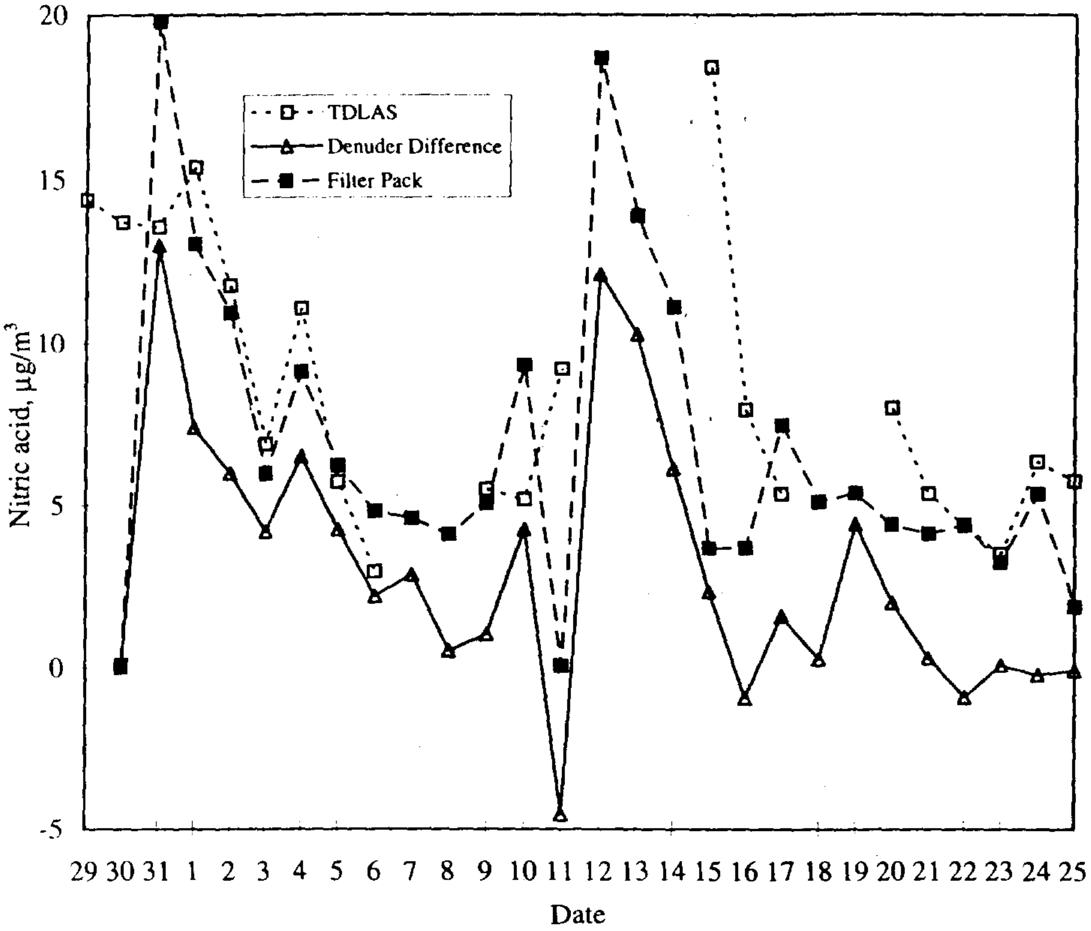


Figure 3-10 Time series plot of nitric acid measured by TDLAS, CADMP denuder difference, and CADMP filter pack, nighttime Claremont

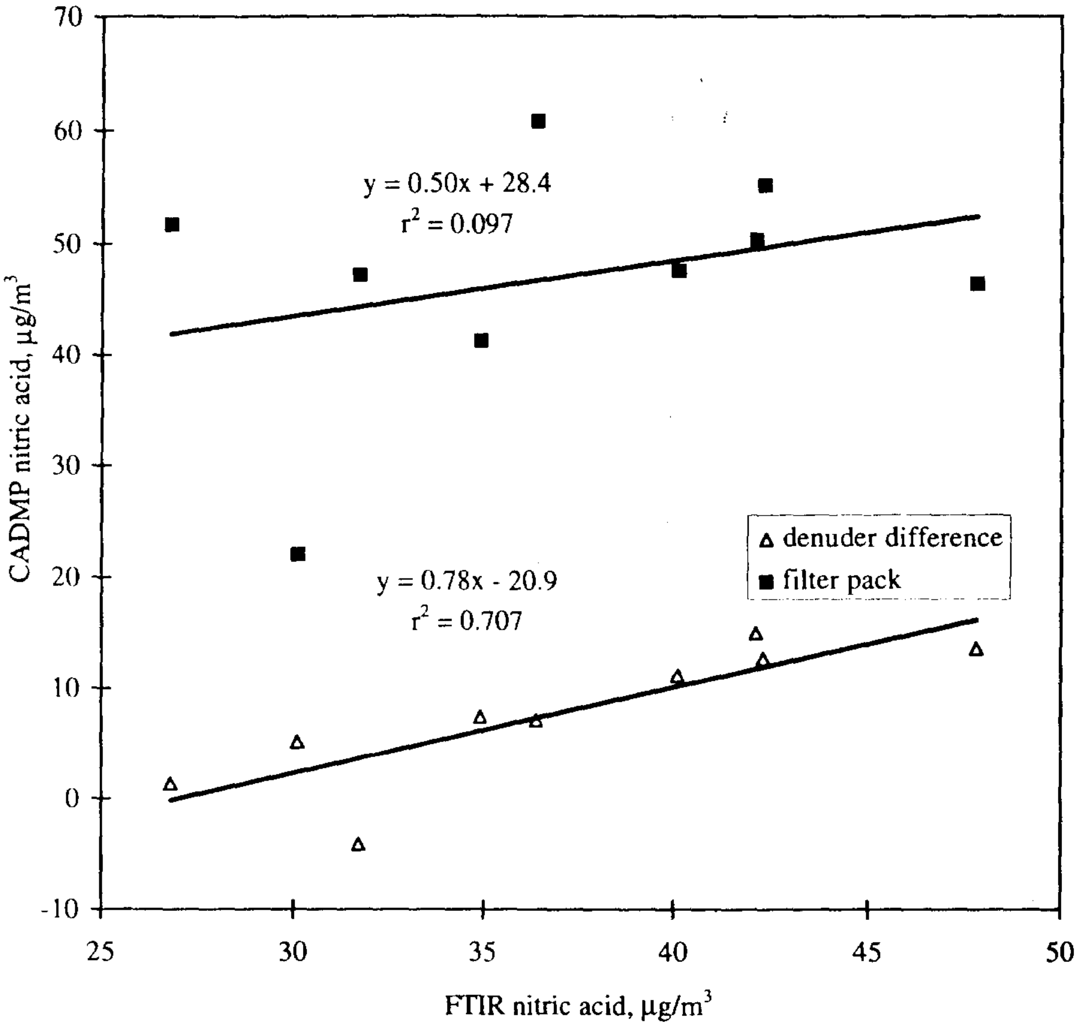


Figure 3-11 CADMP vs. FTIR nitric acid measurements, daytime Claremont (September 11, 12, 13, 14, 15, 16, 19, 20, 22)

efficient in removing nitric acid since it had not been exposed to as much in the preceding two years.

Laboratory experiments, described later, showed these denuders to be sources of nitric acid. We also observed particle shedding from the cyclone during the laboratory evaluation using synthetically generated aerosol. This may account for high negative numbers for nitric acid (if nitrate-containing particles were shed onto the nylon filter below the denuder) and the high variability of the nitric acid measurements. That the denuders failed after less than two years of service since reconditioning is difficult to explain, especially since the 1993 Azusa study showed little degradation after five years of use. This failure may be due to the hot ambient temperatures and high nitric acid concentrations encountered during the Claremont study. Alternatively, the use of a KOH solution to 'recondition' the denuders may have resulted in an alteration of the anodized surface in such a way that may have caused them to fail prematurely. The anodization of surfaces has been found to be necessary for quantitatively removing nitric acid.

Conclusion

Poor agreement was found when comparing CADMP and TDLAS nitric acid data from the ambient air in Claremont. The most likely reason for this is that the denuders of the primary Azusa CADMP sampler were no longer efficiently removing nitric acid.

3.3 Laboratory Evaluations

As described previously, laboratory evaluations of the penetration of nitric acid through the CADMP sampler using synthetically generated sources were conducted for both the whole sampler and for the components.

3.3.1 Whole Sampler Evaluation

The sampler used for this evaluation was the collocated sampler in Azusa. This sampler had been used every day for 30 days in a special study in October 1993, every sixth day until September 1994, and then for nine collection periods in the fall of 1994. The sampling was conducted using the same approach as in the field evaluation but with a synthetic source of nitric acid. Figure 3-12 details the experimental configuration.

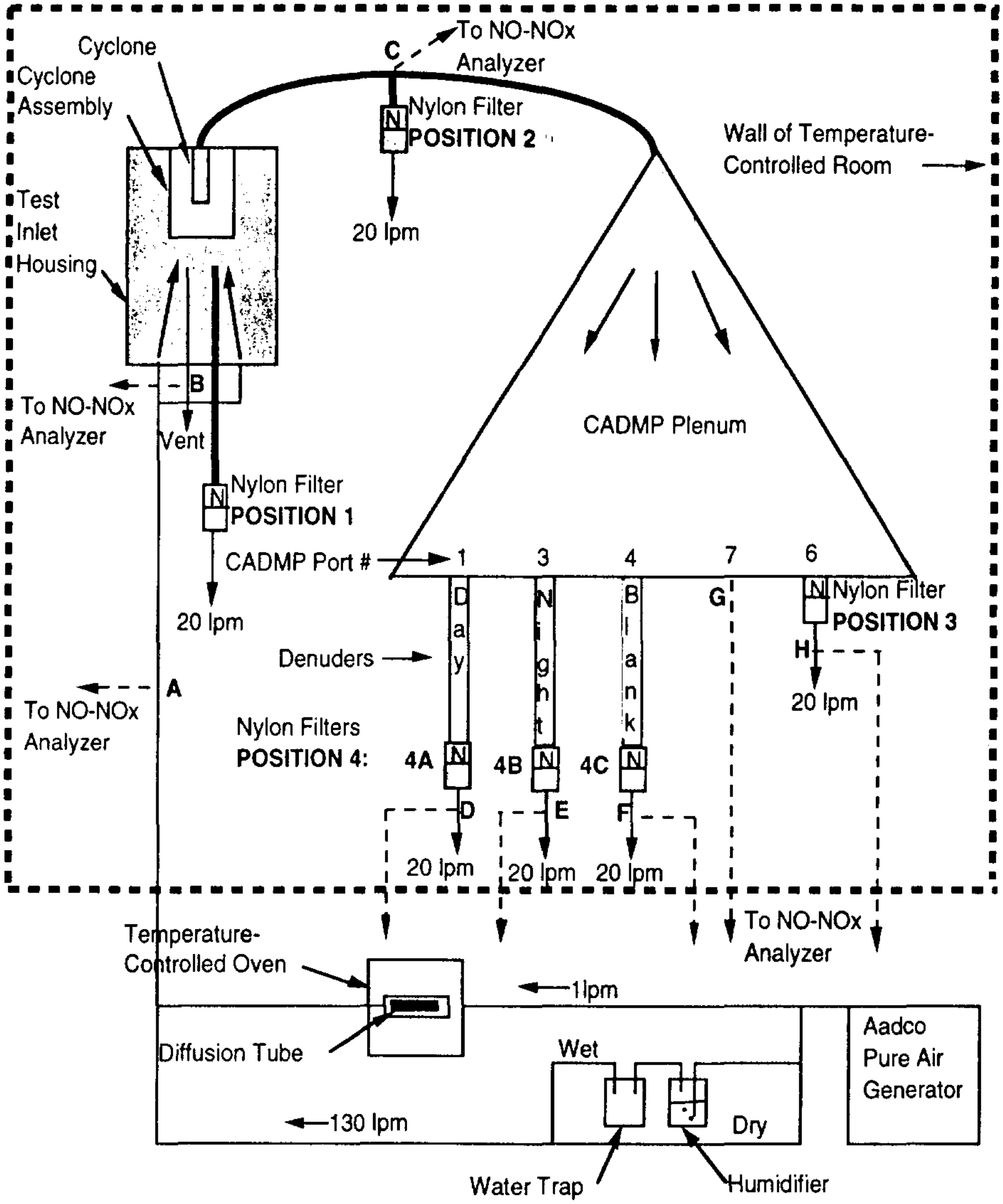


Figure 3-12 Schematic diagram for the laboratory evaluation of the CADMP sampler

3.3.1.1 Nitric Acid Penetration Using a NO-NO$_X$ Analyzer

Overall Objective and Approach

The objective of this study was to evaluate quickly the nitric acid penetration through the CADMP to compare with data obtained by collecting integrated longer-term samples on nylon filters. It was expected that the concentrations could be monitored at all of the positions shown in Figure 3-12, allowing several minutes per point for equilibration of the NO-NO$_X$ analyzer (lettered positions refer to analyzer sampling positions). The approach described in Section 2 needed to be modified, however, as knowledge was gained of the PFA Teflon adsorption/desorption characteristics. The NO-NO$_X$ nitric acid measurement in real time allowed us to characterize the transitory processes which are otherwise averaged when sample substrates are collected over longer periods of time for laboratory nitrate analysis.

While real-time concentrations were beneficial, the evaluation process became more complicated than anticipated. In order to give a better understanding of the experimental approach, the types of experiments conducted are described under the following 'bullets'. Each 'bullet' has its own objective and approach, results, and conclusions section along with additional sections as needed.

- CHARACTERIZATION OF THE TEST INLET HOUSING FOR NITRIC ACID PENETRATION AS A FUNCTION OF TEMPERATURE AND RELATIVE HUMIDITY

Objective and Approach

The objective of this first task was to determine the penetration of nitric acid through the PFA-coated test inlet housing which was designed to enclose the CADMP cyclone assembly. The evaluation was conducted with the CADMP cyclone assembly installed. Unlike the schematic in Figure 3-12, the sample was extracted at the sample point using the shortest practical 1/8 inch PFA tubing (about 30cm) prior to the externally-mounted NO$_X$ converter. The outlet of this converter was connected to NO-NO$_X$ analyzer with 1/8 inch PFA tubing.

Results

The initial evaluation was conducted at a nominal nitric acid concentration of 200 $\mu g/m^3$ at room temperature (20°C). Using dry air (the Aadco specifications for the dew point -70°C or less) at 20°C, the nitric acid concentration at the vent of the test inlet housing (position B) was within 5% of concentration at the inlet prior to the test inlet assembly (position A). When the relative humidity (RH) of the air was increased to 50% by adjusting the moist/dry flow rates the nitric acid concentration at the vent of the test inlet housing immediately dropped to nearly zero and then slowly increased over the following sixteen hours, reaching only 65% of the inlet concentration.

The test inlet housing was then washed with dilute nitric acid (1% by volume), rinsed thoroughly with deionized water, and dried. After purging with 200 $\mu g/m^3$ nitric acid at 50% RH for sixteen hours, the vent (position B) concentration reached 88% of the inlet concentration after eighteen hours. The concentration was then lowered to 28 $\mu g/m^3$, and the temperature (of the small room in which the equipment was set up, which was monitored both within the test inlet housing and in the room and found to be ± 1°C) was raised from 20°C to 37°C; the RH was adjusted to 30% and the system was allowed to equilibrate overnight. Monitoring the nitric acid concentration at the inlet housing, the heater for the room was then turned off. Figure 3-13 shows a temperature and concentration profile with time. Lowering the temperature lowered the nitric acid concentration measured at the vent of the test inlet assembly although the concentration of nitric acid in the input air remained the same. Turning the heater back on caused the nitric acid measured at the test inlet housing vent to rise. The experiment was repeated with no added water to raise the relative humidity, and no changes in nitric acid concentrations were observed with changes in temperature.

Conclusion

Nitric acid was being adsorbed to the walls of the test inlet housing as a function of either temperature, relative humidity, or both.

• CHARACTERIZATION OF THE CADMP PLENUM FOR NITRIC ACID PENETRATION AS A FUNCTION OF TEMPERATURE AND RELATIVE HUMIDITY

Objective and Approach

The objective of this test was to determine the extent to which temperature and humidity effected adsorption/desorption of the PFA-coated surfaces in the CADMP sampler. Since the cyclone assembly could not be exposed without using the test inlet housing, attention was focused on the CADMP plenum in which nitric acid could be directly introduced with a 1/2 inch diameter PFA Teflon line. The field testing had shown that nitric acid penetration through the plenum of the sample was essentially quantitative. A constant 28 $\mu g/m^3$ of nitric acid at 75 ℓpm was introduced into the plenum and sampled at the port 7 plenum outlet (position G in Figure 3-12) with the $NO\text{-}NO_x$ analyzer. The room was maintained at 39°C and the humidity

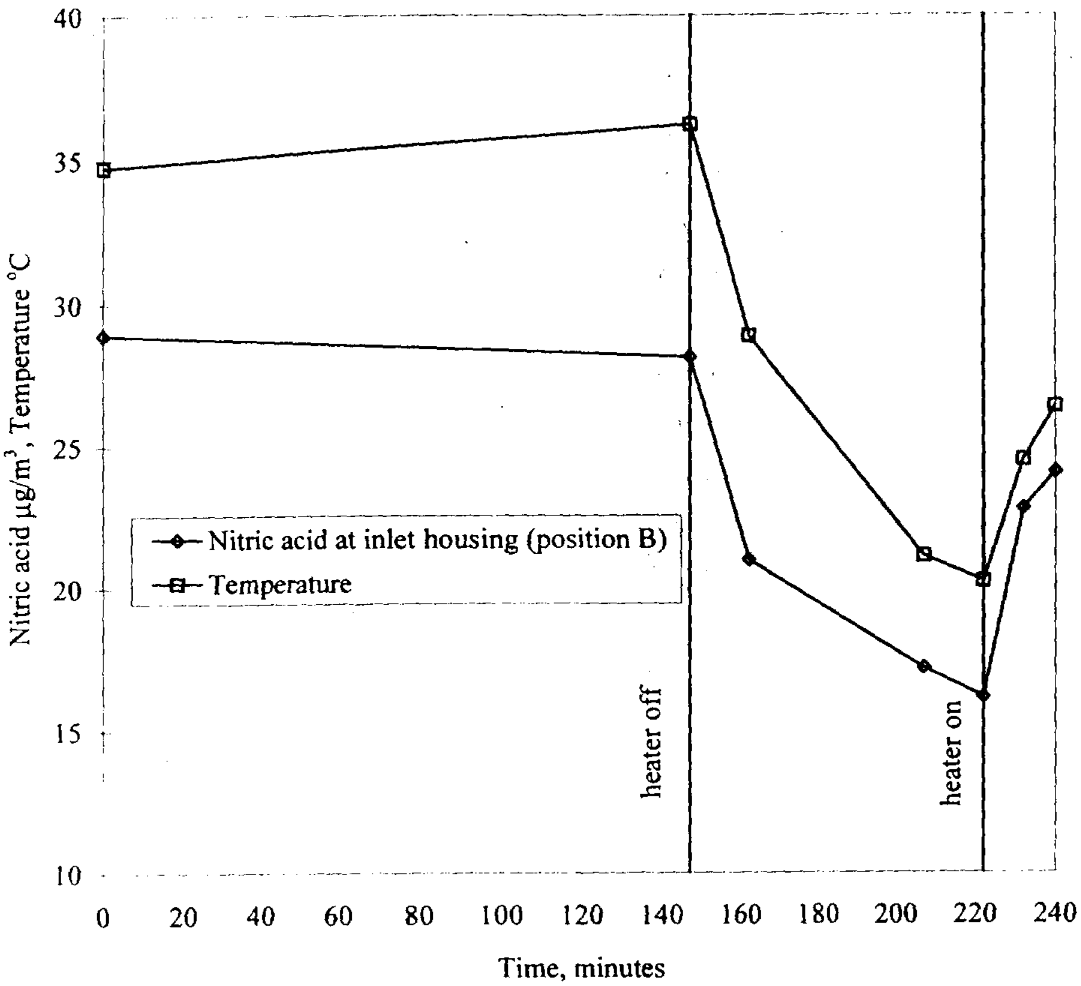


Figure 3-13 Nitric acid at the test inlet housing vent (position B) as temperature changes (RH = 30%, temperature = 37°C)

was 20%. The system was allowed to equilibrate overnight. The effect of cooling and heating at a constant nitric acid input was considered.

Results

Figure 3-14 shows the results of turning off the heater and turning on the air conditioner. The concentration measured at the CADMP plenum outlet immediately started to drop and reached almost zero as the temperature fell to 13°C. The plenum had therefore become a sink for nitric acid. The air conditioner was then turned off and the heater on. The nitric acid measured at the plenum outlet immediately rose, reaching a concentration above that of the source. The plenum had become a source for nitric acid. During this time the nitric acid concentration at the source (a 'T' on tubing prior to the plenum) remained at a constant 28 $\mu g/m^3$.

Conclusion

The CADMP plenum had temperature-induced nitric acid adsorption/desorption properties similar to those observed for the test inlet housing.

- CHARACTERIZATION OF THE CYCLONE ASSEMBLY FOR NITRIC ACID PENETRATION AS A FUNCTION OF TEMPERATURE AND RELATIVE HUMIDITY USING AN FEP FILM TEST INLET BAG.

Objective and Approach

The objective of this test was to evaluate the temperature and humidity responses on the adsorption/desorption characteristics of the CADMP cyclone assembly. Evaluating the cyclone assembly for nitric acid penetration would be complicated by the concurrent changes in concentration occurring in the housing that was needed to enclose the cyclone assembly (it was necessary to enclose the cyclone assembly since there was no convenient plumbing inlet, only a 4 inch square opening). FEP Teflon film was chosen to construct a test inlet bag, because we believed that this film would behave more like extruded, molded, or machined Teflon rather than a Teflon coated metal when exposed to nitric acid. Machined Teflon has been shown to remove less nitric acid than coated surfaces (Appel et al. 1987). The test inlet housing was replaced with a bag constructed from 2 mm thick FEP Teflon film. The Teflon film was heat sealed to form a bag with an opening on one end. The bag was placed over the cyclone assembly, two 1/4 inch PFA Teflon sampling lines were inserted (one for the nitric acid source and the other for the NO-NO_x analyzer), and the end of the bag tied tightly around the tubing connecting the cyclone assembly to the CADMP plenum. With the nitric acid source turned on,

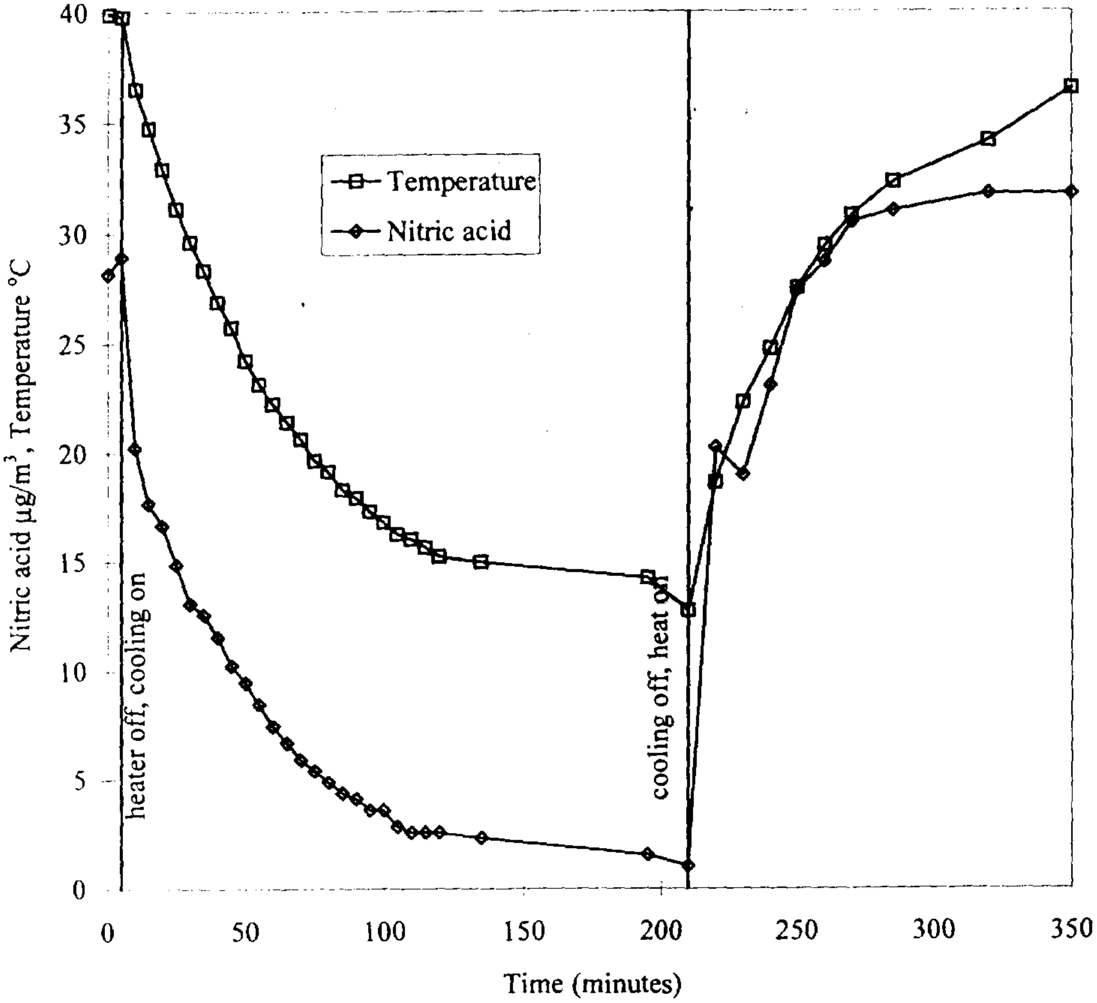


Figure 3-14 Nitric acid concentrations through CADMP plenum while cooling, then heating (constant source of nitric acid of 28µg/m³, RH = 20% at 40°C)

the bag expanded into a chamber. During the tests, the nitric acid within the test inlet bag was monitored with the NO-NO_x analyzer.

Results

Forty-six µg/m^3 of nitric acid at 20% relative humidity were introduced into the cyclone assembly through this bag at 80 ℓpm. The concentration was monitored at the outlet of the cyclone chamber (position C in Figure 3-12) with the NO-NO_x analyzer as the temperature was changed. During the course of the experiment the nitric acid concentration within the test inlet bag did not change more than 2 µg/m^3 (although approximately 30 minutes would be required to achieve a stable reading due to conditioning of the sample lines; this will be discussed later). This indicated that the FEP Teflon did not interfere with the test. Figure 3-15 shows the results. As the temperature stabilized to 40°C , so did the HNO_3. The air conditioner was then turned on and the concentration of nitric acid fell as the system cooled, dropping to nearly zero. Note that the last point on the time series was measured after nearly 18 hours of nitric acid exposure after the air conditioning was turned on. The nitric acid concentration was still 30 µg/m^3 compared to the 46 µg/m^3at the FEP test inlet bag (there was a routine verification that the input concentration had not changed).

After two additional days of exposure to nitric acid at 16°C the concentration at position C finally reached the level of that being introduced into the sampler. The temperature of the sampler was brought back up to 40°C and the nitric acid measured at position C then climbed to over 100 µg/m^3. It slowly dropped to 50 µg/m^3 during the next 24 hours. Similar results were obtained when the original test inlet housing replaced the bag.

Conclusions

These results show that penetration of nitric acid through the cyclone inlet was also a function of temperature and relative humidity and that FEP Teflon film can be used to introduce nitric acid into the CADMP without introducing additional adsorption/desorption effects during the tests

- CHARACTERIZATION OF THE TEST INLET HOUSING FOR NITRIC ACID PENETRATION AS A FUNCTION OF RELATIVE HUMIDITY ONLY.

Objective and Approach

The objective of this test was to determine the affect of relative humidity changes alone on the adsorption/desorption characteristics of nitric acid when passed through PFA Teflon-coated

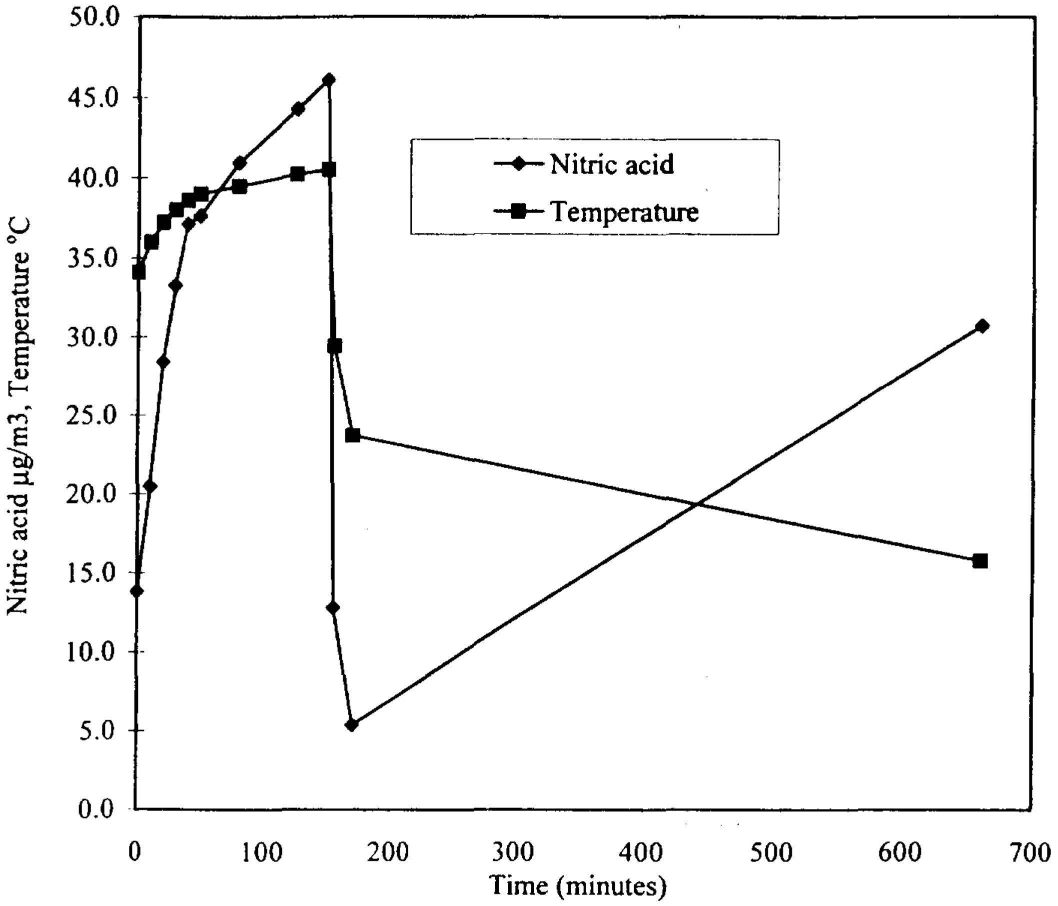


Figure 3-15 Nitric acid measured at the CADMP cyclone assembly (position C) as a function of temperature using an FEP teflon test bag (constant nitric input, RH=20%, temperature 40°C)

aluminum devices. To accomplish this, the test inlet housing was purged at a constant nitric acid concentration with the heater for the humidifier turned off until the concentration of nitric acid at position A was stable at 125 $\mu g/m^3$ (this heater controlled the temperature of the humidifier, not the CADMP sampler, which remained at 20°C for the entire experiment). The heater of the humidifier was then turned on while leaving all flows the same. Since everything else remained untouched, relative humidity was the only variable that was changed and this was done via an electric heating element.

Results

Figure 3-16 shows the results of this experiment as a function of time. Immediately after turning the heater on, the relative humidity started to increase and the nitric acid concentration started to decrease: HNO_3 was almost perfectly inversely correlated with RH. When the humidifier heater was turned off the nitric acid started to rise. The equilibrium of nitric acid adsorption/desorption with relative humidity was not shifted very far or for very long (i.e. the humidity was not changed a great deal nor sampled for very long), otherwise the concentration data would show more of a hysteresis effect and not respond as quickly to changes in humidity.

Conclusion

This experiment gives good support to the idea that the adsorption/desorption processes are relatively humidity dependent (the temperature remained the same during the entire experiment). While it would have been ideal to perform a similar experiment where temperature was the only variable changed, this could not be easily accomplished (heat cannot be added to the system like water; the temperature change would effect the relative humidity).

- CHARACTERIZATION OF THE PFA TEFLON SOURCE AND SAMPLING TUBING FOR NITRIC ACID PENETRATION AS A FUNCTION OF TEMPERATURE AND RELATIVE HUMIDITY.

Objective and Approach

The objective of this test was to characterize the adsorption/desorption characteristics of the PFA Teflon tubing used in the laboratory CADMP evaluation. The time constant for losses and gains for these components would set the lower limit for which changes in a tested component could be ascribed to the component itself and not the test apparatus. The PFA Teflon tubing used for the inlet line of the NO-NO_x analyzer was evaluated by sampling the nitric acid source

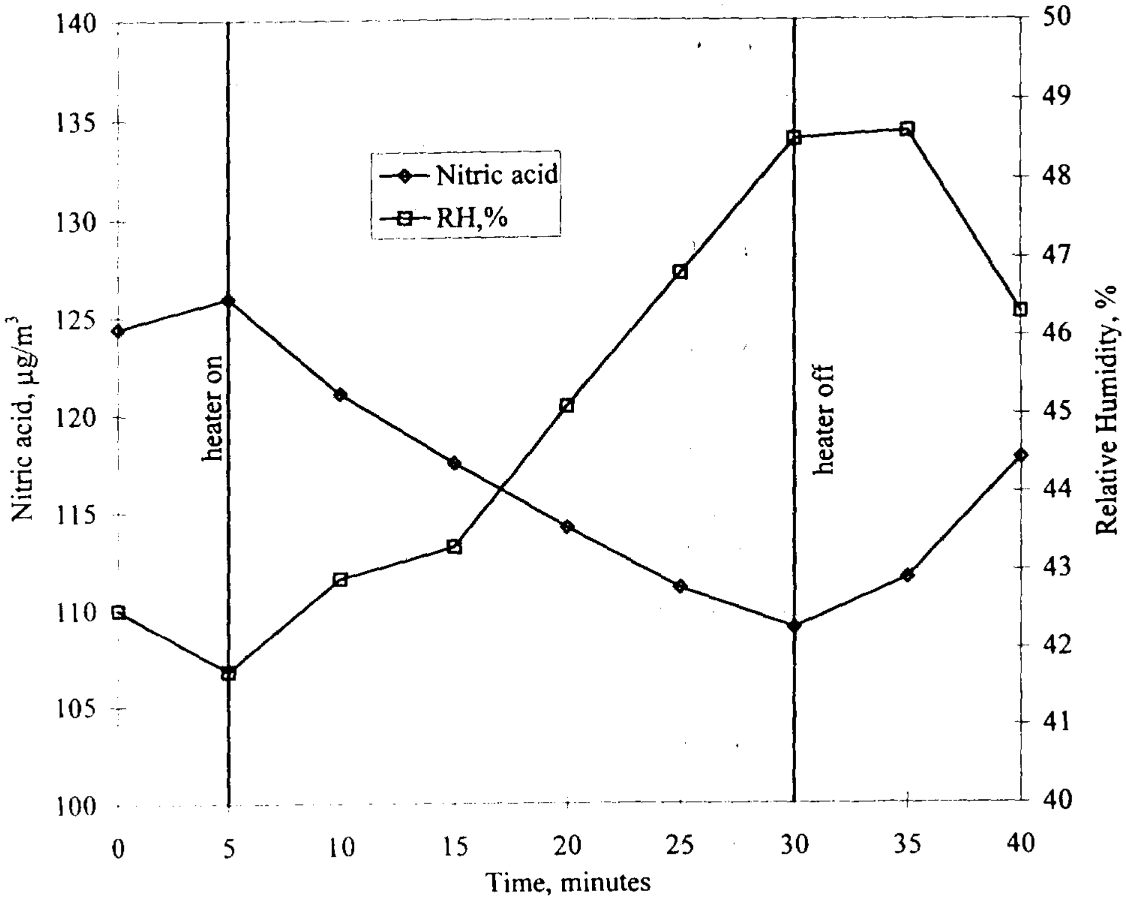


Figure 3-16 Nitric acid concentration measurements with humidity at changes at 20°C (test inlet housing)

line with the analyzer until the concentration reached a constant value, and then sampling zero air (air sampled from the source line before nitric acid was added) and measuring the time for the NO-NO_x response to return to zero.

Results

These tests were all conducted at 20°C and 51 $\mu g/m^3$ nitric acid. Under dry conditions (no added water for humidification) the concentration of nitric acid dropped to 5 $\mu g/m^3$ in about ten minutes and reached the zero concentration in about an hour. A similar time response was obtained when the sampling line was reattached to the nitric acid source. Repeating the tests at 50% RH, it was found that it took about two hours to drop to 5 $\mu g/m^3$ and 12-24 hours, and sometimes longer, to reach zero. In these experiments no changes in concentration or humidity were made to the nitric acid source line. The time response under these conditions included that of the sample lines to the instrument, as there was no way to isolate them from the rest of the system.

This experiment showed that nitric acid was being retained in the PFA sampling line or the NO_x converter. One possibility for this could be adsorption on the few inches of stainless steel tubing going into the converter. It would be difficult to eliminate this since the tubing goes into the heated zone which, at 450°C, is well above the temperature where Teflon can be used. Alternatives could be tried, such as a low temperature specialized converter (e.g., ferrous sulfate) or replacing the stainless steel tubing with quartz or some other material which would not cause nitric acid to be retained. Both of these alternatives would require research and development which would be beyond the scope of this study and may not help meet the objectives, since significant adsorption/desorption effects have already been shown for the CADMP sampler.

Conclusions

The time to reach equilibrium with changes in temperature and relative humidity in the sample lines were far less than those observed when evaluating the concentration of nitric acid at various test positions on the CADMP sampler with the NO-NO_x analyzer. The results of evaluating the CADMP are therefore at least qualitatively valid. When measuring nitric acid at positions where the concentrations are expected to be low or at zero, much time can be saved by testing these positions first before testing positions where there is significant nitric acid (and therefore requiring a significant time for re-equilibration).

- DETERMINATION OF DENUDER NITRIC ACID COLLECTION EFFICIENCY

Objective and Approach

Determining denuder efficiency with the NO-NO_x analyzer, an objective originally proposed as a component of evaluating the overall penetration of nitric acid through the CADMP sampler, was complicated by the adsorption/desorption phenomenon encountered. Once we understood this process, the procedure was changed. When the nitric acid at the outlet of the CADMP sampler (position G in Figure 3-12) had stabilized, the NO-NO_x analyzer was allowed to sample zero air until a steady zero had been reached. By sampling the outlet of a denuder with a properly zeroed NO-NO_x analyzer (it is important to sample at the denuder outlet first, since once exposed to nitric acid a long equilibration time may be necessary to re-establish the zero) the nitric acid concentration can readily be determined if close to zero. If not, a rise in concentration would occur, indicating incomplete denuder scrubbing of nitric acid or a contaminant in the diffusion tube source of nitric acid. Once the denuder outlet concentration is determined, the analyzer can be used to sample the inlet to verify the nitric concentration at the CADMP plenum outlet.

Results

Prior to the first non-blank filter collection period, we measured the nitric acid for all three denuders (positions D, E, and F in Figure 3-12) when sampling 50 $\mu g/m^3$ at a temperature of 20°C and a relative humidity of 26%. Less than 2 $\mu g/m^3$ of nitric acid was observed. Thus the indicated efficiency was greater than 95%. This should be regarded as a lower limit because it is difficult to quantify concentrations at this low level due to several sources of error. For example, Goldan et al. (1983) found up to 15% NO_2 contaminating their nitric acid; this is a species which would pass through the denuder and be detected by the NO-NO_x analyzer. A small amount of retention of nitric acid was also possible in the sample line. In addition, any residual NO_x (from leakage of ambient air during sampling, inefficiency of the pure air system, or contamination of the humidified water) in the zero air would contribute to a lowered measured removal efficiency. Drift of the NO-NO_x analyzer, which at 1.0 $\mu g/m^3$ was near its detection limit, would also contribute to uncertainty of the denuder efficiency measurement. The filter sampling, discussed in the following section confirms this measurement of denuder efficiency.

Conclusion

All three denuders of the Azusa collocated CADMP sampler were operating with over 95% efficiency just prior to the laboratory evaluation of the CADMP sampler for nitric acid penetration by collecting nylon filter samples.

Discussion of the Overall Results of the Laboratory Evaluation

The nitric acid concentrations requiring many hours to stabilize after changes in temperature and humidity caused the experimental approach to be rethought for both meeting the objectives of the study and in the methodology needed. The first question is whether the laboratory experiments can be useful in evaluating the operation of the CADMP (or any other sampler whose design involves significant contact of the sampled air with Teflon-coated surfaces) when sampling under field conditions where the temperature and humidity are varying thoughout the 12-hour sample duration. For example, the CADMP sampler could adsorb nitric acid during the nighttime when temperatures are lower and the relative humidities are higher, then desorb this nitric acid during the day when temperatures are higher and relative humidities are lower. The amount of nitric acid adsorbed depends on the ambient concentrations encountered during the night, which are also constantly changing (it is also possible that ambient nitric acid concentrations are influenced by adsorption/desorption to <u>all</u> surfaces in the environment). These biases depend on several variables interacting in a complex way and are not quantifiable except in direction: nighttime measurements are biased low, daytime measurements are biased high. Once the surfaces have been saturated, however, long-term average concentrations should be reasonably accurate. These sorptive processes may also explain why the nitric acid concentration measured at night during the filter-air experiments was nearly zero, since it would be adsorbed by the surfaces of the CADMP sampler.

Based on these results, the experimental design was modified to cope with entering the temperature-controlled room to change the sampling position of the NO-NO_X analyzer, and thus upsetting the equilibrium of the nitric acid being measured. For subsequent experiments, permanent PFA NO-NO_X sampling lines were attached to the CADMP that extended to the instrument located outside of the environmental chamber. These are shown in the complete diagram for the testing arrangement shown in the figure in Appendix A. While these lines were only about four feet long, it was necessary to sample this length prior to reaching the NO_X converter (we had only one converter and up to seven sample positions). Nitric acid concentrations would still take about half an hour to stabilize until the sampling line conditioned.

In addition, it was realized that when setting up the CADMP sampler for collecting nitric acid on nylon filters, it would be necessary to ensure that the concentration of nitric acid was stable prior to starting the sampling. If not, the results would not be reproducible, since the time to reach concentration equilibrium depended not only on the concentration, temperature or humidity change, but also on the direction in which these changes were effected, i.e., the hysteresis.

With the new NO-NO_x sampling line setup, bypass lines were used with flow regulation to purge the CADMP while waiting for the nitric acid concentration to equilibrate. This was done to minimize the denuders' exposure to nitric acid during the equilibration process. Previously for conditioning, the 130 ℓpm from the nitric acid source had been flowed directly into the CADMP (by blocking the vent of the test inlet housing) and allowing the mixture to vent at the unused (for these preliminary nitric acid measurements using a NO-NO_x analyzer there was no need to set up for filter collection) filter sampling ports. The denuders had therefore been exposed to significant amounts of nitric acid in the testing to date. These were the same bypass lines used with the CADMP in the field (which normally operated at the 75 ℓpm). It was not believed that this would alter the turbulence inside the CADMP plenum significantly, nor would a change in turbulence affect the results of this experiment.

Once changes were made in the sampling lines so that they could be changed without entering the CADMP's temperature-controlled room, the NO-NO_x analyzer was used to determine whether the system had equilibrated prior to collecting samples on filters. These data are presented in the following section discussing the filter sampling.

Overall Conclusions

It was concluded that sampling with the NO-NO_x analyzer is useful only for a qualitative examination of nitric acid through the CADMP, since the surfaces of the sampler (cyclone assembly and plenum) can be both sinks and sources of nitric acid depending on changes of relative humidity and temperature and the previous exposure history to nitric acid. The NO-NO_x analyzer would only be useful to determine that the penetration of nitric acid does stabilize through the components of the sampler under constant environmental conditions.

The NO-NO_x analyzer could be used to determine the efficiency of the nitric acid denuder. It was found that all three denuders were operating with an efficiency of greater than 95%. Since any significant penetration through the denuder is also likely to depend on the actual environmental conditions, it is not suggested that the analyzer be used to attempt to quantify efficiency for adjusting denuder difference nitric acid measurements. The analyzer approach should be used to verify that the denuder is working properly and removes essentially all nitric acid or to set an upper limit for the error of the denuder difference nitric acid measurement.

3.3.1.2 Nitric Acid Penetration Measured by Nylon Filter Collection and Analysis

Objective and Approach

The objective of this study was to evaluate the penetration of nitric acid by sampling for the acid at the various positions with nylon filters. The positions are 1-3 and 4A-4C shown in Figure 3-12. This was done for a range of three temperatures (13, 20 and 37°C), two relative humidities (10 and 50%), and two concentrations (25 and 130 $\mu g/m^3$) as shown in Table 2-1. In all cases, the NO-NO_x analyzer was used to determine that nitric acid concentrations at the test inlet housing and plenum (positions 1 and 3 in Figure 3-12) of the CADMP had stabilized prior to starting collections. Since the room in which the CADMP was temperature-controlled could not be entered, the CADMP was set up so that conditioning and sample collection could be done remotely. Thus, the bypass lines were used to condition the CADMP at a 100 ℓpm inlet flow rate. These lines connected to unused ports of the CADMP so that the flow rate could be maintained without exposing the denuders to nitric acid during the extended time required to reach equilibrium (sometimes up to days at low temperature or high humidity). The filter sampling was then started, and simultaneously the 'bypass' flow used to reach the equilibrium condition was stopped. It should be noted that with this experimental system it was not possible to use the NO-NO_x analyzer when testing the CADMP at high temperature and humidity conditions as the analyzer would not stabilize, most likely due to the condensation of water vapor and the subsequent dissolution of nitric acid.

We also confirmed, as reported previously (Appel et al., 1980), that the nylon filters quantitatively removed nitric acid to within the experimental error of the test system. This was done much like denuder testing, by sampling with a properly zeroed NO-NO_x analyzer.

Equilibration Results

Figure 3-17 shows a typical time to reach equilibrium under warm and dry conditions (which are expected to equilibrate the fastest) when sampling with a NO-NO_x analyzer at the CADMP plenum with the source concentration of 150 $\mu g/m^3$. In this case sampling was alternated between the test inlet housing (position B in figure 3-12) and the outlet of the CADMP plenum (position G in Figure 3-12). Under these conditions, the same concentrations are expected at

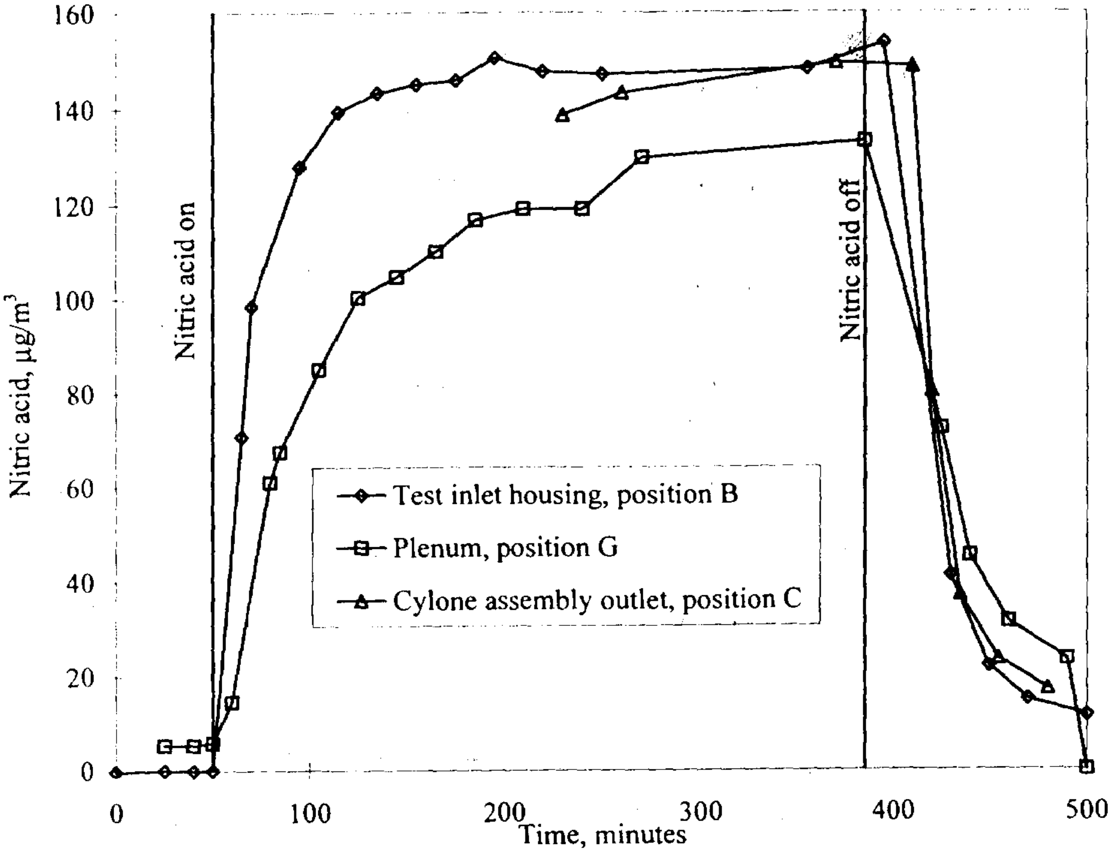


Figure 3-17 Attainment of nitric acid concentration equilibration through the CADMP laboratory test apparatus (37°C, 11%RH)

both sample points, so that analyzer sample line conditioning could not be responsible for all of the differences observed. From the time nitric acid was switched on, it required nearly five hours to equilibrate and when it was switched off, over two hours were required to attain a zero concentration state. It should be noted that these are for hot, dry conditions; equilibration required far longer when the temperature was cool or the relative humidity higher.

Precision Testing

To determine the precision of collecting nitric acid on nylon filters, three pairs of samples were collected directly from the nitric acid source (without using the CADMP sampler), at a nominal 130 μg/m^3 at 20 ℓpm for two hours. All components of the sampling lines were PFA Teflon tubing. At the same time the nitric acid was monitored with a continuous NO-NO$_x$ analyzer in the source line. All nitrate measurements were blank corrected, using as a dynamic blank the mean nitrate for a pair of substrates that sample zero air for a similar period of time under identical conditions. Table 3-2 summarizes the results in units of μg/m^3.

Table 3-2 Measurements to determine the precision sampling nitric acid with nylon filters

NO-NOx Analyzer μg/m^3	Temperature degrees C	Humidity percent RH	Sample Cassette 1 μg/m^3	Sample Cassette 2 μg/m^3	Percent difference between cassettes	Comments
133	20	17	130	144	-11	
117	20	79	242	226	7	
135	20	79	230	268	-17	
0	20	17	0	0		5.1 and 1.3 μg collected
			Mean Std Dev		-7 12	

In order to convert ppb to μg/m^3 under the laboratory temperature and pressure conditions one must divide by 2.56. While the precision was about 12% (in good agreement with our estimate of uncertainty for field collections), the filter samples and analyzer measurements were only in agreement for one of the three sample sets. The dynamic blanks were quite reasonable, averaging 0.3 μg/m^3 nitrate per filter, especially considering that these were full dynamic blanks, including the sampling of zero air. Two trip blanks (filters that were not used but returned to the laboratory in the usual manner in vials), showed an average amount of 0.8 μg nitrate per filter, typical of the expectation from the laboratory. This disagreement between the filter collections and the NO-NO_x analyzer cannot be explained. The calibration of the NO-NO_x analyzer was well characterized, no retention of nitric acid in the sample line was indicated, and the expected concentration (from the diffusion tube release rate and the dilution flow rate) was reached.

Equilibration

Figure 3-18 shows the results from the NO-NO_x analyzer monitoring the nitric acid through the system as it equilibrated and as samples were collected on 3/24/95. Since the sample lines were moved from position to position, the results should be viewed as qualitative since some retention in the sample line was likely occurring. To avoid this, positions of similar nitric acid could have been sampled, either those before or after the denuders, but it would not have been possible to do both on a reasonable time scale for the filter sampling.

Test Results

Table 3-3 summarizes the results of sixteen filter laboratory collection experiments involving various concentrations, relative humidities, and temperatures. The temperature is that of the room in which the CADMP was placed, while the relative humidity was determined with a Fisher Scientific digital hygrometer which sampled air from the CADMP plenum. During these experiments, the NO-NO_x analyzer sampled from either the test inlet housing (position B in Figure 3-12) or the CADMP plenum (position G) to verify stable nitric acid concentrations. The samples collected prior to March 24, 1995 were conducted in the laboratory, since a temperature-controlled room was not necessary (the laboratory was maintained at a constant 20°C).

The NO-NO_x analyzer was used to monitor nitric acid at the test inlet housing (position B). Figure 3-19 is a scatterplot of the nitric acid measured with the analyzer compared to that of the filter measurements at the same position for all tests. While the two are reasonably correlated, with an r^2 value of 0.64, there are a number of outliers where the filter data are anomalously high. Excluding three data points significantly raises the r^2 value to 0.92. Anomalously high values were also observed previously when filter samples were collected for precision determination. The Wilcoxan ranked sum test was applied to the full data set to determine whether the data sets, filter versus analyzer, were equivalent. The result of this test

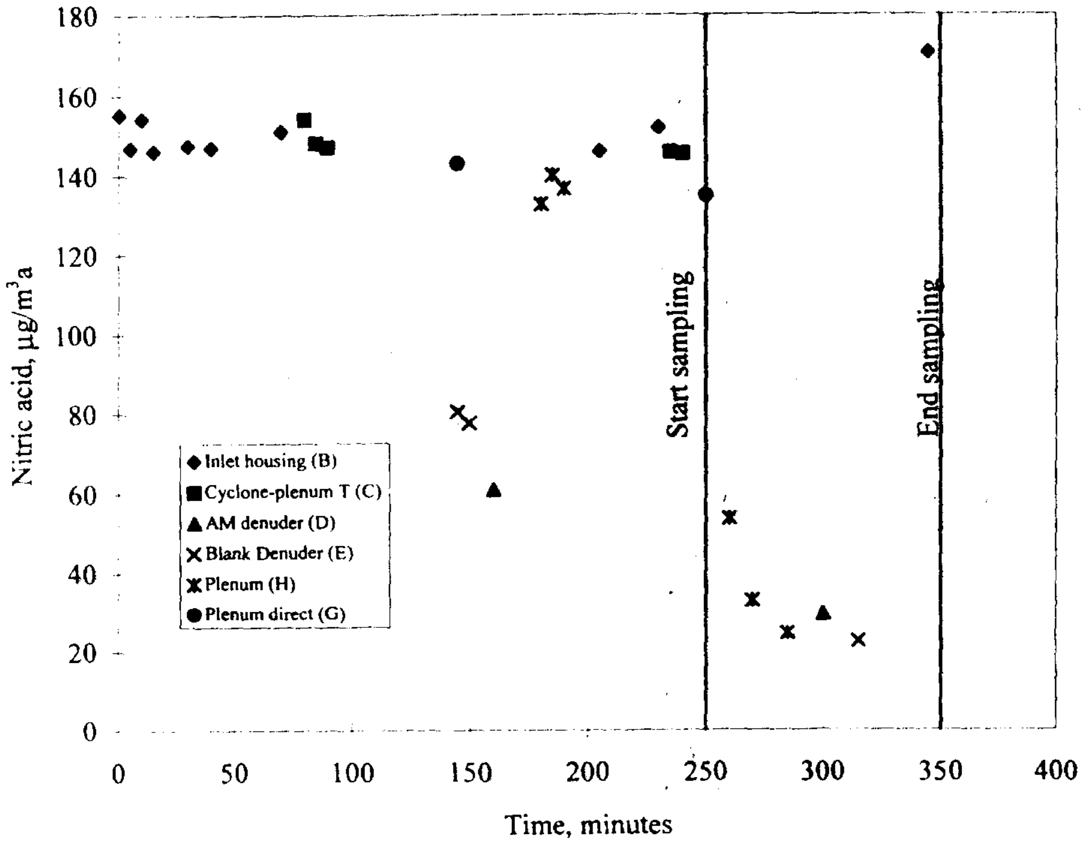


Figure 3-18 NO_x analyzer measurements before and during filter collection 3/24/95

Table 3-3 Summary of nitrate on nylon filters sampling synthetic nitric acid (all values corrected for field filter blanks 0.7µg filter)

Date	Time mins	Temp °C	RH %	Test Inlet Housing (Positions 1,B)		Cyclone Assembly (Position 2)		CADMP Plenum (Position 3)		Day Denuder (Position 4A)		Night Denuder (Position 4B)		Blank Denuder (Position 4C)		Comments
				Analyzer $\mu g/m^3$*	Chamber $\mu g/m^3$	Conc. $\mu g/m^3$	Ratio to Inlet	Conc. $\mu g/m^3$	Ratio to Cyclone	Conc. $\mu g/m^3$	Ratio to Plenum	Conc. $\mu g/m^3$	Ratio to Plenum	Conc. $\mu g/m^3$	Ratio to Plenum	
1/31/95	300	20	41	0.0	5.5	14		19		2.5		0.8		0.8		Dynamic Blank
2/23/95	420	20	52	16	27	5.8	0.21	13	2.24	1.8	0.14	1.3	0.10	1.3	0.10	
2/24/95	420	20	18	23	23	24	1.04	22	0.92	0.4	0.02	0.6	0.03	0.9	0.04	
2/28/95	120	20	11	116	137	116	0.85	69	0.59	1.2	0.02	10.0	0.14	13	0.19	
3/2/95	120	20	85	107	93	104	1.12	32	0.31	1.3	0.04	0.9	0.03	1.0	0.03	
3/13/95	120	20	17	123	94	82	0.87	66	0.80	0.2	0.00	1.4	0.02	1.0	0.02	
3/24/95	120	31	10	142	171	187	1.09	164	0.88	51	0.31	90	0.55	76	0.46	New Test System
3/31/95	120	33	48	137	178	150	0.84	158	1.05	31	0.20	44	0.28	48	0.30	
4/4/95	240	32	48	3.0	1.2	7.0		15		15		12		3.9		Dynamic Blank
4/14/95	417	30	45	33	46	36	0.78	34	0.94	20	0.59	22	0.65	15	0.44	
4/21/95	300	23	47	35	37	34	0.92	35	1.03	13	0.37	18	0.51	18	0.51	
4/25/95	120	25	45	112	210	215	1.02	172	0.80	50	0.29	87	0.51	81	0.47	
4/27/95	300	20	50	84	96.9**	11.5**		7.2**		0.4**		6.0**		5.6**		Static Blank
5/6/95	120	15	52	63	204	85	0.42	ND		ND		112	ND	180	ND	
5/8/95	120	14	53	35	119	142	1.19	190	1.34	93	0.49	127	0.67	113	0.59	
5/12/95	120	15	51	0.0	0.9	2.6		4.7		2.9		0.9		2.2		Dynamic Blank
Means w/o blanks							**0.86**		**0.99**							
Std. Dev. w/o blank							0.29		0.49							
Means w/o blanks, 2/23, 5/ 6, 5/8							**0.95**		**0.81**							
Std. Dev. w/o blanks, 2/23, 5/6, 5/8							0.12		0.23							
Means w/o blanks to 3/13											**0.04**		**0.06**		**0.08**	
Std. Dev. w/o blanks to 3/13											0.05		0.06		0.07	
Means w/o blanks after 3/13											0.37		0.53		0.46	
Std. Dev. w/o blanks after 3/13											0.14		0.14		0.10	

ND= No data available

* Nitric acid expressed as $\mu g/m^3$ nitrate

** Units of µg as there was no flow

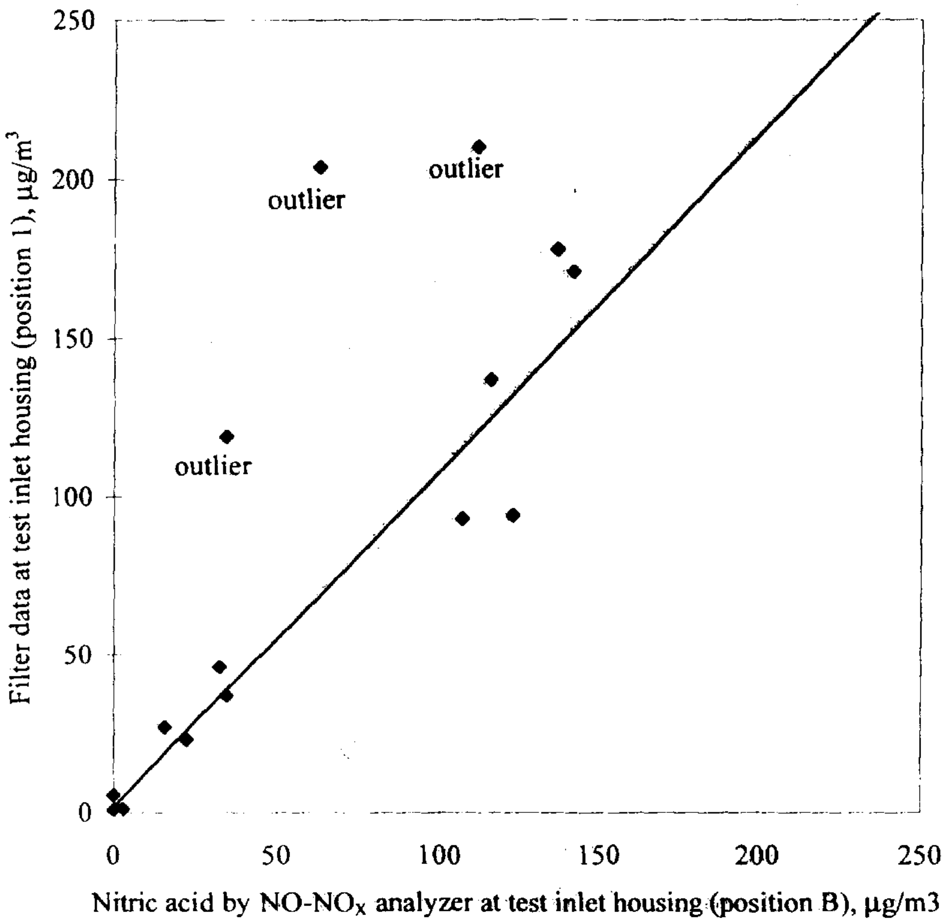


Figure 3-19 Comparison of nitric acid concentrations at the test inlet housing (position B) measured by a NO-NO_X analyzer compared to measurement by nylon filters (r^2=0.64)

was a R- value of 23.5, below the critical value of 30. This indicated that the two data sets were not equivalent at the 95% confidence level, i.e. there was a bias between them. Application of a least squares regression to the data set with the three outliers removed gave a slope of 1.08 with an intercept of 1.7. The two measurement methods were therefore in reasonable agreement, with the analyzer biased somewhat low.

Filter Blank Evaluation

All values in Table 3-3 were corrected for the field blanks, filters that were allowed to remain in the CADMP for a period equivalent to sampling but without any flow through the filter or CADMP sampler. Table 3-3 also shows the results of two other types of blank collections, dynamic and static. Three sets of dynamic blanks were collected, in which pure air without added nitric acid was sampled for periods of time typical of the nitric acid collections. This provides a measure of contamination after a long purge with pure air to 'clean' the surfaces of the sampler. The second dynamic blank was collected before the NO-NO_x analyzer sampling the inlet housing had reached zero concentration. This was done to determine whether the instrumental response was a sampling artifact or whether residual nitric acid was still in the inlet housing. Significant amounts of nitric acid were still released from both the cyclone inlet assembly and CADMP plenum. More importantly, relatively large amounts of nitrate were collected below the daytime and nighttime denuders. This supports the observation, to be discussed later, that the denuder efficiency dropped dramatically between the tests conducted on the 13th and 24th of March. It is possible that nitric acid retained on the denuder surfaces was slowly being 'chromatographed' through the denuder. The dynamic blanks were much lower during the first and third collections. These samples were not collected until the NO-NO_x analyzer monitoring the inlet had fully equilibrated to zero. The first dynamic blank collection showed significant nitric acid from both the cyclone assembly and CADMP plenum. The dynamic blanks from the third collection interval may have also been less than the others since the temperature was lower (15°C compared to 20°C and 32°C) which would promote nitric acid retention on the exposed surfaces.

In the static blank, nylon filters were loaded into the sampler but no flow was allowed to pass through them. The rest of the sampler was equilibrated to 90 $\mu g/m^3$ nitric acid (determined from the NO-NO_x analyzer sampling from the test inlet housing) by using bypass lines to draw the test mixture through the sampler. The static blanks were allowed to stay in the sampler for 36 hours, far longer than the few hours normally needed to re-equilibrate the system after entering the room to install the filter sampling cartridges. This test must therefore be considered a worst case and was meant to determine whether the nylon filters would adsorb any nitric acid (presumably by diffusion) under these conditions. Having the filters installed into the sampler during equilibration was necessary since, as previously mentioned, the equilibrium would be upset when the temperature-controlled room was opened to install filter substrates, while the actual filter sampling flow could be controlled remotely (this approach was used starting on September 24th, 1995). The amount of nitrate collected is shown in Table 3-3 in μg/filter (all other filter sample analyses have been divided by the 2-5 m^3 of air sampled) as attainment of equilibrium, for each test varied in terms of time, which was dependent on temperature, concentration, humidity, and previous exposure history. Since these variables are different for each run, the static blank values should not be used for correcting data, but can provide an indication of the errors present. Since over 100 μg of nitrate is typically collected from the test inlet housing, cyclone assembly, and CADMP plenum (positions 1-3 in Figure 3-12), the worst case static blank represents less than 10% of this amount for both the cyclone assembly and CADMP plenum. On the other hand, a very significant amount of nitrate was collected on the nylon filter sampling from the test inlet housing. This would explain why the concentrations measured at this point by filter collection were generally higher than that of the NO-NO_X analyzer for the experiments conducted after March 23rd, although it was not possible to rationalize how the inlet static blank could be exposed to more nitric acid than the sample collected between the cyclone assembly and the CADMP plenum or at the CADMP plenum outlet. This is yet another reason why the nitric acid concentrations should not be corrected for the static blank.

Discussion

The mean loss of nitric acid was 14% in the cyclone assembly, but the standard deviation was twice this. The ratios of nitrate at the cyclone assembly outlet (position 2) to the test inlet housing (position 1) varied significantly, in a way not explainable by the temperature, concentration, or relative humidity variations. Figure 3-20 is a scatterplot of the nitric acid measured by the filter collections at the cyclone assembly outlet (position 2) compared to the test inlet housing (position 1). Except for one data point, the plot appears to be linear. Further examination of this outlier (collection on 5/6/95) shows the concentration of nitric acid at the test inlet housing to be over twice as high for the measurement at the same point with the NO-NO_X analyzer, in addition to being over twice as high as the concentration determined at the cyclone assembly by the filter measurement. This point might be anomalously high due to collection of nitric acid during the time it was loaded in the sampler without flow while the sampler was equilibrating. The static blank at this position was also quite high during that test as described earlier. A similar argument could be made for the data collected on 2/23/95 although the differences are not as large. For these reasons it was felt to be justified to exclude

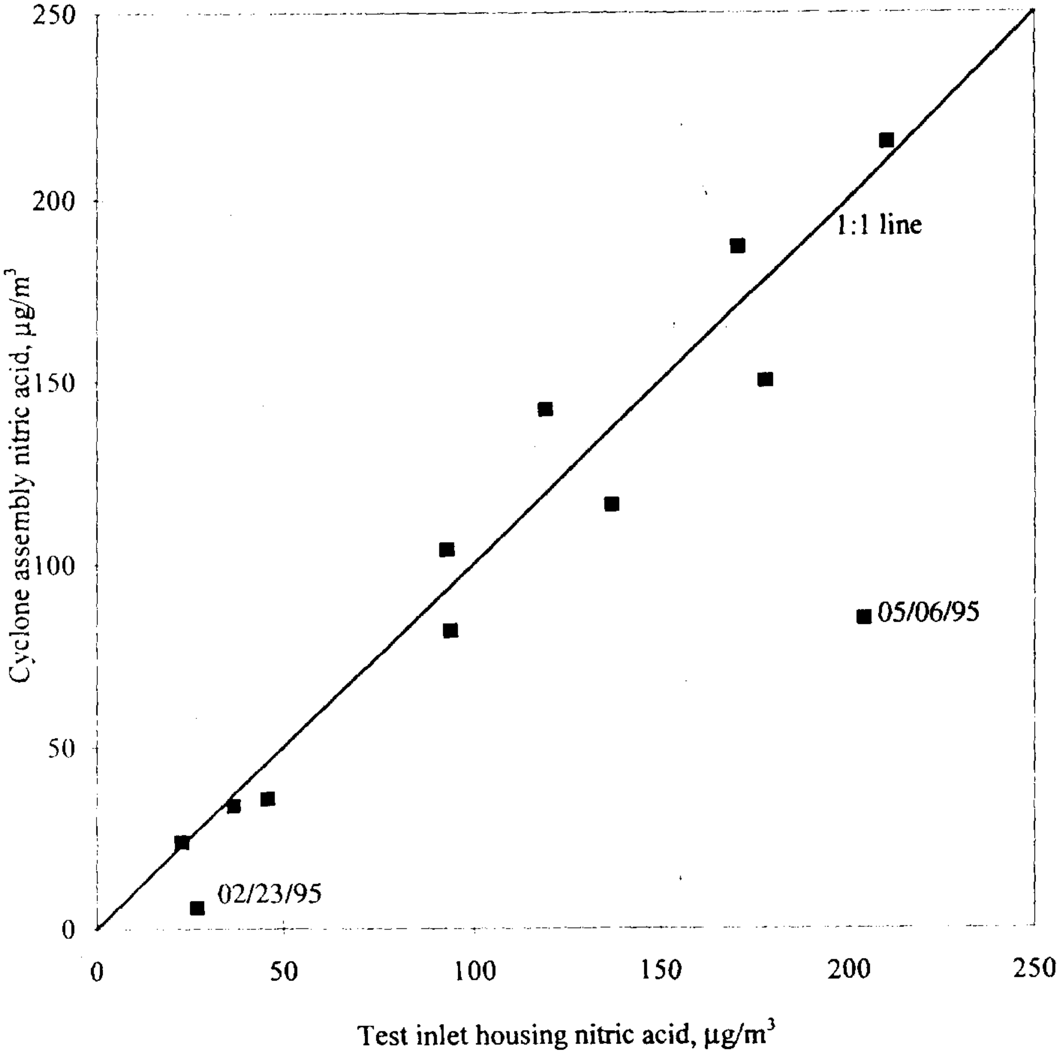


Figure 3-20 Filter-based laboratory nitric acid, cyclone assembly outlet vs. test inlet housing (position 2 vs. position 1)

these two points during further data analysis. Application of the Wilcoxan Ranked Sum Test for the remaining eleven data points showed that the concentrations at both the test inlet housing and cyclone assembly outlet were equivalent at the 95% confidence level ($R^+ = 31$, $R^- = 25$, $T_C = 11$). It was therefore concluded that no statistically significant loss of nitric acid occurred between the inlet housing and the cyclone assembly outlet. This applies only to the equilibrium conditions used in the laboratory exposures.

The mean penetration of nitric acid from the cyclone assembly to the CADMP plenum was 99% or quantitative within the experimental error. Figure 3-21 is a plot of the nitric acid measured from the filter collections at the cyclone assembly outlet compared to the CADMP plenum outlet. There was no justification for exclusion of the outlier collected on 3/2/95 from this data set. Application of the Wilcoxan Ranked Sum Test indicated that the two data sets were equivalent ($R^+ = 46$, $R^- = 20$, $T_C = 14$). It was concluded that the CADMP plenum quantitatively passed nitric acid under these conditions within the experimental error.

The mean penetration of nitric acid from the test inlet housing to the CADMP plenum outlet was calculated to be 0.81 with a standard deviation of 0.32. Figure 3-22 shows a scatterplot of the nitric acid concentration measured by the filters at position 3 compared to position 1. There was no justification for the removal of the outliers. Application of the Wilcoxan test showed that the data sets were not equivalent ($R^+ = 56$, $R^- = 10$, $T_C = 14$). A least squares linear regression yielded a slope of 0.89 and intercept of 0.89, but the r^2 value was only 0.69. Removal of the outlier (while the removal of this data point could not be justified, it was thought to be quite unlikely that the concentration after the CADMP plenum would be nearly twice that of the test inlet housing), collected on 5/8/95, had little effect on the slope, dropping to 0.86, but improved the r^2 value to 0.87. It is concluded that there was a statistically significant loss of nitric acid when measured from the inlet to the CADMP plenum. This was about 15%, near the estimated uncertainty of 12%.

Conclusions

- Until the collection made on March 24th, all three denuders were operating with over 90% efficiency. This efficiency is similar to that measured during the sampling of filtered ambient air during the daytime. After that date, their efficiencies dropped markedly, with the daytime denuder dropping the most. This may be due to it having received more exposure to nitric acid during the year of routine CADMP filter collection.

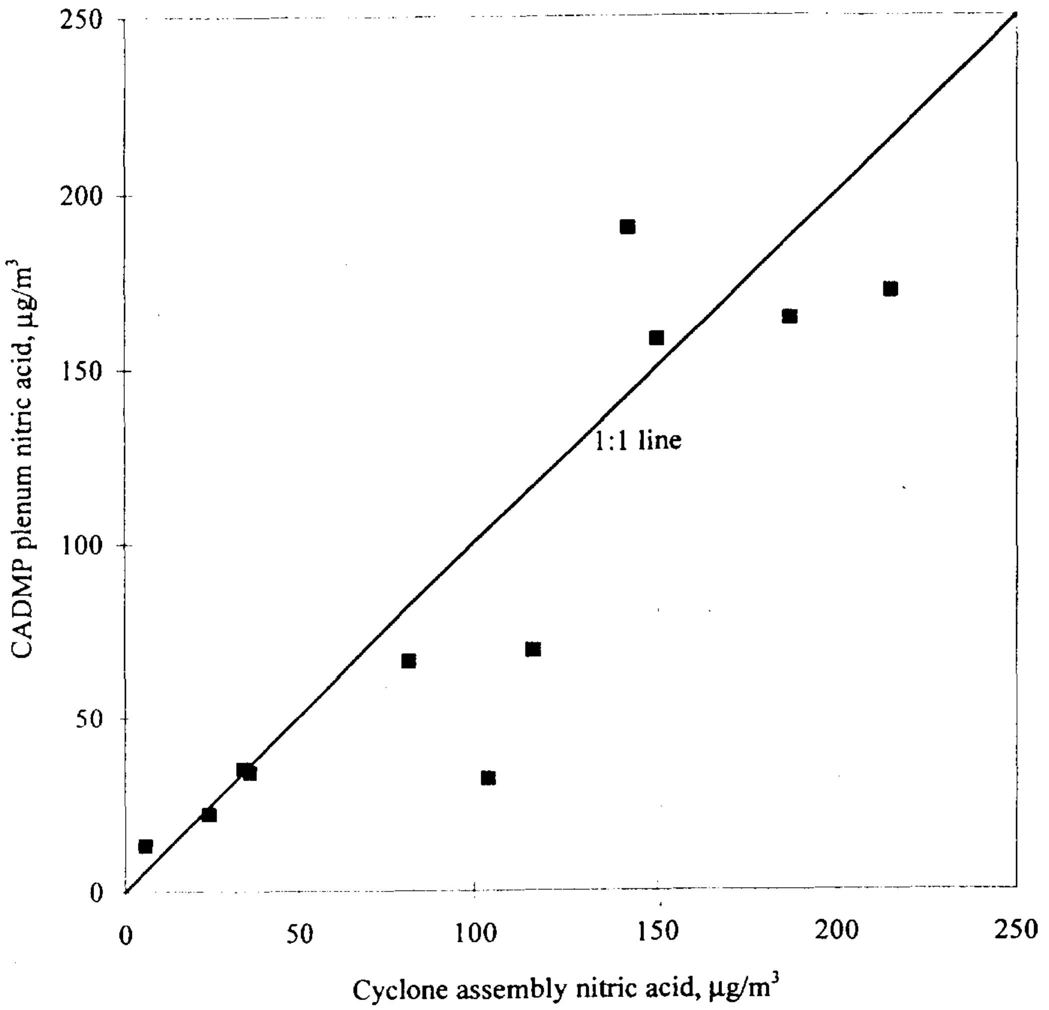


Figure 3-21 Filter-based laboratory nitric acid, CADMP plenum vs. cyclone assembly outlet (position 3 vs. position 2)

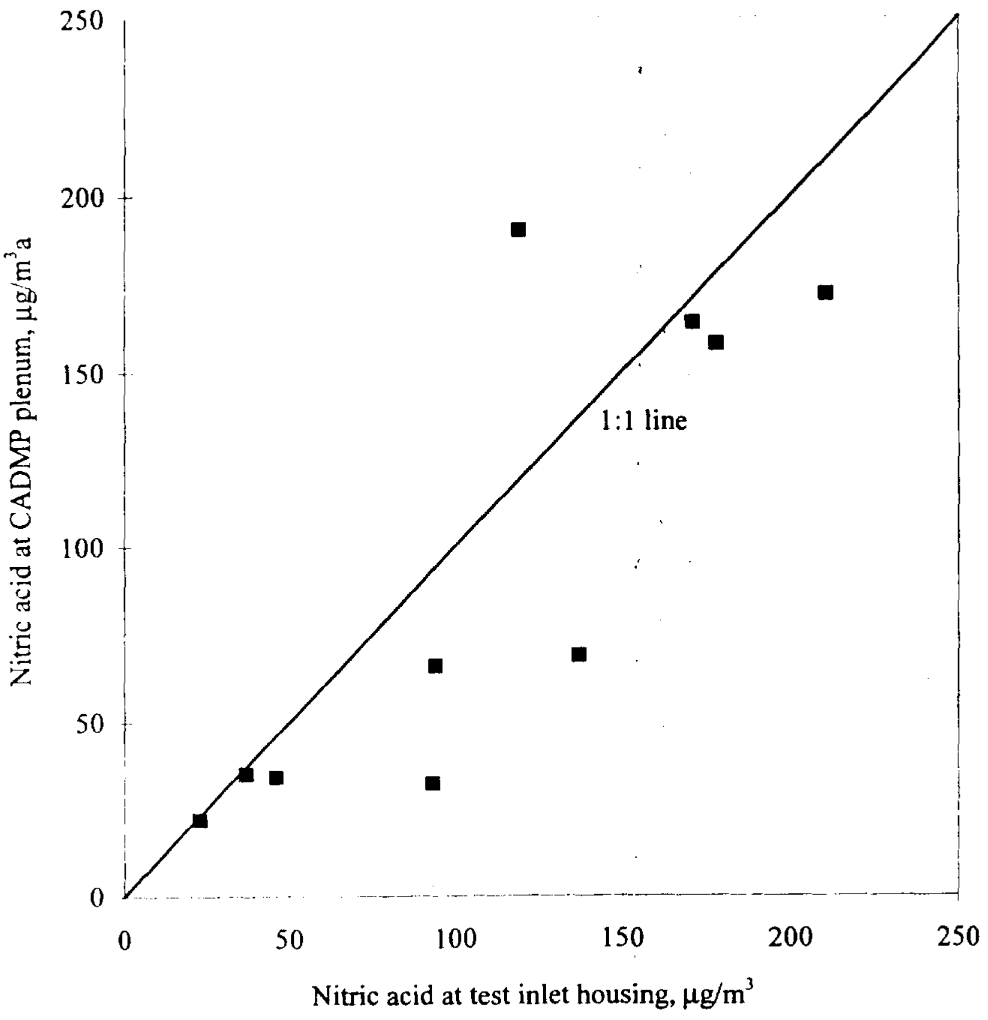


Figure 3-22 Filter-based laboratory nitric acid, CADMP plenum vs. test inlet housing (position 3 vs. position 1)

- The dynamic blanks show nitric acid is still being desorbed from the cyclone assembly and CADMP plenum. When the denuders were working properly virtually no nitric acid was observed after them.

- No statistically significant loss of nitric acid occurred between the test inlet housing and the cyclone assembly outlet or between the cyclone assembly outlet and the CADMP plenum outlet . The loss of nitric acid from the test inlet assembly to the CADMP outlet showed a statistically significant loss of nitric acid of approximately 15%, near the estimated uncertainty of 12%.

- While the penetration of nitric acid through the cyclone assembly and CADMP plenum are in good agreement with the daytime field evaluations, it is not sure if this is a valid comparison or not since we waited for the nitric acid concentrations to stabilize in the laboratory while the changing temperature and humidity conditions in the field may not allow this to happen. The changes of the environmental factors under field conditions could have been slow enough for nitric acid concentrations, on the average, to appear to be at equilibrium, although always lagging the changes in temperature and relative humidity. Sampling total losses through the system most likely produced a larger, and therefore more quantifiable, change in nitric acid concentration than separate component analysis for both the field and laboratory studies.

3.3.1.3 PAN Penetration

Objective and Approach

The objective of this study was to determine whether PAN was retained by nylon filters, the cyclone assembly, or the CADMP plenum. The approach was similar to that described in the last section, except that a synthetically generated source of PAN was used to expose the test apparatus. PAN concentrations were again monitored with a NO-NO_x analyzer at various positions through the CADMP sampling system.

Unlike the nitric acid measurements, PAN concentration readily stabilized throughout the CADMP sampler in a matter of minutes. Since the NO_x analyzer would readily equilibrate when switched to different sampling positions the concentrations were monitored at various points during the sample collection. The NO_x sampling was conducted during the filter sampling runs at positions B-H shown in Figure 3-12. The NO-NO_x analyzer sampled the test inlet housing (position B in the figure), the outlet of the cyclone assembly (position C), the CADMP plenum outlet (position G), the CADMP plenum outlet, below the nylon filter (position H), and below the filters after the three denuders (positions D, E, and F). The analyzer sampled below the filters at positions 3 and 4A-C since it was not physically possible to sample in front of the filters. At least one analyzer measurement was made at each measurement point during the course of a filter collection run. Nylon filters were collected at positions 1-3 and 4A-C.

Results

Table 3-4 summarizes the blank corrected data from nine filter collections performed under varying concentrations, temperatures, and relative humidities. It is obvious that nylon filters have very little affinity to collect PAN. This is most evident at the measurements below the denuders, which were invariably near the values when the sampler was exposed to zero air. Since significant amounts of PAN were measured by the NO-NO_x analyzer at the outlets of the denuders, it is therefore certain that the filters were exposed to significant PAN concentrations. During the first four runs, which were conducted under warm conditions, it is likely that some outgasing of nitric acid from previous experiments was occurring from the CADMP sampler. This was evidenced by the denuder filter nitrate and NO-NO_x analyzer concentration always being lower than the other sample points within the CADMP. In addition, sample position 6 (the CADMP filter without a denuder) yielded the highest filter-based nitrate concentration for all four runs. This position would be expected to have the highest levels since outgasing would be contributed by all of the components upstream. Finally, after run four, when the temperature was cooled, no significant nitrate was collected by the filters. This is consistent with the CADMP sampler becoming a sink for nitric acid when cooled. These experiments definitively show that for the CADMP sampler, PAN is not an interferent when measuring nitric acid.

Conclusion

Nylon filters do not adsorb significant amounts of PAN nor is PAN retained by the components of the CADMP sampler.

Date	Temp °C	RH %	Test Inlet Housing (Positions 1,B)		Cyclone Assembly (Postions 2, C)		CADMP Plenum (Positions 3,H)		Day Denuder (Positions 4A,D)		Night Denuder (Positions 4B,E)	Blank Denuder (Positions 4C, F)		Plenum Port 7 (position G)
			Analyzer μg/m^3*	Filter μg/m^3	Analyzer μg/m^3*	Filter μg/m^3	Analyzer μg/m^3*	Filter μg/m^3	Analyzer μg/m^3*	Filter μg/m^3	Filter μg/m^3	Analyzer μg/m^3*	Filter μg/m^3	Analyzer μg/m^3*
8/1/95	31	20	123	5	120	5	100	7	118	1	1	100	1	
8/1/95	29	20	53	2	53	4	50	5	45	1	1	45	1	55
8/2/95	30	50	105	4	105	4	90	10	85	3	2	83	2	103
8/2/95	30	50	53	4	53	5	45	12	45	4	2	43	2	
8/3/95	15	50	95	3	100	3	85	4	83	2	1	73	1	95
8/3/95	16	20	105	1	100	2	83	2	83	1	1	75	1	95
8/4/95	15	20	40	1	45	1	38	1	40	1	1	38	1	40
8/7/95	15	50	38	1	38	2	35	2	45	1	1	35	1	35
8/8/95**	15	50	0	1	0	2	13	2	20	1	1	13	1	8
Means w/o blank			76.4	2.6	76.8	3.3	65.8	5.4	68.0	1.8	1.3	61.5	1.3	70.5
Std. Dev. w/o blank			30.5	1.4	29.6	1.4	24.1	4.3	21.4	1.2	0.5	20.1	0.5	30.6

* PAN expressed as μg/m^3 nitrate

** Dymanic Blank

Table 3-4 Summary of Nitrate on Nylon Filters Sampling Synthetic PAN

3.3.2 Component Evaluation

3.3.2.1 Nitric Acid Collection Efficiency and Retention Measurements

Results for the penetration of nitric acid through the $PM_{2.5}$ cyclone are shown in Table 3-5. For the 'dirty' cyclone, the experiments to measure nitric acid penetration under warm, dry conditions show greater concentrations downstream of the cyclone than on the reference filter. Essentially the 'dirty' cyclone acts as a source of nitric acid. This same cyclone under humid, room temperature conditions appears to be a sink for nitric acid, with penetration efficiencies of 31% to 45% as measured by the second and third of the high humidity experiments (Run Nos. 5 and 6). The results from Run No. 4, when the temperature was first lowered and the RH raised, gives an intermediate value for nitric acid penetration between a source and a sink.

Results from the 'cleaned' cyclone, also shown in Table 3-5, never shows the cyclone as a source of nitric acid. The initial experiment done after cleaning the cyclone shows only 30% penetration under hot dry conditions. However, a subsequent experiment for hot, dry conditions yield 91% penetration of nitric acid. For humid conditions the penetration drops to 75 ± 8%.

Results from the testing of denuders are given in Table 3-6. For all conditions tested, the denuders that had been used for sampling for over two years acted as a source rather than a sink for nitric acid. Downstream nitric acid concentrations are as high as 500 $\mu g/m^3$, or as much as a factor of 10 greater than the input nitric acid concentration. In contrast, the penetration of nitric acid is low through the 'blank' denuder, that is the denuder which had simply sat in the sampler box without ambient air being pulled through it. While the unused 'blank' denuder behaved as expected, the results for used denuders were unexpected. Further experiments would be needed to fully understand the processes involved. However, it is clear that the denuders used in the field eventually act as a source of nitric acid, analogous to the 'dirty' cyclone results described above.

The pertinent results from the nitric acid penetration experiments are summarized as follows:

- Laboratory testing of the nitric acid penetration showed satisfactory performance for clean cyclones and for the 'blank' denuder that had not been used for ambient sampling.

- Denuders and cyclones which had been used for routine operations in the field for a period of two years without cleaning performed poorly. Both denuders and cyclones appeared to release previously deposited nitric acid.

Run	T (°C)	RH (%)	Δt (min)	Cyclone Flow (lpm)	Reference (μg/m3)	Cyclone (μg/m3)	Penetration (%)
Experiments with "Dirty" Cyclone:							
1	29-34	22-25	35	102	36	136	378
2	25-31	26-37	140	102	33	66	197
3	30-31	26-30	40	101	61	166	272
4	22-23	79-91	33	101	18	13	74
5	22-23	81-96	35	99	11	4	31
6	23-23	54-70	30	101	153	69	45
Experiments with "Clean" Cyclone:							
8	30-33	26-32	45	100	46	14	30
9	28-30	30-35	32	103	47	43	91
10	27-28	73-85	55	103	42	49	115
11	22-23	69-78	65	101	22	18	84
12	22-23	68-87	40	101	22	15	67
Experiments after ammonia exposure:							
13	24-25	74-78	34	101	27	14	51
14	24-25	75-81	52	102	51	47	92

Table 3-5 Cyclone nitric acid penetration results

				Denuder	Reference	HNO3 Downstream of Denuders			HNO3 on Test Filters		Downstream/Reference		
Run	T	RH	Δt	Flow Rate	HNO3	Den#1	Den#3	Den#4	Ny FF	Ny BF		(%)	
ID	(°C)	(%)	(min)	(L/min)	(μg/m3)	(μg/m3)	(μg/m3)	(μg/m3)	(μg/m3)	(μg/m3)	Den#1	Den#3	Den#4
15	27-30	28-33	33	19 - 21	39	264	115	2	27		676	294	5
16	30-40	18-28	55	18 - 21	2	271	52	1	9				
19	25-26	35-36	30	21 - 22	40	520	368	5	36	0	1288	911	11
20	27-41	16-39	110	16 - 25	0	8	49	3		2			
21	24-25	59-79	40	20 - 23	33	467	165	6	34	0	1410	500	19
22	20-23	37-45	85	19 - 27	2	75	38	4		0			
23	21-22	82-99	37	19 - 21	22	135	235	4	33	1	616	1078	19
24	21-26	38-51	60	20 - 20	4	231	128	6		1			
25	24-26	33-39	55	18 - 21	2	150	157	18		2			

Key:

Den#1= Denuder used for daytime sampling
Den#3= Denuder used for night time sampling
Den#4= Denuder on blank leg, not used for sampling
Ny FF= Front filter on test nylon filter pack
Ny BF= Back filter on test nylon filter pack
Reference HNO3= Nitric acid measured on reference nylon filter

Table 3-6 Measured nitric acid concentration and penetration from laboratory testing of CADMP denuders and nylon filters

From these experiments, it is concluded:

- The anodized aluminum surfaces of the denuders, as well as the dust-lined surfaces of the 'dirty' cyclone, appear to act like a chromatographic column, first retaining and then releasing nitric acid.
- The CADMP samplers require regular maintenance for collection of reliable nitric acid data. These were specified in the Field Operations Manual (Bowen et al., 1990), but apparently not followed.

3.3.2.2 Particle Collection Characteristics of $PM_{2.5}$ Cyclone

3.3.2.2.1 Cyclone Collection Efficiencies

The measured upstream and downstream aerosol concentrations and the calculated penetration as a function of aerodynamic particle diameter for the ungreased and greased cyclones (both were cleaned) are shown in Figure 3-23. The standard deviation of each of the average frequency distributions, N_d and N_u, used to calculate P in equation #2, was estimated from the time variation of the one-minute samples used in each average. This was done in a manner that accounts for the effect of the smoothing process. The error limits for P of $\pm$ two standard deviations shown in Figure 3-23 were calculated by propagation of errors from the calculated uncertainties in the N values.

The penetration through the ungreased cyclone is compared to that of the greased cyclone in Figure 3-24 as a function of aerodynamic diameter. The 50% cutpoint is 2.35 ± 0.16 µm for the clean cyclone and 2.57 ± 0.13 µm for the greased cyclone, in good agreement with each other and within the expected value of 2.5 µm.

In fact, the two penetration curves are in agreement within experimental error up to approximately 4.5 µm. Above 4.5 µm, there is indication that more particles penetrate the clean cyclone than the greased cyclone.

3.3.2.2.2 Particle Reentrainment

The time-dependence of particle penetration through the cyclones above threshold sizes of 3 to 4 µm is shown in Figure 3-25. For the greased cyclone, these penetrations are essentially constant showing no significant trends as a function of time. For the clean cyclone, the penetrations for each of the threshold diameters start off comparable to the average

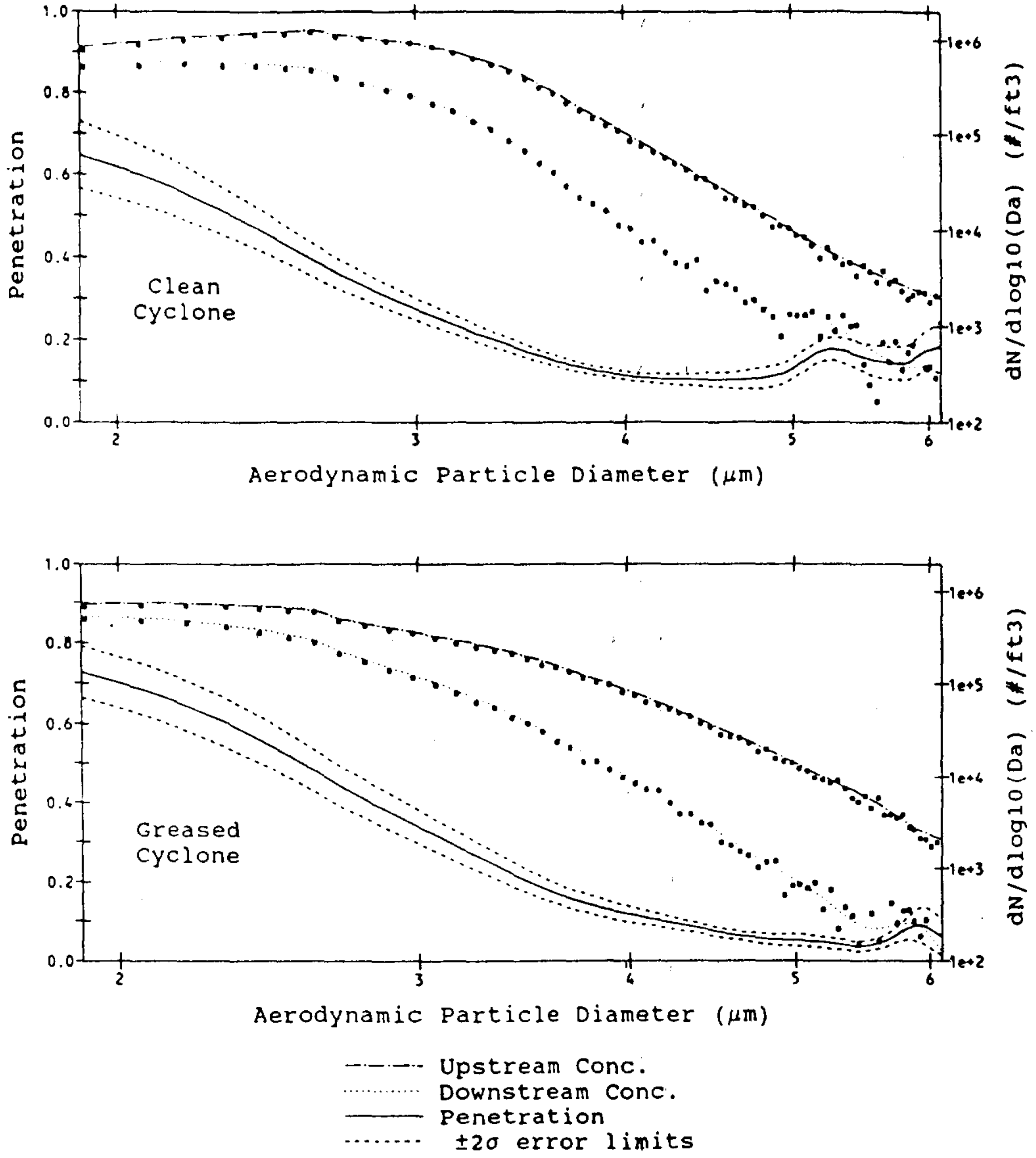


Figure 3-23 Upstream and downstream particle concentrations (solid circles) and corresponding particle penetration values (solid lines) for cleaned and greased cyclones

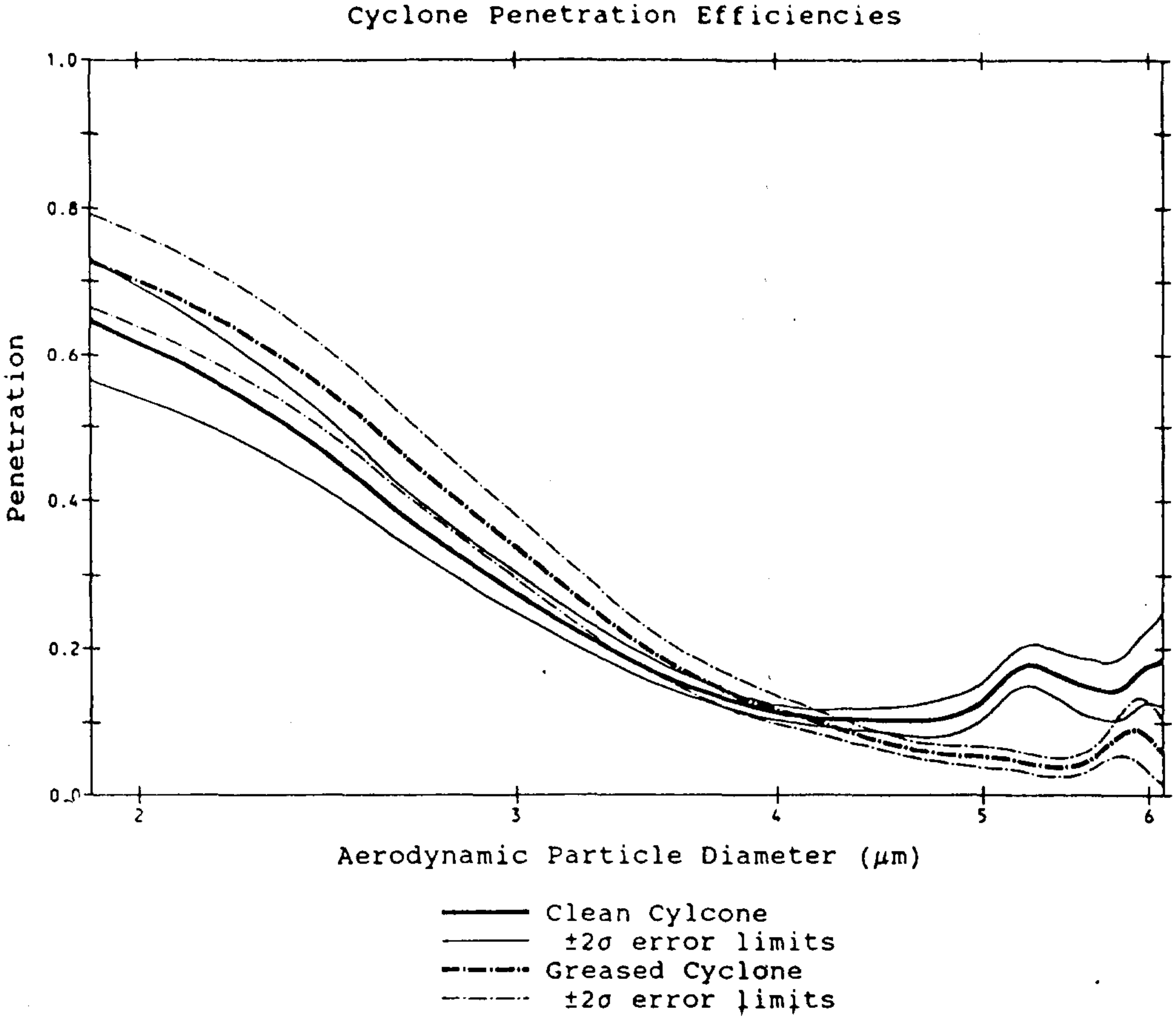


Figure 3-24 Particle penetration for cleaned and greased cyclones, showing 2σ error limits from counting statistics

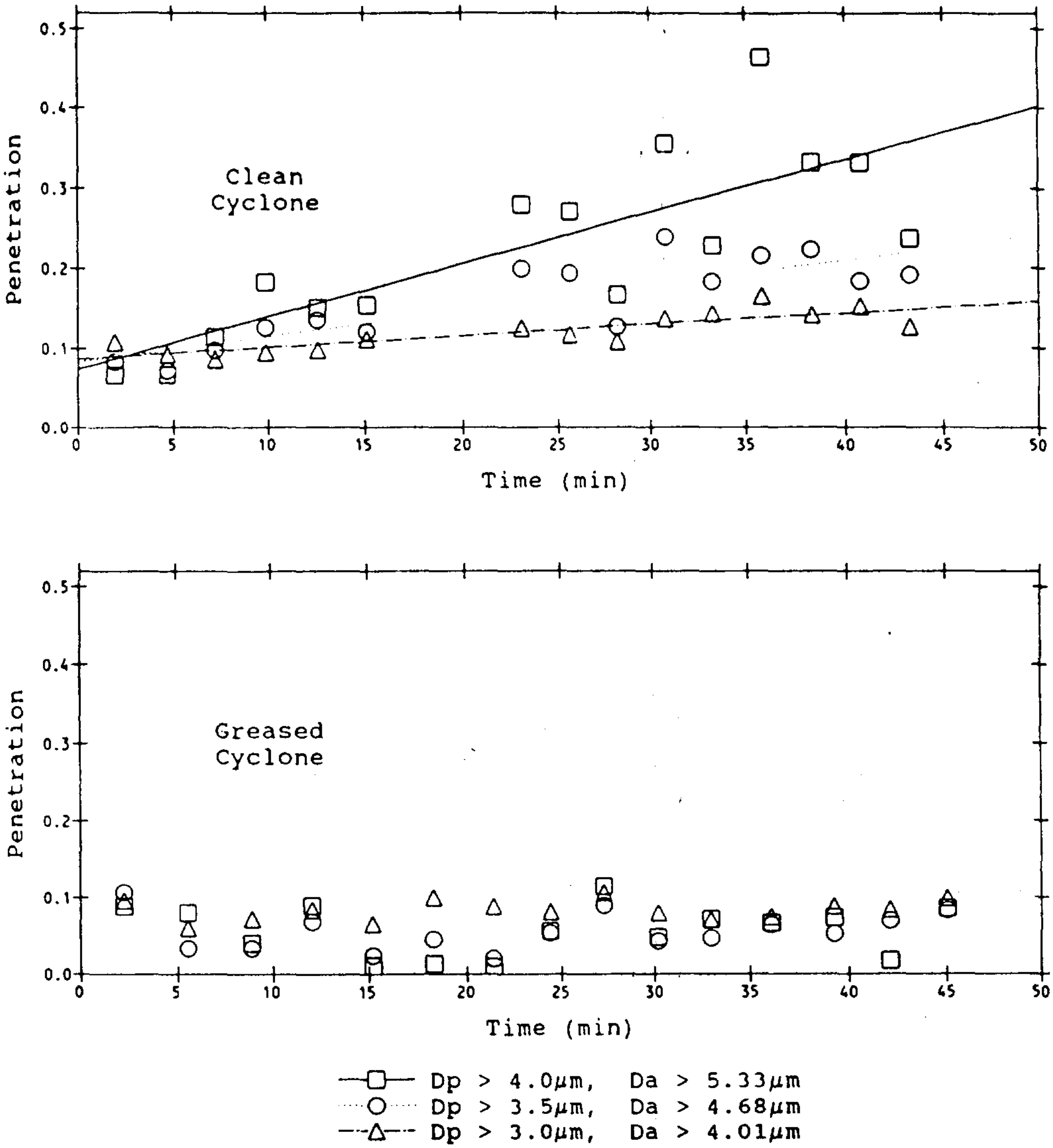


Figure 3-25 Particle penetration in clean and greased cyclone as a function of run time for particles above threshold diameters of 3μm, 3.5μm and 4μm

penetrations for the greased cyclone but increase significantly as time passes. The input concentration to the cyclone is essentially constant during this time so the only thing that is changing in the cyclone is the accumulated collected particle load.

It is postulated that the apparent increase in penetration of large particles over time is actually caused by shedding of particles from an increasing particle load. Let N_u' be the number of particles larger than D_p entering the cyclone per unit time (input rate) and let $P_>$ be their penetration. Then $(P_>)\cdot N_u'$ is the output rate, $(dP_>/dt)\cdot N_u'$ is the shed increase rate and $(1-P_>)\cdot N_u'$ is the net load increase rate. The ratio of the last two quantities, $(dP_>/dt)/(1-P_>) = k_s$, represents the fraction of load shed per unit time. If k_s is independent of $P_>$ then half of a given load (ignoring added load) would be shed in time $T_{1/2} = \ln(2)/k_s$. Figure 3-24 shows linear fits to the $P_>$ vs. t data for the clean cyclone and Table 3-7 shows the parameters of these fits and the corresponding calculated fractional load shed rates and load half-lives.

Table 3-7. Fractional Particle Load Shed Rates and Load Half-Lives for the Ungreased Cyclone while Sampling Particles.

$D_{p,min}$ (μm)	$D_{a,min}$ (μm)	$P_>(t_{mid})$	$dP_>/dt$ (min^{-1})	k_s (min^{-1})	$T_{1/2}$ (min)
4.0	5.33	0.222	6.56×10^{-3}	8.43×10^{-3}	106
3.5	4.68	0.157	3.27×10^{-3}	3.88×10^{-3}	212
3.0	4.01	0.120	1.43×10^{-3}	1.63×10^{-3}	484

Key:

$D_{p,min}$ = threshold geometric particle diameter
$D_{a,min}$ = aerodynamic diameter of threshold
$P_>(t_{mid})$=penetration of particles greater than threshold diameter at midpoint time
$dP_>/dt$ = rate of change of penetration $P_>$
k_s = fraction of load shed per min
$T1/2$ = inferred half life of particle deposited within cyclone.

To examine whether the shed of particles results from airflow though the cyclone, or from particles entering the cyclone, shed rates were examined for sampling particle free air. After collecting particle penetration data for approximately 45 minutes, the aerosol nebulizer excitation circuit was turned on while maintaining constant flows. After about 8 minutes, upstream and downstream 'background' concentrations were measured for another 11 minutes for accumulated total sampling times of 3-5 minutes each. The upstream background concentrations did not go to zero, perhaps as a result of particle shedding from the aerosol transport tubes.

After turning off the nebulizer the concentration of particles for D_p>4 mm decreased by about a factor of 4 and concentrations of smaller particles decreased by much greater factors. The upstream background concentrations for the two cyclones were essentially the same but the downstream background concentrations of large particles for the clean cyclone were significantly higher, possibly indicative of continuing particle shedding from the cyclone.

Estimates of the particle shed rate in the ungreased cyclone before and after the nebulizer was turned off are shown in Table 3-9 for the same three size classes as in Table 3-7. In this table N_d' is the number of particles larger then D_p exiting the cyclone per unit time where the subscripts C and G are for the ungreased and greased cyclones, respectively. The subscript *b* refers to background counts measured while sampling particle-free air. $N_{d,C}'$ represents the clean cyclone output rate just before the nebulizer was turned off as estimated from the linear fits to the penetration data in Figure 3-24. The other output rates, $N_{d,G}'$, $N_{db,G}'$ and $N_{db,C}'$, were relatively constant over time and were calculated as averages over all appropriate one-minute samples. If it is assumed that the greased cyclone behaves the same as the clean cyclone, except without shedding, then $N_{d,C}'$ and $N_{d,G}'$ represent particles penetrating the same cyclone with and without shedding, respectively. Their difference, $N_{d,C}'-N_{d,G}' = N_{s,C}'$, therefore represents the clean cyclone shed rate just before turning off the nebulizer. Similarly, $N_{db,C}'-N_{db,G}' = N_{sb,C}'$ represents the clean cyclone shed rate after turning off the nebulizer.

Though the load of collected particles in the clean cyclone was essentially the same just before and after turning off the nebulizer, the shed rates as shown in Table 3-8 decreased by factors ranging from 2.8 to 4.3. It should be noted that these numbers are based on OPC count rates which are about 20 times less than those shown in Table 3-8 and therefore have substantial uncertainties due to Poisson statistical fluctuations.

These data suggest that the particle shedding is, at least in part, associated with the cyclone input aerosol concentration. Previously collected particles may be knocked off the collection surface by large particles impacting on the surface. As noted above, the cyclone input concentration of particles for D_p > 4 mm decreased by a factor of about 4 when the nebulizer was turned off. This factor is in line with the decrease in shed rate. Estimates of the rate of impaction of particles greater than D_p on the cyclone collection surface are shown in Table 3-9.

Table 3-8. Comparison of the Downstream Particle Count Rates for Sampling Particle-Laden and Particle-Free Air.

$D_{p,min}$ (μm)	$D_{a,min}$ (μm)	$N_{d,C}'$ (#/min)	$N_{d,G}'$ (#/min)	$N_{s,C}'$ (#/min)	$N_{db,C}'$ (#/min)	$N_{db,G}'$ (#/min)	$N_{sb,C}'$ (#/min)
4.0	5.33	512	89	424	184	33	151
3.5	4.68	884	272	612	269	72	198
3.0	4.01	2674	1536	1138	437	176	262

Key:

$D_{p,min}$ = threshold geometric particle diameter

$D_{a,min}$ = aerodynamic diameter of threshold

$N_{d,C}'$ = Particles per minute measured downstream of clean cyclone with particles generator on

$N_{db,C}'$ = Particles per minute measured downstream of clean cyclone with particles generator off

$N_{d,G}'$ = Particles per min. measured downstream of greased cyclone with particles generator on.

$N_{db,G}'$ = Particles per min. measured downstream of greased cyclone with particles generator off.

Table 3-9 Comparison of Cross-sectional Area of Impacting Particles to Deposit Area within the Cyclone.

$D_{p,min}$ (μm)	$D_{a,min}$ (μm)	N_u' (#/min)	N_i' (#/min)	A_i' (cm^2/min)	A_i'/A_c (min^{-1})
4.0	5.33	1.42×10^3	1.40×10^3	2.77×10^{-4}	8.87×10^{-6}
3.5	4.68	3.90×10^3	3.75×10^3	5.28×10^{-4}	1.69×10^{-5}
3.0	4.01	1.78×10^4	1.64×10^4	1.53×10^{-3}	4.91×10^{-5}

Key:

$D_{p,min}$ = threshold geometric particle diameter

$D_{a,min}$ = aerodynamic diameter of threshold

N_u' = particle count rate upstream of cyclone

N_i' = number of particles per minute depositing in cyclone

A_i' = cross-sectional area of particles deposited per minute

A_c = area inside cyclone exit tube

The impaction rate in the clean cyclone is estimated as the input rate times the collection efficiency neglecting shedding. The latter quantity is approximated as 1 minus the size-dependent penetration through the greased cyclone. For particles larger than D_p, N_u' is the number input rate for the clean cyclone, N_i' is the number impaction rate, and A_i' is the particle cross sectional area associated with N_i'. Most of the aerosol in the cyclone was observed to collect on the inner surface of the smaller diameter exit tube with calculated surface area $A_c = 31.2$ cm^2. The ratio A_i'/A_c is then an estimate of the fraction of the cyclone collection surface covered by aerosol per unit time. This is noted to be several orders of magnitude smaller than the calculated values of k_S (Table 3-7) which represent the fraction of collected aerosol shed per unit time. Thus, if particle knock-off is the primary mechanism of particle shedding, then either large particles can be knocked off by much smaller particles or incoming large particles knock off collected large particles from an area of the collection surface several orders of magnitude greater than their own cross-sectional area.

The particle shedding could be significant in the field performance of this cyclone. The loading within the cyclone for these experiments for which shedding is observed was approximately 280 μg of particles. In contrast, the cyclone would collect over 100 mg of particulate matter over two years of every sixth day sampling. (A depositing coarse particle concentration at 10 $\mu g/m^3$ sampled at 0.1 m^3/min over 120 days yields 170 mg of particle deposit). Thus the amount of deposit within the cyclone for which shedding was observed in the laboratory is several orders of magnitude smaller than would be expected for a year of field operations in the CADMP network.

The experimental results show the following:

- Ungreased and greased cyclones performed the same within experimental uncertainty for particles with aerodynamic diameters less than about 4.5 μm.
- After operating for a period of time, the ungreased cyclone large particle net collection efficiency begins to drop, possibly because previously collected particles were being knocked off by incoming large particles impacting on the collection surface.

It is noted that the laboratory measurements from which these results were obtained were conducted with the axis of the cyclone oriented horizontally. It is not known whether these results would be affected by a change in the cyclone orientation.

It is concluded:

- Regular cleaning of the cyclone is needed to prevent re-entrainment of previously deposited particles.

3.4 Reconciliation with Previous CADMP Evaluations

3.4.1 CADMP Original Evaluation

Some evaluation of nitric acid penetration through the PFA Teflon-coated cyclone was conducted by the Desert Research Institute (DRI) of the University of Nevada in Reno during the development of the sampler, but was not reported. This was a non-systematic test to identify potential problems, since the components of the design had been previously studied and reported (Watson, 1996). The results were summarized by Ashbaugh (1994b). In the final configuration, with all Teflon-coated surfaces treated with a solution of dilute nitric acid, the nitric losses ranged from 0-10%. Extensive evaluation was outside of the DRI project scope, and variations with temperature and relative humidity were not quantified (Watson, 1996). The results of approximately 15% loss of nitric acid obtained from both laboratory and field evaluations on a sampler that had been used for more than a year in the field were in good agreement.

3.4.2 1993 TDLAS Comparison

A study to compare nitric acid measured using the Azusa primary and collocated samplers with a tunable diode laser absorption spectrometer (TDLAS) was conducted at Azusa in October 1993. The results of this study were briefly reviewed in an informal report (Ashbaugh and Motallebi, 1994). The number of data points collected in this study is limited due to changing variables ('as is' vs. reconditioned and alternating 'daytime' and 'nighttime' denuders) and missed data due to replumbing, reconditioning, and other reasons.

This study used the Azusa primary CADMP both in 'as is' and, later in the study, in 'reconditioned' states. The 'as is' condition, as far as could be determined, implied that cleaning or reconditioning had been implemented since installation five years ago. The collocated sampler had been reconditioned in late 1992 and installed at Azusa for collocated weekly sampling over a two month period prior to the study.

While the data set was too small for a quantitative comparison of data, four important qualitative conclusions could be drawn from the data presented:

- The CADMP nitric acid measurements were 20 to 70% of the TDLAS measurements, even after the primary sampler was reconditioned. More striking was the large variability between the two measurement methods.

- The primary CADMP nitric acid measurements, before or after reconditioning in October 1993, were similar to those of the reconditioned collocated sampler during this study.

- No major differences were observed as a function of denuder history and, therefore, total exposure to nitric acid. These denuders ranged from the most exposed (primary 'daytime'), to virtually unexposed (the primary 'blank'), and to reconditioned.

- A bias existed between the particulate nitrate measured by the primary and collocated samplers in Azusa prior to the TDLAS comparison study. The primary sampler always showed higher particulate nitrate, especially in the daytime. This would be indicative of nitric acid penetrating the denuder, to be monitored as particulate nitrate. This is supported by the diurnal pattern, since daytime concentrations of nitric acid are higher than nighttime. This bias may not have been observed during the October study when temperatures were lower, and, as shown from our laboratory evaluations, the denuder may function more efficiently

DRI evaluation of the new CADMP samplers indicated 90-100% penetration of nitric acid. Our experiments have shown that about 85% of the nitric acid was available to the total nitrate filter pack in the collocated Azusa sampler a year after the TDLAS comparison study. It was determined that the denuders for the collocated CADMP were still functioning with over 90 per cent efficiency in both field and early laboratory evaluations. Thus CADMP should not be biased more than 25% lower than the TDLAS, and this should be a relatively consistent bias. There are a variety of reasons to explain the bias between the CADMP sampler and the TDLAS:

- Additional losses of nitric acid may have occurred in the CADMP due to the temperature and relative humidity conditions at the time of sampling.

While it has shown dependence in the laboratory, our field evaluation (also in October) did not indicate such losses. The data analysis by Tuazon et al. (1995) also did not support this.

- The TDLAS values are biased high.

The TDLAS could be high due to calibration techniques or volatilization of particulate nitrate. A calibration problem was encountered with the purity of the water used, but this was apparently resolved in the final data set. Our more recent comparison with the FTIR in Claremont does show the TDLAS to be higher. If, however, this bias was caused by adsorption/desorption occurring on the Teflon prefilter of the TDLAS, the magnitude of the bias would depend on the specific sampling conditions (such as temperature profiles, nitric acid concentration & ammonia concentration) and could not be applied to the Azusa study.

There is potential for volatilization of nitrate from the Teflon filter used on the inlet system of the TDLAS, the well known volatilization artifact. These filters were changed daily, but the time of day they were changed would be important for effect of volatilization on the measurements. If, for example, they were changed in the early morning, there would be little immediate difference in the TDLAS measurement since temperatures are relatively cool and volatilization would be slow. The situation could be quite different by early afternoon.

Tuazon et al. (1995) did not find evidence of particulate nitrate volatilization based upon diurnal profiles of nitric acid, PAN, and ozone which did not show nitric acid 'trailing'. All of these species generally follow a diurnal pattern similar to temperature, therefore the lack of 'trailing' may not rule out volatilization of particulate nitrate during the day on the TDLAS Teflon filter. The equilibrium of ammonium nitrate with gaseous ammonia, and nitric acid with temperature would be established on a time scale of minutes. The examination of ozone, PAN, and nitric acid diurnal profiles to determine volatilization of nitrate from filters is an indirect approach. It is well known that particulate nitrate is volatilized from Teflon filters to release nitric acid (Forrest et al., 1982). This is the reason that the denuder approach is needed in the first place. This volatilization artifact could be estimated directly using the CADMP data by subtracting the nitrate on the Teflon filter from the nitrate on the nylon filter below the denuder; this difference would be a measure of the particulate nitrate that volatilized from the Teflon filter.

As pointed out by Tuazon et al. (1995) there could be local pollutants which would bias the TDLAS high due to a spectroscopic interference, yet not be retained by nylon filters. These pollutants would therefore not interfere with the CADMP nitric acid measurement. Such pollutants could be either local emissions or more regional pollutants which are specific for the Azusa area.

- The CADMP measurements are low due to leaks in the sampler or filter cassettes.

Presumably careful flow checks were made to minimize these problems. Leaking cassettes are a particular problem unless the flow at the cassette inlet is checked each time they are used. While this could explain some of the anomalously low values when comparing the two CADMP samplers, it is unlikely that both samplers would have similar and chronic leakage problems.

- The nitrate measured on the CADMP filters are biased low due to the analytical method.

There is potential for losses of nitrate during storage and shipment. Presumably during this special study all samples were immediately refrigerated after sampling until extracted in the laboratory (this is not the case for the routine CADMP samples). Recovery of nitrate from filters can be problematic if published protocols, which have been well developed, are not followed. Conversations with the MLD analyst have indicated that proper protocols are in place. Presumably the MLD laboratory has also been subjected to round robin evaluations using ambient samples.

4.0 SUMMARY AND CONCLUSIONS

4.1 Summary

Audits of the Azusa CADMP Samplers

The flow rates of the primary and collocated Azusa CADMP samplers were independently measured and found to be within a few percent of that expected by the site operator. The visible portions of the sampler's interior were noticeably dirty.

Filtered Ambient Air Evaluation of Nylon Filters

The efficiency of nylon filters to collect nitric acid and other nitrogenous species was assessed using a filterpack consisting of a Teflon front filter and two nylon back filters. For samples collected in Riverside about 25% of the nitrate was found on the first back filter, indicating either collection inefficiency for nitric acid or adsorption of an interfering nitrogenous species. Collocated sodium chloride-coated filters collected less nitrate than the nylon filter (with very little nitrate on the second filter or third backup filters; this indicated high collection efficiency), therefore an interferent was suspected. Peroxyacetyl nitrate (PAN) was later shown not to collect on nylon filters so nitrous acid was the likely interferent. For the Claremont samples, the nitrate on the second nylon filter was less than 10% of that on the first, suggesting a mix of pollutants different from that of the Riverside sampling.

Filtered Ambient Air Evaluation of the Losses of Nitric Acid Through the CADMP

Ambient air at Azusa was used as a source of nitric acid by removing particles with Teflon filters. The Azusa collocated CADMP sampler was used and nitric acid was sampled with nylon filters at four locations: (1) within the inlet housing, (2) between the cyclone and the CADMP sampling plenum, (3) at the exit of the CADMP sampling plenum, and (4) at the outlet of the denuder. The Azusa sampler had been used for a year since being refurbished. A series of 12 hour samples was collected for both daytime (6 am-6 pm) and nighttime (6 pm-6 am) intervals during periods of moderate air pollution (peak ozone of approximately 0.10 ppm). While the nighttime results were inconclusive due to low nitric acid concentrations, the daytime samples showed nitric acid losses of approximately 15% through the cyclone and plenum, while the denuder efficiency was over 90% (losses of nitric acid through the cyclone and plenum separately were within the experimental uncertainty).

Laboratory Evaluation of the Penetration of Nitric Acid Through the CADMP

Synthetically generated nitric acid was used to evaluate nitric acid penetration through the Azusa collocated CADMP sampler under a variety of concentrations, temperatures, and relative humidities. Nitric acid was measured at the locations described in the filtered air experiment with both a NO-NO_x analyzer and nylon filters.

- Measurement of Nitric Acid With a NO-NO_x Analyzer

The NO-NO_x analyzer allowed real-time concentration measurement. This feature lead to the discovery of significant temporally changing sorptive properties of nitric acid to the PFA Teflon-coated aluminum surfaces of the sampler as a function of temperature, relative humidity, and previous nitric acid sampling history. PFA Teflon-coated surfaces (including those of the CADMP cyclone assembly and plenum) were found to adsorb nitric acid when the temperature was lowered or the humidity raised, and to release nitric acid that had been adsorbed when the temperature was raised or the relative humidity lowered. All three of the denuders were found to be approximately 90% efficient in removing nitric acid.

- Measurement of Nitric Acid With Nylon Filters

The penetration of nitric acid through the sampler was evaluated by allowing the nitric acid concentration to equilibrate prior to filter sampling; a process that would often require many hours to days. The filtration results, under these conditions, were similar to those for filtered ambient air, with the cyclone assembly and CADMP plenum passing about 85% of the nitric acid. The denuders were originally over 90% efficient in removing nitric acid, but suddenly lost much of their efficiency. This was most likely due to the long exposure times needed to achieve concentration equilibrium.

Laboratory Evaluation of the Penetration of Nitric Acid Through the CADMP

The penetration of nitric acid through the sampler and nylon filters was evaluated in the laboratory using the synthetically generated PAN. Measurements of PAN were made at the sampling positions discussed above with a NO-NO_x analyzer. Nylon filters were simultaneously collected. PAN did not exhibit the surface losses observed for nitric acid using the NO-NO_x analyzer nor was it retained by nylon filters.

Comparison of Nitric Acid Measured with a CADMP Sampler Compared to a TDLAS

Nitric acid measurements obtained with the Azusa primary CADMP were compared to those of a TDLAS and FTIR during a 28-day study in August-September at Claremont. The correlation of nitric acid concentrations between the CADMP and the TDLAS was less than 0.36 and the CADMP was, on average, four to eight times lower. In addition, many values, even in the daytime sampling period, were at or below zero. This is evidence that the denuders had lost significant efficiency, which was further supported by the laboratory evaluation.

Laboratory Evaluation of Nitric Acid Penetration Through CADMP Components

- Cyclone Assembly

The cyclone inlet assembly and denuders from the primary Azusa CADMP were then evaluated in the laboratory for nitric acid penetration using synthetically prepared nitric acid. Sampling was done before and after each component with nylon filters. These components were tested in the same way as after the Claremont sampling and no attempt was made to monitor the concentration until equilibration was achieved. Under warm, dry conditions the cyclone inlet assembly behaved as a source of nitric acid, with the concentration at the outlet over twice that of the laboratory source. When tested under cool, moist conditions the nitric acid penetration ranged from 31 to 74%. These tests were re-run after cleaning the cyclone inlet assembly and the results showed that after a conditioning run, the penetration of nitric acid ranged from 67 to 115%.

- Denuders

Similar tests were performed on the three denuders used with the CADMP (one for daytime, one for nighttime, and one for field blank collection). While the denuder used to collect field blanks operated with approximately 90% efficiency, the two others were, under all temperature, humidity, and concentration conditions, sources of nitric acid (the outlet concentration was often an order of magnitude higher than the inlet concentration). The denuder as a source of nitric acid would explain the field measurements where the nitric acid concentrations were reported to be negative (more nitrate collected after the denuder compared to without the denuder).

Evaluation of Particle Penetration Through the CADMP Cyclone

The particle collection efficiency of the cyclone was also tested in the laboratory using synthetically generated aerosol. There were only slight differences in cut-points between clean and greased cyclones. When sampling particles greater than the cut-point, the greased cyclone maintained high removal efficiency, while the removal efficiency of the ungreased cyclone became significantly lower after 30 minutes of sampling, which is indicative of particle shedding. If this shedding occurs while sampling ambient air, it is likely to cause a positive artifact in the measurement of fine particulate nitrate and possibly a positive artifact for nitric acid measurements (large particles are more likely to settle within the denuder and contribute to 'apparent' nitric acid).

4.2 Conclusions

We have found that the CADMP sampler, when reconditioned annually and perhaps cleaned more often, maintains high nitric acid penetration and high denuder efficiency. The sampler is therefore useful in measuring nitric acid, although the values will generally be biased 10-20% low due to wall losses and the inefficiency of the denuders to remove all nitric acid and pass all nitrate-containing particulate matter. This bias is typical of all filtration-based methods of measuring nitric acid, although it has been reduced by some of the recent specialized samplers. This study has produced a number of significant findings:

- Laboratory evaluations of nitric acid penetration using either a NO-NO_x analyzer or nylon filters may not be directly comparable to ambient performance due to the ability of nitric acid to adsorb and desorb from the CADMP's Teflon-coated aluminum surfaces as a function of temperature, relative humidity, and exposure history.

- The sorptive properties of the CADMP may bias the measurements, especially during periods of rapid temperature change.

- A NO-NO_x analyzer can be used to determine denuder efficiency quickly on synthetically generated nitric acid.

- Aluminum-based denuders can be exposed to nitric acid under both laboratory and field conditions to the extent that their removal efficiency drops dramatically, and in some cases, may actually become a source of nitric acid.

- It is likely that nylon filters partially collect an unidentified nitrogenous species as nitrate from the ambient air in the South Coast Air Basin. While the effect on the nitric acid measurement has not been determined, it is likely that this artifact contributes to the amount of particulate nitrate measured.

- PAN has been shown not to interfere in the measurement of nitric acid or particulate nitrate when using nylon filters to collect nitric acid.

The sorptive behavior of nitric acid as a function of surface type, temperature, humidity, and exposure history precludes providing any exact correction factor for the nitric acid measured by the CADMP. Thus our original idea of flushing the CADMP sampler with synthetically generated nitric acid in the field and measuring the penetration with a NO-NO_X analyzer is not practical, or even particularly useful, except to measure denuder efficiency. However, it was useful to determine that nitric acid concentrations within the sampler had stabilized.

The denuders of the collocated Azusa CADMP were operating with high efficiency after a year of field use and significant laboratory exposure to nitric acid at concentrations well above that typically encountered in ambient air. This supports the results of the field sampling of filtered ambient air that showed the efficiency for this sampler was over 90%. The denuders can therefore be expected to retain efficiency for at least a year on the CADMP sampling schedule (the CADMP field operations procedure recommends re-anodizing once per year), but is likely to fail over several years at sites with high nitric acid concentrations, such as Azusa. The amount of sampling possible until the CADMP fails may be related to a number of ambient environmental conditions, such as nitric acid concentrations, length of exposure, temperature, humidity, and co-pollutants. For this reason we cannot predict when denuders should be reconditioned, but have shown that annually should be sufficient since Azusa probably represents the highest total exposure of nitric acid in terms of ppm-hours.

The ungreased Bendix 240 cyclones used with the CADMP sampler have nearly identical cutpoints as when greased. Particle shedding was observed with the ungreased Bendix cyclones but not with the greased cyclones. While this has the potential to bias particulate nitrate high, the magnitude of the effect under ambient conditions is not known.

5.0 RECOMMENDATIONS

While the CADMP represented the best compromise for a routine field network using the technology available at the time, recent direct denuder measurement techniques may offer a more accurate measurement of nitric acid and particulate nitrate for future monitoring programs. These include the Two-Week Sampler and shorter term adaptations (Fitz and Hering, 1996), the Harvard annual denuder (Koutrakis et al., 1993) and a new type of denuder currently being developed under ARB funding (Fitz, 1996).

Of particular concern is the sorptive behavior of nitric acid to the Teflon-coated surfaces within the CADMP. While nitric acid penetration was found to be reasonable under the conditions of the evaluations, there are potential pitfalls under other conditions, particularly when temperature and humidity are rapidly changing. Under these conditions an equilibrium concentration may not be maintained.

The following recommendations are suggested should the CADMP remain in service at its current use rate:

- The samplers' interior surfaces should be cleaned annually, and the cyclone cleaned at least quarterly. It has been shown that particle shedding could introduce error in both nitric acid and particulate nitrate measurements and cleaning the cyclone regularly would minimize these errors. The laboratory testing showed that a cleaned cyclone was less likely to be a sink or source of nitric acid.

- New denuders should be installed annually or cleaned and re-anodized as it has been shown that they can fail under ambient conditions. Denuders should be tested in the laboratory before and after use on synthetically generated nitric acid. The 'reconditioning' of the denuders with NaOH may work for a year, but this treatment is not advised based on the failure observed.

- Measuring nitric acid at night may not be useful and its importance should be re-evaluated. The spectroscopic measurements showed that the concentrations were low and it is also likely that under nighttime conditions of temperature and humidity the CADMP's surfaces will become sinks for nitric acid.

- Routine (annual) evaluation of the sampler using filtered ambient air would provide an effective method of quality control.

- The use of nylon filters, though convenient, should be rethought due to the potential artifact collection observed from non-nitric acid species, especially in the South Coast Air Basin. The magnitude of this artifact could be estimated by using nylon filters in series. Alternatively, the use of NaCl-coated filters should be considered since they were shown to collect nitric acid efficiently and did not display the same degree of sampling artifacts as the nylon filters. Perrino et al., (1990) found that these filters did not adsorb nitric acid.

- The 1994 and 1995 Azusa nitrate and nitric acid data should be evaluated to determine when the denuders failed. This could be done by comparison with either the collocated sampler, when available, or from drops in the nitric acid/ozone ratio.

- A particle size separation device less subject to particle shedding should be considered. While shedding was observed with the synthetically generated aerosol, it is difficult to estimate the effect of nitric acid or particulate nitrate on ambient measurements. Particles greater than two μm generally do not contain large amounts of nitrate, but there have been exceptions, especially near coastal areas where sea salt aerosol may be present, or if the source is agricultural or industrial.

6.0 REFERENCES

Appel B.R., Povard V. and Kothney E.L. (1987) Loss of nitric acid within inlet devices for atmospheric sampling. Presented at 1987 EPA/AWMA Symp.: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 3-6, 1987.

Appel B.R., Wall S.M., Tokiwa Y. and Haik M. (1980) Simultaneous nitric acid, particulate nitrate and acidity measuements in ambient air. *Atmospheric Environment,* **14,** 549-554.

Ashbaugh L.L (1994a) Personal communication.

Ashbaugh L. (1994b) Proposed Further Tests of the CADMP Sampler, Informal internal report, California Air Resources Board.

Ashbaugh L.L., Chow J.C. and Watson J.G. (1991) Atmospheric acidity data quality and measurement characteristics for California's acid deposition monitoring program. Paper 91-89.7 Presented at the 84th Annual AWMA Meeting, Vancouver, British Columbia, June 16-21.

Ashbaugh L. and Motallebi N. (1994) CADMP Sampler Comparison with the TDLAS Sampler. Informal internal report, California Air Resources Board.

Blanchard C. (1993a) Comments on validation of the CADMP dry-deposition data. Memo to Nehzat Montallebi dated March 3,1993.

Blanchard C. (1993b) More on validation of the CADMP dry-deposition data. Memo to Nehzat Motallebi, April 9, 1993.

Bowen J.L, Watson J.G., Chow J.G, Egami R.T., Frazier C.A. and Gertler A.W. (1990) Field Operations Manual for the California Acid Deposition Monitoring Program. Final Report California Air Resources Board Contract A6-076-32.

Fitz D.R. (1996) Development and evaluation of a novel diffusion denuder for ambient air sampling. Presented at the Air and Waste Management Association West Coast Section meeting 'Fine Particulate Matter:The New Challenge' Newport Beach, CA, March 6-8.

Fitz D.R. and Hering S.V (1996) Further Evaluation of a Two-Week Sampler for Acidic Gases and Fine Particles. Final Report , California Air Resources Board Contract 93-339.

Fitz D. R. and Zwicker J. (1988) Design and Testing of the SCAQS Sampler for the SCAQS Study, 1987. Final Report California Air Resources Board Contract A6-077-32.

Forrest J., Spandau D.J., Tanner R.L. and Newman L. (1982) Determination of atmospheric nitrate and nitric acid employing a diffusion denuder with a filter pack. *Atmospheric Environment,* **16,** 1473-1485.

Harris G.W., Carter W.P.L., Winer A.M., Pitts J.N. Jr., Platt U. and Perner D. (1982) Observations of nitrous acid in the Los Angeles atmosphere and implications for predictions of ozone-precursor relationships. *Environmental Science and Technology* **16,** 1414-1419.

Joseph D.W. and Spicer C.W. (1978) Chemilumenescent method for atmospheric monitoring of nitric acid and nitrogen oxides. *Analytical Chemistry,* **50,** 1400-1403.

Luhrmann F.W., Roberts P.T., Hering S.V., Avol E.L., and Colome S.D. (1994) Pase II Final Report, Appendix A: Exposure Assessment Methodology. Final Report California Air Resources Board Contract A033-186.

Koutrakis P., Sloutas C., Ferguson S.T., Wolfson J.M., Mulik J.D. and Burton R.M. (1993) Development and evaluation of a glass honeycomb denuder/filterpack system to collect atmospheric gases and particles. *Environmental Science and Technology,* **27,** 2437-2501.

Perrino C., DeSantis F. and Febo A. (1988) Uptake of nitrous acid and nitrogen oxides by nylon surfaces: Implications for nitric acid measurement. *Atmospheic Environment,* **22,** 1925-1930.

Perrino C., DeSantis F. and Febo A. (1990) Criteria for the choice of denuder sampling technique devoted to the measurement of atmospheric nitrous and nitric acids. *Atmospheric Environment,* **24,** 617-626.

Rogers C.F., Watson J.G. and Matrhai C.V. (1989) Design and testing of a new size classifying isokinetic sequential air sampler. *Journal of the Air Pollution and Control Association,* **39,** 1569-1576.

Sanhueza E., Plum C.N. and Pitts J.N. Jr. (1984) Positive interference of nitrous acid in the determination of gaseous HNO_3 by the NO_x chemilumenescence-nylon cartridge method: Applications to measurements of ppb levels of HONO in air. *Atmospheric Environment,* **18,** 1029-1031.

Sickles J.E.II and Hodson L.L. (1989) Fate of nitrous acid on selected collection surfaces. *Atmospheric Environment,* **23,** 2321-2324.

Stephens E.R., Burleson F.R. and Cardiff E.A. (1965) The production of pure peroxyacyl nitrates, *Journal of the Air Pollution and Control Association,* **15,** 87-89.

Tombach I.H., Allard D.W., Drake R.L. and Lewis R.C. (1987) Western Regional Air Quality Studies-Visibility and Air Quality Measurements: 1981-1982. Electric Power Research Institute Document EA-4903, Palo Alto, CA.

Tuazon E. C., Blanchard C.L., Hering S.V., Lucas D. and Mackay G.I. (1995) A Review of Nitric Acid Measurements by Tunable Diode Laser Absorption Spectrometry (TDLAS). Final Report California Air Resources Board Contract 93-300.

U.S. Environmental Protection Agency (1984) Quality Assurance Handbook for Air Pollution Monitoring Systems: Volume I, Principles, Document EPA-600/9-76-005, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC. (December)

U.S. Environmental Protection Agency (1987) Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD). Document EPA-450/4-87-007. Office of Air Quality Panning And Standards, Research Triangle Park NC 27711 (May).

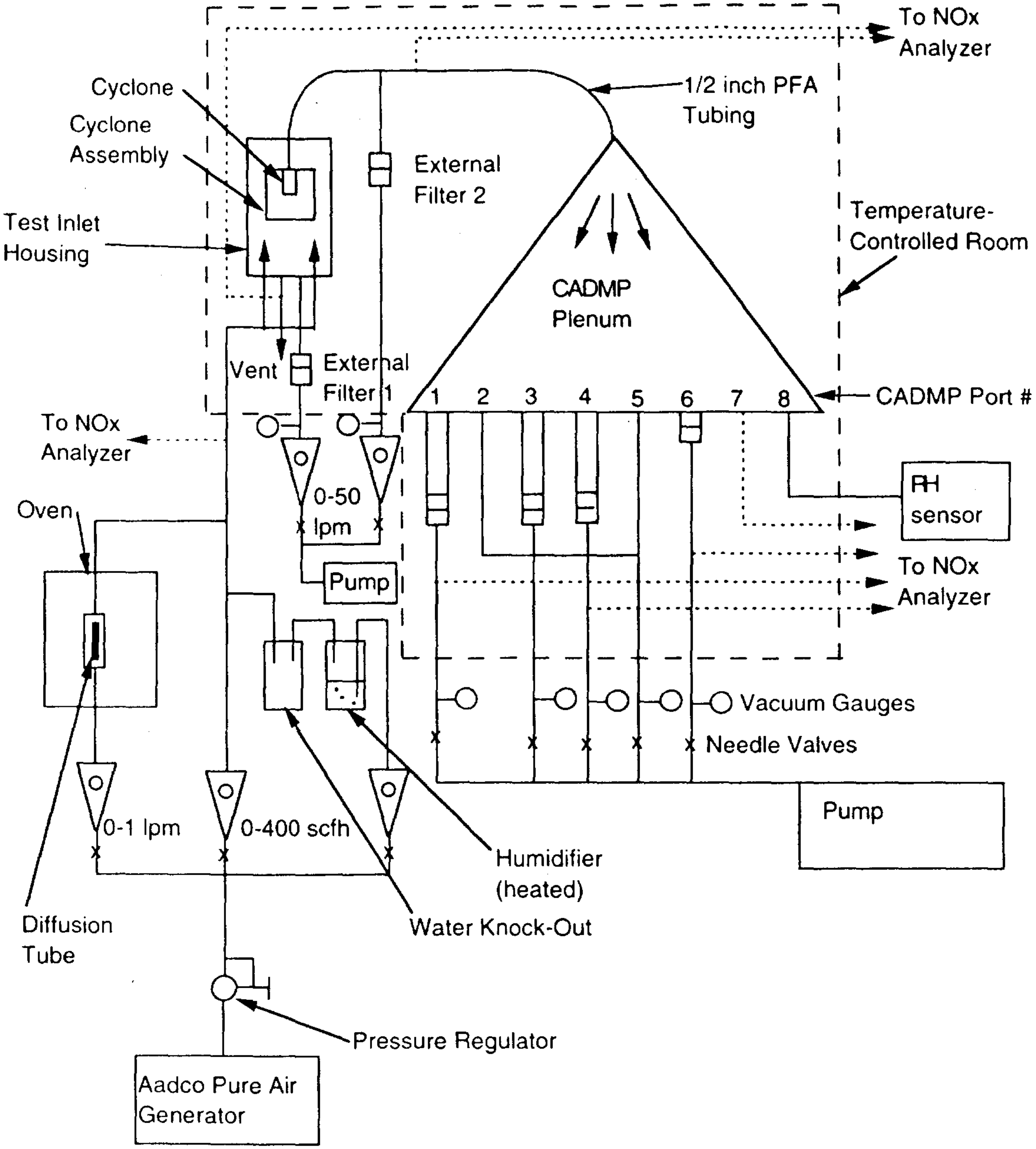
Watson J.G. (1993) Personal communication.

Watson J.G., (1996) Personal communication.

Watson J. and Chow J. (1991) Measurement of Dry Deposition Parameters for the California Acid Deposition Monitoring Program. Final Report California Air Resources Board Contract A6-076-32.

Winer A.M., Peters J.W., Smith J.P. and Pitts J.N. Jr. (1974) Response of commercial chemilumenescent NO-NO_2 analyzers to other nitrogen-containing compounds. *Environmental Science and Technology* **8**, 1118-1121.

APPENDIX A



Schematic Diagram of Apparatus to Perform a Laboratory Evaluation of the Whole CADMP Sampler for Nitric Acid Penetration (for PAN a compressed gas cylinder replaces the diffusion source).

APPENDIX B

Audit at Azusa on CADMP Sampler Performed by CE-CERT

Date: August 16, 1994
Project: RT38
Auditor: K. Bumiller
Site tech: Lee Lewis w/CARB Phone 818-575-6991
Site phone: 818-969-5630
Arrived on site at 08:00 hr.
Left site at 11:30 hr.

Review of site operations:

Cleaning and maintenance:

The primary sampler was lasted cleaned 10/20/93 and the collocated cleaned in Sacramento before being shipped to site for set up and calibration in June of 1993. There is not a fixed scheduled for cleaning or maintenance.

Calibration:

The primary sampler was last calibrated on 10/20/93, while the collocated was last calibrated on 07/20/93. ARB uses mass flow meters, and based on the calibration records provided to the auditor, the flow rates were set directly in standard units and not corrected to volumetric units by applying the temperature and pressure corrections at the time of calibration. The mass flow meters are calibrated by ARB and are traceable to volumetric standards.

Flow checks:

All flows are check before the samples are unloaded and flow are recorded on the field data sheet. After new sample are loaded the sampler, flows are set to the last reference value determined from the last calibration. Samplers are flow-checked once per month with rotameters as cross check of the calibration.

Sample shipping and storage:

Sample filters are prepared by the ARB lab in Sacramento and send to the site operator in filter holders. After sampling, the operator returns the sample to ARB. The samples are not temperature controlled before or after the sample is collected.

Other:

On site meteorological system was not working. There is no maintained or QC program for the meteorological system. The 1/2" line that connects the Cyclone to the sampler was dirty and may have caused a loss of sample.

Site location:

Site is located at the SCAQMD Azusa site. The sampler is located on the roof of a one story industrial building, with a flat roof. The sampler inlet height is 5 meters above ground level. There are many other samplers located on this roof. The surrounding area is a mix of light industrial and residential housing. There is a metal working shop southeast of the sampler inlet at ground level. During the audit the shop activities include metal cutting and welding. The site shelter has a small vent on the roof, apparently for a water heater.

Siting Designation:

The characteristics of the site are consistent with EPA spatial scale of "Neighborhood".

Audit Results:

The audit was conducted using a dry test meter traceable to NIST standards. Flows were timed to the nearest hundredth of a second. Flow rates were corrected by a calibration curve applied to the dry test meter to give actual liters per minute (alpm) and converted to standard units (298°K and 760mm pressure) to give standard liters per minute (slpm). While the details of the audit measurements are provided in the attached spreadsheet, the following tables summarize the comparison of audit measure flows with the reference determined by the site operator (in standard units):

Primary sampler

Port ID	Audit (slpm)	Reference (slpm)	percent difference
Port 1 day	20.1	20.0	0.5%
Port 2 day	34.8	36.5	-4.9%
Port 2 night	35.7	36.5	-2.2%
Port 3 night	20.5	20.0	2.4%
Port 5 day	20.4	20.0	2.0%
Port 6 day	37.0	36.5	1.4%
Port 6 night	36.9	36.5	1.1%
Port 7 night	19.2	20.0	-4.2%
Total day	108.8	113.0	-3.9%
Total night	108.5	113.0	-4.1%

Collocated sampler Port ID	Audit (slpm)	Reference (slpm)	percent difference
Port 1 day	20.3	20.0	1.7%
Port 2 day	37.5	36.5	2.7%
Port 2 night	37.4	36.5	2.3%
Port 3 night	20.7	20.0	3.3%
Port 5 day	20.8	20.0	3.7%
Port 6 day	37.9	36.5	3.8%
Port 6 night	36.3	36.5	-0.6%
Port 7 night	21.4	20.0	6.6%
Total day	115.1	113.0	1.8%
Total night	114.7	113.0	1.5%

Note that the per cent differences are based on the standard units relative to the audit flow rates. The differences observed are minor and are to be expected due to day-to-day variability and precision of the sampler's flow measurement system.

University of California, Riverside

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Flow Audit Report

Date:	08/16/94	Analyzer:	CADMP Sampler
Time:	09:00	SN:	Collocated Azusa
Location:	Azusa	Audit by:	Kurt Bumiller

Dry gas meter SN: 7812471
Dry gas meter type: Rockwell Model S-275

El Monte ATIS pressure:	29.86 "HG	Altitude factor:	0.6431 "HG
Site Altitude:	600 Ft	Site pressure:	742.3 mm HG

Measurement:	Total flow day	Total flow night	Port 1 day	Port 2 day	Port 5 day
Start volume (liters):	5494.08	6881.76	7703.04	7929.60	7816.32
End volume (liters):	6145.44	7476.48	7788.00	8099.52	7901.28
Meter press. (mm Hg.):					
Time (sec):	336.00	308.00	248.00	269.00	243.00
Indicated volume (liters):	651.4	594.7	85.0	169.9	85.0
Gas temperature:	26.3	27.2	28.1	28.8	28.8
Indicated flow (lpm):	116.3	115.9	20.6	37.9	21.0
Corrected flow (alpm):	118.4	118.3	21.0	38.9	21.5
Corrected flow (slpm):	115.1	114.7	20.3	37.5	20.8
Reference (slpm):	113.0	113.0	20.0	36.5	20.0
% difference:	1.8%	1.5%	1.7%	2.7%	3.7%

	Port 6 day	Port 3 night	Port 2 night	Port 7 night	Port 6 night
Start volume (liters):	8127.84	8326.08	8453.52	8651.76	8779.20

End volume (liters):	8297.76	8411.04	8623.44	8750.88	8949.12
Meter press. (mm Hg.):					
Time (sec):	266.00	244.00	270.00	275.00	278.00
Indicated volume (liters):	169.9	85.0	169.9	99.1	169.9
Gas temperature:	28.4	21.1	29.3	28.6	30.0
Indicated flow (lpm) :	38.3	20.9	37.8	21.6	36.7
Corrected flow (alpm):	39.3	20.9	38.8	22.2	37.8
Corrected flow (slpm):	37.9	20.7	37.4	21.4	36.3
Reference (slpm):	36.5	20.0	36.5	20.0	36.5
% difference:	3.8%	3.3%	2.3%	6.6%	-0.6%

Comments:
Flows were set to last
calibration reference flow rate
by site operator.

	slpm		slpm
Port 1 day	20.3	Port 3 night	20.7
Port 2 day	37.5	Port 2 night	37.4
Port 5 day	20.8	Port 7 night	21.4
Port 6 day	37.9	Port 6 night	36.3
Sum	116.6	Sum	115.7
Measured total	115.1	Measured total	114.7
Reference	113.0	Reference	113.0

University of California, Riverside

Center for Environmental Research and Technology

Flow Audit Report

Date:	08/16/94	Analyzer:	CADMP Sampler
Time:	10:30	SN:	Primary Azusa
Location:	Azusa	Audit by:	Kurt Bumiller

Dry gas meter SN: 7812471
Dry gas meter type: Rockwell Model S-275

El Monte ATIS pressure:	29.86	"HG	Altitude factor:	0.6431	"HG
Site Altitude:	600	Ft	Site pressure:	742.3	mm HG

	Total flow day	Total flow night	Port 1 day	Port 2 day	Port 5 day
Start volume (liters):	9232.32	10025.28	10761.60	10874.88	11101.44
End volume (liters):	9798.72	10591.68	10846.56	11073.12	11243.04
Meter press. (mm Hg.):					
Time (sec):	309.00	310.00	251.00	338.00	412.00
Indicated volume (liters):	566.4	566.4	85.0	198.2	141.6
Gas temperature:	33.5	34.8	37.5	37.8	40.0
Indicated flow (lpm) :	110.0	109.6	20.3	35.2	20.6
Corrected flow (alpm):	114.6	114.7	21.4	37.2	21.9
Corrected flow (slpm):	108.8	108.5	20.1	34.8	20.4
Reference (slpm):	113.0	113.0	20.0	36.5	20.0
% difference:	-3.8%	-4.1%	0.5%	-4.7%	2.0%

	Port 6 day	Port 3 night	Port 2 night	Port 7 night	Port 6 night
Start volume (liters):	11299.68	11582.88	11766.96	11993.52	12163.44
End volume (liters):	11526.24	11738.64	11965.20	12135.12	12361.68
Meter press. (mm Hg.):					
Time (sec):	364.00	452.00	330.00	438.00	319.00
Indicated volume (liters):	226.6	155.8	198.2	141.6	198.2
Gas temperature:	40.7	41.4	40.7	42.3	41.7
Indicated flow (lpm) :	37.3	20.7	36.0	19.4	37.3
Corrected flow (alpm):	39.8	22.1	38.4	20.8	39.9
Corrected flow (slpm):	37.0	20.5	35.7	19.2	36.9
Reference (slpm):	36.5	20.0	36.5	20.0	36.5
% difference:	1.2%	2.2%	-2.3%	-4.1%	1.1%

Comments:
Flows were set to last
calibration reference flow rate
by site operator.

	lpm		lpm
Port 1 day	20.1	Port 3 night	20.5
Port 2 day	34.8	Port 2 night	35.7
Port 5 day	20.4	Port 7 night	19.2
Port 6 day	37.0	Port 6 night	36.9
Sum	112.3	Sum	112.2
Measured total	108.8	Measured total	108.5
Reference	113.0	Reference	113.0

APPENDIX C

A.2 Wilcoxan Rank Sum Test for Paired Data

The hypothesis to be tested in this case, normally called the null hypothesis, is:

H_0: The median of the population of all possible differences is zero; that is, Y_i is as likely to be larger than X_i, as X_i is likely to be larger than Y_i.

This hypothesis can also be expressed as the two population distributions being equivalent, with the same mean and standard deviation.

The steps to be taken in this analysis are:

A-1 Obtain the differences and absolute differences between each pair of data:

$$d_{ABi} = X_i - Y_i$$

$$|d_{ABi}| = |X_i - Y_i|$$

A-2 Sort d_{AB_i} from the lowest to the highest value and rank them numerically.

A-3 Calculate

$$R^- = \sum_{i=1}^{n} |d_{AB}|_i \text{ for } all\ d_{AB_i} < 0$$

$$R^+ = \sum_{i=1}^{n} |d_{AB}|_i \text{ for } all\ d_{AB_i} > 0$$

A-4 Find the smallest value among R^- and R^+ (designated by T) and compare this with T_c, the tabulated critical value (see Table A-2).

If $T > T_c$, accept H_0, and the two populations are equivalent. If $T < T_c$ then go to the next step.

A-5 Perform modified regression analysis to confirm the hypothesis that the data sets are not equivalent.

Note: If the number of paired samples is greater than 25, T is approximately normally distributed with mean and standard deviation:

$$u_T = \frac{n(n+1)}{4}$$

$$\sigma_T = \sqrt{\frac{n(n+1)(2n+1)}{24}}$$

Therefore, we can compute:

$$Z = \frac{T - u_T}{\sigma_T}$$

and complement the test with the following comparison:

- with T, u_T and σ_T obtain Z.
- with n and a given probability (say 95% of confidence or $\alpha = (0.05)$ obtain Z_c from statistical tables.

Then if $Z < Z_c$ we accept the null hypothesis, and the samplers or sampling methods are equivalent.

As an example, the data from Table 5 in the main text can be summarized as follows:

$$R^- = 41.5$$

$$R^+ = 78.5$$

Then $T = 41.5$

From Table A-2 we have $T_c = 30$.

$T_c > T$, then both sampler populations are equivalent, with a 95% of confidence.

TABLE A-2. Critical values of T in the Wilcoxon Rank sum test for a paired experiment. These critical values assume a two tailed distribution; i.e., the first data point in a pair might be either larger or smaller than the second. Thus, we use P = 0.1 or $\alpha = 0.05$ for each tail. This implies that we are accepting a 5 percent probability that we might reject the hypothesis of equal population distributions when the hypothesis is true.*

Number of Pairs n	Critical Value of T T_c
5	1
6	2
7	4
8	6
9	8
10	11
11	14
12	17 n 21
n 13/14	26
15	30
16	36
17	41
18	47
19	54
20	60
21	68
22	75
23	83
24	92
25	101
26	110
27	120
28	130
29	141
30	152
31	163
32	175
33	188
34	201
35	214
36	228
37	242
38	256
39	271
40	287
41	303
42	319
43	336
44	353
45	371
47	389
48	427
49	446
50	466

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*This table is summarized from the more complete Table 9 in Mendenhall (1971).

APPENDIX D

	DAYTIME			NIGHTTIME		
Start Date	TDLAS $\mu g/m^3$	CADMP,$\mu g/m^3$ Denuder Difference	CADMP,$\mu g/m^3$ Filter Pack	TDLAS $\mu g/m^3$	CADMP,$\mu g/m^3$ Denuder Difference	CADMP,$\mu g/m^3$ Filter Pack
8/29/95	37.52	-10.23	10.11	14.40		
8/30/95	48.21	0.24	0.51	13.72	0.03	0.11
8/3/95	57.53	27.41	60.45	13.59	13.02	19.80
9/1/95	59.09	11.09	30.20	15.38	7.40	13.06
9/2/95	61.54	16.38	46.28	11.78	6.00	10.94
9/3/95	58.94	9.37	35.62	6.90	4.20	5.99
9/4/95	33.52	9.64	30.98	11.07	6.51	9.11
9/5/95	30.56	6.27	25.81	5.74	4.26	6.24
9/6/95	25.80	0.97	23.35	2.96	2.19	4.83
9/7/95	32.84				2.86	4.61
9/8/95		3.73	21.99		0.53	4.10
9/9/95		1.58	27.12	5.51	1.03	5.07
9/10/95	24.72	-21.71	0.18	5.20	4.26	9.32
9/11/95	37.80	5.17	21.99	9.21	-4.54	0.06
9/12/95	51.10	13.56	46.41		12.12	18.70
9/13/95		11.12	47.57		10.28	13.91
9/14/95		14.95	50.35		6.14	11.11
9/15/95	54.78	12.67	55.18	18.41	2.34	3.68
9/16/95	31.33	7.45	41.28	7.93	-0.93	3.68
9/17/95	30.36	3.96	48.22	5.36	1.58	7.46
9/18/95	36.40	4.03	48.50		0.26	5.12
9/19/95	52.77	7.11	60.67		4.43	5.38
9/20/95	35.51	-4.13	47.18	7.98	1.99	4.41
9/21/95	16.68	1.64	42.87	5.37	0.30	4.13
9/22/95	21.16	1.36	51.71	4.37	-0.91	4.39
9/23/95	19.93	6.39	43.68	3.50	0.07	3.23
9/24/95	15.67	-1.52	39.42	6.35	-0.22	5.36
9/25/95	14.38	-1.66	23.33	5.75	-0.09	1.86

Appendix D Nitric acid measurements at Claremont by the CADMP and TDLAS