EVALUATION OF A SAMPLING METHODOLOGY FOR ACIDIC SPECIES

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ABSTRACT

A novel diffusion denuder sampling technique has been evaluated to provide a sampling methodology to replace that used during the first phase of the California Acid Deposition Monitoring Program. The approach is based on a new style of diffusion denuder to sample acidic and basic gases and particulate ammonium nitrate. A coated fabric is used as the denuder substrate. This substrate can be loaded directly into a standard filter holder. This approach allows direct denuder sampling with no additional capital costs and simplifies the coating and extraction process.

This denuder approach was evaluated in the laboratory with various chemical coatings to test the removal efficiency for nitric acid, nitrous acid, formic acid, acetic acid, ammonia, ozone, peroxyacetyl nitrate, and sulfur dioxide. Nitric acid collection efficiency on sodium chloride coated denuder substrates was used to assess more than twenty materials. After field testing denuder particle penetration and nitric acid collection efficiency of the four initially selected materials, one material was chosen for additional laboratory evaluation. The collection efficiency of an all-cotton fabric (material #5 in this report) — coated with sodium chloride for nitric acid, sodium carbonate for nitrous acid, and phosphoric acid for ammonia — were evaluated in the laboratory and found to have collection efficiencies ranging from 80-100% and therefore suitable for sampling if two denuders were used in series. Collection efficiencies of sodium carbonate coated denuders for sulfur dioxide and carboxylic acids were lower and more variable.

Particle retention, which would cause a denuder to have a positive bias for gas concentration measurements, was evaluated by ambient air sampling using particulate sulfate as the reference aerosol. Material #5 showed the lowest particle retention, ranging from around 0% to 17%. Preliminary field evaluations were conducted in Riverside, CA, while an extensive evaluation was conducted in Claremont, CA, collocated with a Fourier transform infrared spectrometer (FTIR) with a long, open optical path to quantify nitric acid, ammonia, and formic acid, and a tunable diode laser absorption spectrometer (TDLAS) to measure nitric acid in an enclosed cell. Also collocated were two denuder difference samplers, one designed by the South Coast Air Quality Management District to measure ammonia and nitric acid, and the current CADMP sampler to measure nitric acid. Nitric acid collection efficiency using four denuder materials was found to be over 90% at 2 and 10 L/min whether the denuder was coated or not; two fabric denuders are therefore recommended for sampling. The nitric acid measured by the TDLAS was highly correlated (r^2 = 0.90) with the SCAQMD measurements collected at night (1700-1100 hours PDT), although the TDLAS was an average of 33% higher. The FTIR data were collected only during the daytime sample collection period (1100-1700 hours PDT) and considered the reference method since the measurement did not perturb the sample. Although there were gaps in the data precluding direct comparison, none of the other three measurement methods for nitric acid showed high correlation with the TDLAS during the

daytime sampling periods, and all three were significantly lower on the average (22-33%). The FTIR was higher than the TDLAS in the morning and lower in the afternoon, possibly due to the volatilization of ammonium nitrate by TDLAS sampling components. The highest daytime correlation (r^2 = .76) was found between the FTIR and the CE-CERT denuder measurements. Denuders were also found to remove 80% of the ammonia whether coated with citric acid or not. Comparison of single periods of replicate samples showed the CE-CERT denuder measurement of ammonia to be 37% higher than the FTIR while that for formic acid was 72% higher than the FTIR.

Prototype sampler designs for measuring nitric acid, nitrous acid, ammonia, and ammonium nitrate were collocated in Bakersfield with other samplers as part of the IMS95 study.

The development of this new type of denuder resulted in a sampling method which could be based on commercially available low volume samplers. Adaptations of these are recommended rather than fabricating a specialized sampler to replace the CADMP.

TABLE OF CONTENTS

PAGE

VOLUME 1

LIST OF FIGURES

PAGE

LIST OF TABLES

PAGE

VOLUME 2

1.0 INTRODUCTION

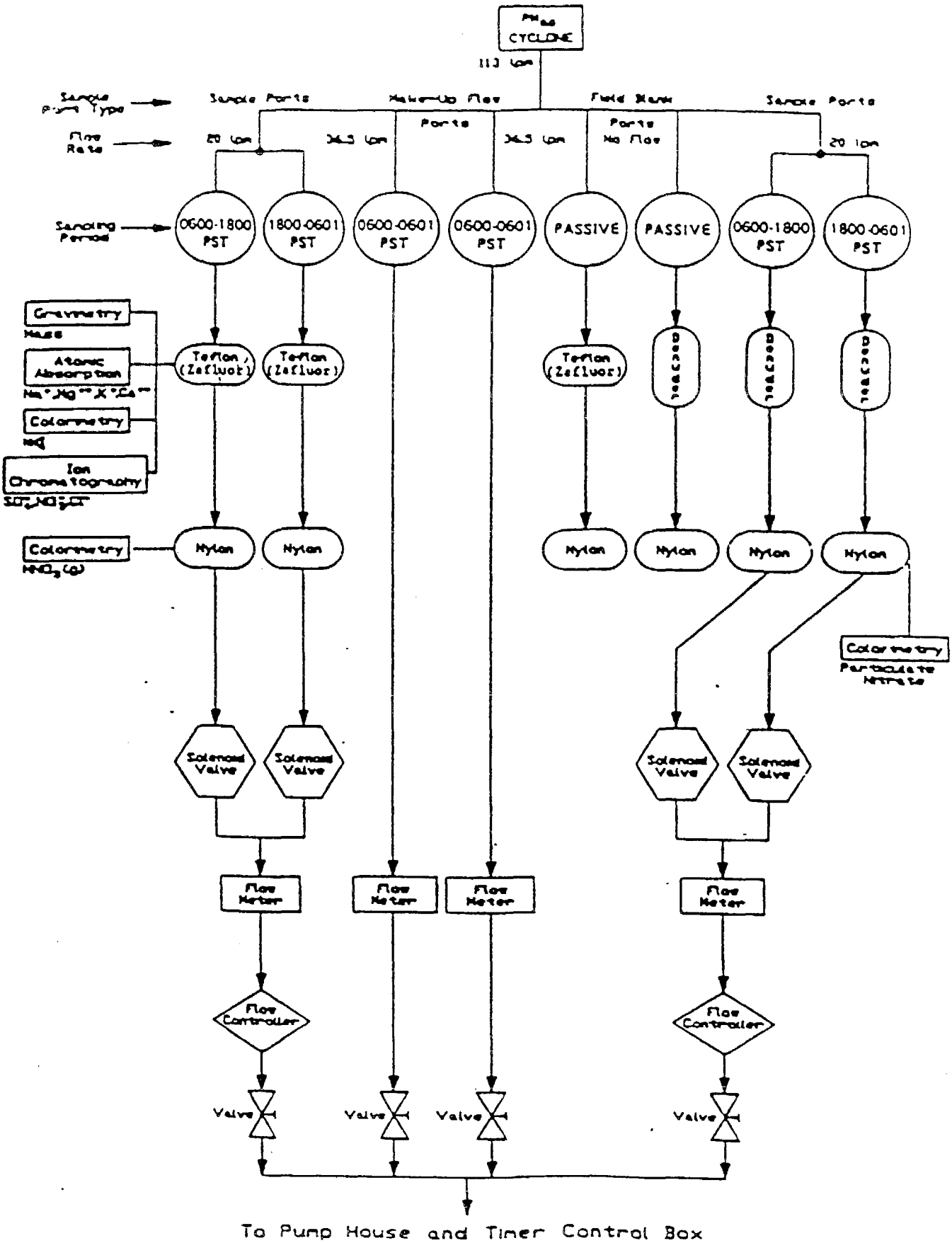
1.1 Background

The deposition of acidic particles and gases can have significant environmental consequences. In California, the long-term accumulation of nitrogen in the soil is the most serious, leading to soil acidification, decreased forest productivity, and losses of wildlife habitat (Mautz, 1995). The California Acid Deposition Monitoring Program (CADMP) was designed to assess the levels of acidic deposition within the State. In this 5-year program beginning in 1989, the Air Resources Board estimated acidic deposition fluxes using a model that required measuring both meteorological parameters and the concentrations of the acidic species. To meet these needs an aerosol sampling system was designed, constructed, and deployed at ten sites throughout California (Watson and Chow, 1991; Chow et al., 1993).

This sampling system, referred to as the CADMP sampler, consists of two units, one for $PM_{2.5}$ (particulate matter less than 2.5 μm aerodynamic diameter) and the other for PM_{10} (particulate matter less than 10 μm aerodynamic diameter). The PM_{10} unit collected parallel samples on Teflon and quartz filters for particle analysis. The Teflon filter was analyzed for sulfate, nitrate, chloride, ammonium, sodium, magnesium, calcium and potassium. The $PM_{2.5}$ unit collected two samples of particles less than 2.5 mm aerodynamic diameter, one on a Teflon-nylon filter pack without a nitric acid denuder, and the other on a nylon filter after a denuder (which consisted of anodized aluminum tubes). Figure 1-1 shows a schematic drawing of the $PM_{2.5}$ unit (Watson and Chow, 1991). The Teflon filter was analyzed for the same species as the PM_{10} Teflon filter while the nylon back filters were analyzed for nitrate. The difference between the total nitrate measured by the filter pack and that by the nylon filter below the denuder was a measure of gaseous nitric acid by the "denuder difference" approach. The nitrate on the nylon filter without the denuder was a measure of nitric acid by the "filter pack" approach.

The data from collocated samplers operated during 1988 and 1989 in Sacramento, CA, were analyzed (Ashbaugh et al., 1991; Chow et al., 1993). Correlations with regression coefficients greater than 0.92 were found for gravimetric mass, particulate sulfate and nitrate, sulfur dioxide, nitrogen dioxide, and ammonia. The precision for nitric acid values by denuder difference was not as good as for the particulate nitrate. The filter pack method, which simply assays nitric acid after particle removal has been shown to be subject to collection artifacts. A positive bias may result from the volatilization of particulate nitrate from the particle filter (Appel et al., 1980) while a negative interference occurs when the nitric acid reacts with particulate material collected on the filter itself (such as NaCl, sulfate, or alkaline crustal material). Since the filter pack is a direct rather than a

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



difference method, it is capable of greater sensitivity, which is especially useful for sites with low concentrations.

Ashbaugh and co-workers (1991) compared daytime values of nitric acid by the denuder difference and filter pack methods at ten sites throughout the state for the first year of operation. At sites with the highest concentrations – Bakersfield, Long Beach, Los Angeles, and Azusa – the average filter pack values were approximately twice those obtained by denuder difference. No other nitric acid measurements were available for comparison. Subsequent data analysis (Blanchard, 1993a,b) has raised questions regarding the performance of the sampler for nitric acid measurement. In the 3.5 years of data analyzed, Blanchard found a gradual decrease in the ratio of denuder difference nitric acid to filter pack nitric acid measurements. The filter pack nitric acid showed seasonal trends following expectations, and correlated with ozone. Denuder difference nitric acid showed the same seasonal trend in the first year's data, but in subsequent years the seasonal trend gradually diminished. Also, the ratio between denuder difference nitric acid and ozone concentrations decreased. At the Azusa and Los Angeles sites Blanchard also found particulate nitrate 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. On the other hand, comparisons between CADMP and the routine PM_{10} samplers showed good agreement for mass, sulfate, nitrate and ammonium ion concentrations. Blanchard concluded there were no significant errors due to leaks or flow rate instabilities. However, he did conclude that the denuders may have become ineffective after several years of use.

In October of 1993, a side-by-side nitric acid comparison test was conducted in Azusa between the CADMP sampler and a Tunable Diode Laser Absorption Spectrometer (TDLAS) operated by Unisearch. Overall, the CADMP values were approximately a factor of two lower than the TDLAS. Differences between CADMP samplers were variable (Ashbaugh, 1994a). The data have been reviewed by Tuazon et al. (1995). Based on the high ratios of nitric acid to ozone compared with previous studies when the TDLAS was collocated with a long pathlength Fourier transform infrared spectrometer (FTIR), they concluded that the nitric acid concentrations measured in Azusa by the TDLAS were higher than expected. This did not appear to be due to a volatilization artifact from the Teflon filter used in the sample line of the TDLAS. Interferences from local emissions in the industrial area were suspected, but not likely.

Recent work (Fitz and Hering, 1996) has shown that nitric acid is reversibly adsorbed by the PFA-Teflon-coated surfaces of the housing for the size-selective inlet and the sampling plenum as a function of temperature, humidity and prior exposure. The overall loss of nitric acid to these surfaces was found to average 15%, although short-term concentration variability due to changes in temperature and humidity would vary by nearly 100% higher or lower. In addition, Fitz and Hering

(1996) noted that the nitric acid denuder may become saturated with nitric acid to such a degree that it could function as a source.

The CADMP also showed operational deficiencies. Both the PM_{10} and $PM_{2.5}$ units have plenums which are difficult to reseal after removing for cleaning, thus discouraging such cleaning. Cleaning of the size-selective inlets was also a cumbersome process, which was not undertaken on a routine basis. Other problems included damage of the Teflon filters upon startup, loosening of o-ring friction fit between the filter holders and the plenum, and variable flow rates.

Since the design of the CADMP, advances have been made in denuder technology for sampling semi-volatile species such as nitric acid. The direct denuder approach, in which nitric acid is adsorbed on a denuder coating and quantified, is generally favored over the denuder difference method due to its greater sensitivity and freedom from saturation, which leads to a negative bias in measuring nitric acid concentrations. Several types of denuder have been developed along with specialized size-selective inlets to minimize nitric acid adsorption. This includes the annular denuder (Possanzini et al., 1983), coiled tubing (Pui et. al., 1990), honeycomb denuders (Koutrakis et al., 1993), and nuclepore filters (Luhrmann et al., 1994). While these denuders offer several advantages over the denuder difference approach used by the CADMP, a large capital investment in denuder hardware is needed for routine field measurement programs. They also require size selective inlets, which not only add to the cost of the sampler, but also are likely to adsorb the reactive gases being measured.

1.2 Diffusion Denuder Sampling Methodology

Ambient particulate matter contains semi-volatile species which are in a temperature-dependent equilibrium between the gas and solid phases (Appel et al., 1980; Spicer et al., 1982). Ammonium nitrate is one such particulate species. At ambient temperatures, ammonium nitrate is in equilibrium with a substantial amount of ammonia and nitric acid. Higher temperatures shift the equilibrium to the gas phase, while lower ones shift the equilibrium to the particulate phase. At a given temperature, *in-situ* spectroscopic measurements have shown the equilibrium constant to be quite variable in ambient air, although regression plots against the inverse of absolute temperature yielded free energy and enthalpy changes consistent with laboratory studies (Doyle et al., 1979). The variability may be due to humidity and whether the aerosol is internally or externally mixed (Stelson and Seinfeld, 1982; Hildemann et al., 1984; Jacob et al., 1986). Under otherwise constant conditions, increases of one gas will therefore result in decreases of the other gas (resulting in additional solid phase ammonium nitrate).

After ammonium nitrate is collected on a filter, it is therefore subject to these equilibrium shifts, which can increase or decrease the amount of ammonium nitrate retained on the filter (Zhang and

McMurry 1987). Both ammonia and nitric acid gases also are subject to acid-base reactions with previously collected particulate matter, resulting in ion formation, and therefore transformation to the particulate phase. In order to accurately sample nitric acid, ammonia, nitrate and ammonium in the phases as they exist in the atmosphere, diffusion denuding techniques have been developed (Shaw et al., 1982; Forrest et al., 1982; Possanzini et al., 1983; Ferm and Sjodin, 1985, Ferm, 1986). Diffusion denuders are devices that remove gaseous components, while allowing particles to pass through them. This is physically possible due to the much higher diffusion rate of gases compared with typical ion-containing atmospheric particulate matter. Denuders are therefore used to remove nitric acid and ammonia. While the removal of these species will result in their replacement by volatilizing ammonium nitrate, this does not occur during the short period of time the particles are passing through the denuder (Forrest et al., 1982). The remaining ammonium and nitrate can then be collected on specially treated filters which prevent further volatilization.

While denuder technology can result in the accurate measurements of these species, its application to routine sampling is difficult due to the cost and complexity of sampling equipment. Two approaches have been used in the past: direct denuder and denuder difference. In the direct denuder approach (Possanzini et al., 1983; Ferm, 1986; Allegrini et al., 1987; Vossler et al., 1988) the adsorbent layer of the denuder is extracted and analyzed for either nitrate or ammonium (separate denuders are used for nitric acid and ammonia since different sorbent coating are required). This method requires the denuder to be recoated after each sampling period, usually a labor-intensive laboratory procedure. Normally annular denuders are used, which are precision sampling devices costing several hundreds of dollars each. For field sampling, therefore, a stock of eight to ten denuders is required, resulting in a major capital investment and increased operating costs.

Another denuder-based method is the denuder difference approach (Shaw et al., 1982; Forrest et al., 1982, John et al., 1988). In this method, the denuders are not extracted after sampling, and two sampling lines are used, one with a denuder and one without. These denuders are designed for high adsorptive capacity so they can be used for many sample collection periods before requiring reactivation or replacement. Both lines then collect samples on specially coated filters, which prevent further volatilization. The filter used on the line without the denuder also retains the corresponding gas-phase component. Both filters are extracted and the ion of interest quantified. The concentration on the filter with the denuder is a measure of the particulate concentration, while that of the filter without the denuder is the total concentration for gas particulate phases. The difference in concentration between the two filters is therefore a measure of the gaseous concentration. While this approach requires considerably less labor and capital investment than the direct denuder method, the difference technique is subject to greater measurement uncertainty for the gas phase species. In addition, denuder surfaces must be occasionally renewed. This applies to the denuders for nitric acid which used anodized aluminum denuder surfaces. While they were thought to have infinite capacity

for removing nitric acid (John et al., 1988), we have recently found that break-through is possible under both laboratory and ambient air conditions (Fitz and Hering, 1996).

Another limitation with conventional denuders is that it is necessary to remove large particles (usually greater than 2 μm aerodynamic diameter) containing the species to be measured since they might deposit in the long, narrow channels typically necessary to allow gases to diffuse to the treated surface, thus resulting in a positive interference. Size selective inlets, however, present another surface to which nitric acid and ammonia may deposit. This could result in measurements with a negative bias. At the same time, ammonium nitrate might volatilize from particles collected in the inlet, resulting in a positive bias.

1.3 Objectives

Nitric acid in the atmosphere may pose a significant health risk and environmental hazard. The acid plus ammonia forms ammonium nitrate particulate matter primarily in the $PM_{2.5}$ size range, a particulate range for which a new Federal ambient air quality standard is being developed. Based on the above discussion, there is a need for an improved sampler to measure the concentration of acidic species in the atmosphere. Rather than using annular and honeycomb types of denuder, we suggested a new approach with the potential of offering greater measurement sensitivity and selectivity at a lower capital and operating cost. The direct objectives of this study were to evaluate this new type of denuder and then to apply this technology to design a sampler to replace the CADMP used by the ARB for monitoring acidic species in California, although such a sampler would be useful for monitoring any environment.. This denuder would offer the following potential advantages:

- Direct denuder approach for maximum sensitivity
- Ability to sample reactive gases without a size selective inlet
- Simplicity in operation
- Low cost

The denuder evaluation resulted in an optimum sampling substrate configuration. A sampler was then designed to meet or exceed the precision and accuracy of the CADMP sampler. The species to be monitored by this sampler include nitric acid, nitrous acid, ammonia, sulfur dioxide, nitrate, and ammonium.

Previous studies have shown that ions such as sulfate, nitrate and ammonium particles are found primarily in the $PM_{2.5}$ faction since they are largely produced by gas-to-particle conversions of sulfur dioxide, oxides of nitrogen, and ammonia. Large particulate nitrate, presumably due to the reaction of nitric acid with sodium chloride aerosol from sea salt, is one possible exception (Wall et.

al., 1988). Mass measurements for acid deposition studies should therefore exclude particles greater than 2.5μm aerodynamic diameter, which are mainly crustal in origin, and do not contain these species.

The sampling flow rate and duration for a particular study are determined by such factors as the detection limits required, the resources to service samplers and analyze substrates, and denuder capacity. The detection limits of the CADMP, sampling a nominal 14.4 m^3 on 47 mm substrates, was found to be adequate to evaluate acidic deposition. Table 1-1 shows the range of concentration for daytime and nighttime samples collected by the CADMP at both urban and rural sites. All of the daytime samples were usually above the lower quantifiable limit (LQL), Even at night over 90% of samples for the species of interest, except for nitric acid, were above the LQL at the urban sites; for non-urban sites this value drops to the 50-90% range.

Due to changes in meteorological conditions and pollutant concentrations, separate samples need to be collected during the day and night. While the CADMP sampler provided for one daytime and one nighttime collection period every six days, a more robust characterization of the concentrations could be made if sampling were conducted every day. Recent work (Luhrmann et. al., 1994; Fitz and Hering, 1996; Hering, 1996; and Hering and Chow, 1996) has shown that collected samples would be stable for collection periods as long as two weeks. We therefore propose collecting samples over seven-day periods on two sample trains, one for the daytime, the other for the nighttime.

The design goal for the sampler, based on the denuder technology developed during this project, is a unit that will measure all of the parameters available from the CADMP sampler. In order to sample 14.4 m^3 of air with this approach, a minimum flow rate of 2.86 L/min will be required. Thus a design goal is to have a sampling methodology capable of operating 47 mm substrates with at least this flow rate, and preferably much higher to facilitate sample collection when greater time resolution is desired. The sampler design will allow simpler routine maintenance, greater selectivity, and improved durability compared with current denuder-based sampler designs.

Table 1-1. Analytical specification for urban and non-urban samples collected from California Acid Deposition Monitoring Program (CADMP), May 3, 1988, to September 25, 1989

URBAN SITES

Chemical Species	Size	Analysis Method (a)	NDC (b) (µg/m3)	LQL (c) (µg/m3)	Daytime Range (e) of Urban Concentration (d (µg/m3)	Total No. of Samples	Percent Sample Exceeded		Nighttime Range (e) of Urban Concentration (d (µg/m3)	Total No. of Samples	Percent Sample Exceeded	
							NDC (b)	LQL (c)			NDC (b)	LQL (c)
Particle Mass	PM 2.5	Gravimetry	0.67	1.7	0.50 to 132.54	479	100	99	0.00 to 187.53	474	89	98
Particle Mass	PM 10	Gravimetry	0.67	1.7	0.00 to 213.17	479	100	99	0.00 to 196.74	478	100	100
Sodium (Na+)	PM 2.5	AA	0.004	0.04	0.00 to 1.92	478	96	90	0.00 to 2.25	475	96	89
Sodium (Na+)	PM 10	AA	0.004	0.052	0.00 to 6.27	487	99	97	0.00 to 6.49	484	99	97
Magnesium (Mg ++)	PM 2.5	AA	0.0027	0.0083	0.00 to 0.35	485	98	92	0.00 to 0.35	477	97	90
Magnesium (Mg++)	PM 10	AA	0.0027	0.0063	0.002 to 0.85	488	100	99	0.003 to 0.85	484	100	99
Potassium (K+)	PM 2.5	AA	0.0066	0.024	0.00 to 0.69	485	92	80	0.00 to 1.13	476	91	76
Potassium (K+)	PM 10	AA	0.0066	0.034	0.00 to 1.76	478	89	96	0.00 to 1.51	475	99	96
Calcium (Ca++)	PM 2.5	AA	0.033	0.046	0.00 to 2.00	485	72	59	0.00 to 2.34	477	51	38
Calcium (Ca++)	PM 10	AA	0.033	0.041	0.001 to 2.39	489	99	99	0.00 to 3.50	484	96	96
Ammonium (NH4+)	PM 2.5	AC	0.066	0.096	0.00 to 18.46	467	95	94	0.00 to 24.64	467	87	96
Ammonium (NH4+)	PM 10	AC	0.066	0.15	0.00 to 26.43	468	99	96	0.00 to 24.09	467	98	96
Chloride (Cl-)	PM 2.5	IC	0.066	0.13	0.00 to 3.24	419	28	17	0.00 to.30	417	37	26
Chloride (Cl-)	PM 10	IC	0.066	0.13	0.00 to 4.55	407	65	51	0.00 to 9.74	406	77	67
Sulfate (SO4=)	PM 2.5	IC	0.066	0.36	0.00 to 21.92	467	99	97	0.00 to 21.91	472	99	96
Sulfate (SO4=)	PM 10	IC	0.066	0.18	0.00 to 29.43	467	100	100	0.00 to 27.44	469	99	99
Sulfur Dioxide (SO2)	Gas	IC	0.022	0.29	0.00 to 28.45	441	99	98	0.00 to 41.06	443	98	87
Nitrogen Dioxide (NO2)	Gas	IC	0.025	0.39	0.00 to 370.00	477	89	98	0.00 to 254.98	471	98	98
Ammonia (NH3)	Gas	AC	0.032	0.14	0.00 to 38.33	497	99	99	0.00 to 30.09	490	99	99
Nitrate (NO3)	PM 10	IC	0.066	0.1	0.00 to 37.91	469	99	98	0.00 to 51.23	469	99	99
Nitrate (NO3)	PM 2.5	IC	0.066	0.12	0.00 to 27.64	470	95	94	0.00 to 31.28	472	95	94
Nitrate (NO3)	Undenuded											
	PM 2.5	IC	0.034	0.41	0.004 to 54.48	471	100	95	0.004 to 31.64	473	97	66
Nitrate (NO3)	Denuded											
	PM 2.5	IC	0.034	0.34	0.00 to 49.27	464	100	99	0.00 to 51.67	462	100	98
Nitric Acid (HNO3)	Gas	IC	0.066	0.41	0.00 to 37.28	429	82	78	0.00 to 12.35	437	39	25

Continued next page

Table 1-1 (Continued)

NON-URBAN SITES

Chemical Species	Size	Analysis Method (a)	NDC (b) (µg/m3)	LQL (c) (µg/m3)	Daytime Range (e) of Urban Concentration (d) (µg/m3)	Total No. of Samples	Percent Sample Exceeded NDC (b)	Percent Sample Exceeded LQL (c)	Nighttime Range (e) of Urban Concentration (d) (µg/m3)	Total No. of Samples	Percent Sample Exceeded NDC (b)	Percent Sample Exceeded LQL (c)
Particle Mass	PM 2.5	Gravimetry	0.67	1.7	0.00 to 48.82	179	87	79	0.00 to 177.87	172	84	80
Particle Mass	PM 10	Gravimetry	0.67	1.7	0.00 to 90.55	172	97	93	0.00 to 182.30	163	92	87
Sodium (Na+)	PM 2.5	AA	0.004	0.040	0.00 to 1.50	183	73	60	0.00 to 0.96	178	70	52
Sodium (Na+)	PM 10	AA	0.004	0.952	0.00 to 2.93	177	87	77	0.00 to 2.48	170	84	64
Magnesium (Mg++)	PM 2.5	AA	0.0027	0.0083	0.00 to 0.16	183	87	66	0.00 to 0.12	178	83	63
Magnesium (Mg++)	PM 10	AA	0.0027	0.0063	0.00 to 0.47	177	92	85	0.00 to 0.48	170	88	81
Potassium (K+)	PM 2.5	AA	0.0066	0.24	0.00 to 0.55	182	80	60	0.00 to 0.91	177	78	60
Potassium (K+)	PM 10	AA	0.0066	0.034	0.00 to 2.39	173	89	68	0.00 to 1.81	166	93	64
Calcium (Ca++)	PM 2.5	AA	0.033	0.046	0.00 to 0.38	183	42	29	0.00 to 0.75	178	38	28
Calcium (Ca++)	PM 10	AA	0.033	0.041	0.00 to 0.76	177	79	75	0.00 to 1.34	170	71	66
Ammonium (NH4+)	PM 2.5	AC	0.066	0.096	0.00 to 2.33	178	78	71	0.00 to 1.96	172	78	74
Ammonium (NH4+)	PM 10	AC	0.066	0.149	0.00 to 7.50	167	92	78	0.00 to 2.63	159	90	78
Chloride (Cl-)	PM 2.5	IC	0.066	0.128	0.00 to 2.59	158	23	16	0.00 to 1.84	151	25	13
Chloride (Cl-)	PM 10	IC	0.066	0.131	0.00 to 3.15	148	38	26	0.00 to 1.85	134	36	23
Sulfate (SO4=)	PM 2.5	IC	0.066	0.36	0.00 to 4.27	178	94	78	0.00 to 6.12	171	92	78
Sulfate (SO4=)	PM 10	IC	0.066	0.18	0.00 to 3.60	166	97	92	0.00 to 4.85	155	94	88
Sulfur Dioxide (SO2)	Gas	IC	0.022	0.29	0.00 to 2.96	158	73	46	0.00 to 3.90	154	71	42
Nitrogen Dioxide (NO2)	Gas	IC	0.025	0.39	0.00 to 18.11	170	15	14	0.00 to 30.91	162	22	20
Ammonia (NH3)	Gas	AC	0.032	0.14	0.00 to 13.96	179	98	89	0.00 to 15.69	172	88	80
Nitrate (NO3)	PM 10	IC	0.066	0.104	0.00 to 6.00	166	85	80	0.00 to 4.91	155	79	75
Nitrate (NO3)	PM 2.5	IC	0.066	0.116	0.00 to 4.98	178	64	56	0.00 to 4.47	171	57	52
Nitrate (NO3)	Undenuded											
	PM 2.5	IC	0.034	0.41	0.00 to 7.79	183	89	58	0.00 to 3.38	177	80	44
Nitrate (NO3)	Denuded											
	PM 2.5	IC	0.034	0.34	0.00 to 8.41	180	99	59	0.00 to 10.63	173	97	55
Nitric Acid (HNO3)	Gas	IC	0.066	0.41	0.00 to 9.80	171	63	47	0.00 to 2.64	163	44	21

(a)
IC: Ion Chromatography
AC: Automated Colorimetry
AA: Atomic Absorption Spectrophotometry

(b) Minimum Detectable Concentration (MDC) is the concentration at which instrument response equals the standard deviation of the response to a known concentration of zero.
(c) Lower Quantifiable Limit (LQL) equals the standard deviation of dynamic field blanks as determined from the CADMP sampling program.
(d) Urban sites include: Fresno, Sacramento, Collocated Sacramento, Bakersfield, Santa Barbara, Long Beach, Los Angeles, and Azusa.
(e) Assumes extraction of half filter in 10 ml for particle samples and extractions of entire filter in 10 ml for impregnated filters with a nominal volume of 15.5 m3.
(f) Non-urban sites include: Gasquet, Yosemite, and Sequoia.

2.0 DENUDER EVALUATION AND COMPARISON METHODS

The denuder sampling approach that we proposed is based on diffusion research for devices used to remove very fine particles. These devices, known as diffusion batteries, are used to size-resolve submicron particles *in-situ*. They were originally constructed using a single long channel, then made more compact, but more difficult to fabricate, by using tubing bundles. These evolved to honeycomb structures, and finally wire screens (Sinclair, 1986). This development is analogous to the development of diffusion denuders for sampling semi-volatile species, which started with tubing bundles (Shaw et al., 1982), progressed to annular geometries (Possanzini et al., 1983), and then to honeycomb structures (Koutrakis et al., 1993).

Our approach uses a cloth fabric as the denuder substrate, analogous to the wire screen denuders for collecting very fine particles in diffusion batteries. The finer the mesh, the greater the deposition by either particles or gases. In the case of particles, the wire of the mesh is typically 10 μm in diameter with a spacing of 20-50 μm. Typically over one hundred such screens are necessary to remove submicron-sized particles. Since the diffusion coefficient for gases is several orders of magnitude higher than for particulate matter, a single screen, which need not be as fine, could be used. Cloth, with a typical thread size of 100 μm spaced on centers of 250 μm, leaving an open grid of 150 μm (typical dimensions for cloth), would be sufficient. In addition, an adsorbent material would allow the cloth to be coated with a variety of chemicals for selectively removing target gases. The denuders therefore could be soaked in solutions of citric acid, sodium chloride, triethanolamine, and potassium carbonate, which would adsorb ammonia, nitric acid, nitrogen dioxide, and sulfur dioxide, respectively.

2.1 Theoretical Basis

The feasibility of the concept was first evaluated by using the theory developed for wire diffusion screens (Cheng and Yeh, 1980).

The equation to describe the fractional penetration of a particle (P) is given by

$$P=\exp\left(-AnPe^{-2/3}\right) \qquad (1)$$

where:

$$A = \frac{2\beta ah}{\pi(1-a)r}$$

where:

ß = 2.7

a = solid surface fraction = 0.345

r = fiber radius in cm

h = screen thickness in cm

n = number of screens

P_e = Peclet number = $2r\ U_0/D$

where:

U_0 = undisturbed flow velocity

D = Diffusion coefficient

Assuming a denuder is treated with a chemical that quantitatively removes a target gas upon contact with the denuder surface, we can calculate the theoretical denuder efficiency. To apply this equation to nitric acid, for example, for a 4.0 cm diameter cloth sampling at 10 L/min, the dimensions of the cloth grid cell and the diffusion constant for nitric acid at room temperature, 0.12 cm^2/sec are used. This results in a penetration of 0.02 or 2%. On the other hand, using the diffusion coefficient of a 0.1 µm particle (6×10^{-6} cm^2/sec) results in a penetration of greater than 99%.

Since cloth substrates have not previously been used as gaseous diffusion denuders, laboratory testing was needed to optimize the denuder geometry and coating material. Additional testing was needed to determine whether the laboratory performance could be maintained under actual field sampling conditions. Field testing was also used to evaluate the penetration of particulate matter through the denuder.

2.2 Efficiency Definitions and Estimation Methods

Denuder collection efficiencies were determined by three methods depending on the measurement approach used and the number of and type of denuders stacked in series. All of these methods assume that the collection efficiency of each denuder is identical.

Method 1 (uses measured concentration of adsorbed ions for two denuders in series):

$$E = (1 - L_2/L_1)*100 = \text{Percent Efficiency} \qquad (2)$$

where:

L_1 = ion load measured on first denuder in series

L_2 = ion load measured on second denuder in series

This calculation assumes that the collection efficiencies of each denuder are equal and remain constant during sampling. When collection efficiencies decrease with increased loading, this formula will underestimate collection efficiency.

Method 2 (uses continuous analyzer concentrations before and after a single denuder):

Comparison of the concentrations upstream and downstream of the single denuder as measured by the continuous analyzer. This method requires knowing the zero point and linearity of the analyzer, but the span factor of the analyzer is not needed. Instantaneous efficiency is given by:

$$E = (1 - (C_d - Z)/(C_u - Z))*100 \quad (3)$$

where:

C_d = analyzer response downstream of denuder

C_u = analyzer response upstream of denuder

Z = analyzer response to zero air

Instantaneous efficiencies generally decreased with sampling time and were determined at approximately six-hour intervals from the continuous chart recorder traces. These efficiencies were averaged and weighted by time duration. The average efficiency, therefore, corresponds to the collection efficiency of the front denuder as determined by ion analysis.

At very high collection efficiencies (e.g. for HONO), zero drift limits the precision of the efficiency determination. At very low collection efficiencies (e.g. for PAN), drift in the input concentration and analyzer span limit the precision of the efficiency determination.

Method 3 (uses both measurement of adsorbed ion and continuous analyzer data for the first of two or more denuders in series):

Extracted ions on the single denuder (or the primary denuder of the denuder stack) were compared with the ion loadings calculated from test gas concentration and the sample flow rates. This method requires accuracy in the analytical concentrations, the sample flow rate, the sample duration, and either the span of the analyzer or the permeation rate plus the dilution air flow rate.

$$E = (L_1/(C_{in}*V))*100 \quad (4)$$

where:

C_{in} = input concentration determined from instrument response or from permeation rate and dilution flow rate

V = sample volume determined from sample flow rate and duration

L_1 = load on the single or primary denuder

2.3 Denuder Substrates

The denuders were cut into 47 mm circles with a custom-made 47 mm arch punch and installed in Savillex 47 mm filter holders. Cloths of a variety of weave patterns and materials were evaluated. Table 2-1 summarizes the materials used. Fabrics with higher porosity were chosen, since they would be expected to remove less particulate matter. Appendix A fully describes the procedures for preparing, handling, and analyzing sampling substrates.

Table 2-1. Fabric denuder materials evaluated in the laboratory

Material #	Material Type	Material #	Material Type
1	35/65 cotton-synthetic blend	11	polyester
2	cotton-polyester blend	12	silk
3	rayon-polyester	14*	silk
4	rayon-acetate	15	nylon
5, 5A	cotton	16	nylon
6	cotton	17	polyester
7	cotton	18	cotton
8	cotton	19	50/50 cotton-polyester blend
9	nylon	20	cotton
10	polyester		

* There was no Material #13.

2.4 Denuder Coatings

Denuders were coated by dissolving the coating material in a 50/50 (v/v) solution of methanol/water which also contained 2% glycerol by volume. The concentration of the denuder coating solution is expressed as the mass percentage of coating agent in solution. Denuders were dipped in this solution and allowed to drain and air dry, after which they were immediately sealed in polyethylene bags and stored in a refrigerator at 4°C. Appendix A describes the coating procedure in more detail.

The following denuder coating materials were evaluated:

- Sodium Chloride (2% and 9%)

  Sodium chloride denuder coatings have been shown to be more selective at removing nitric acid than any other coating material reported in the literature (Perrino et al., 1990). The NaCl-coated denuder was evaluated in the laboratory for the penetration of nitric and nitrous acids, PAN, sulfur dioxide, and formic and acetic acids. Denuders were extracted with a carbonate buffer (of the same composition recommended by Dionex for ion chromatography of nitrate, nitrite, and sulfate) and analyzed for nitrate. Since nitric acid was felt to be the most important acid to be monitored, denuder substrate materials were initially

screened to determine the removal efficiency. For this screening, only the continuous NO-NO_x analyzer (Thermoenvironmental Model 42) was used to determine denuder efficiency.

- Sodium Carbonate (2%)

  Coated on a filter, this base has been shown to be effective in removing nitrous acid, carboxylic acids, and sulfur dioxide (Ferm and Sjodin, 1985; Grosjean and Parmar, 1990, Allegrini et al., 1987). The denuders were evaluated for the penetration of these species. Denuders were extracted with a carbonate buffer and analyzed for nitrate, nitrite, and sulfate. Denuders exposed to carboxylic acids were extracted in deionized water and analyzed for acetate and formate.

- Citric Acid (2% and 9%)

  Filters coated with this acid have been shown to be effective in removing ammonia (Bos, 1980). The denuder was evaluated for the removal of this species.

- Phosphoric Acid (2% and 9%)

  Denuders coated with citric acid were found to have both limited efficiency and capacity for removing ammonia. Phosphoric acid coating was tested for collecting ammonia (Stevens et al., 1978) to determine whether its efficiency and capacity exceeded that of the citric acid coating.

- 2% Potassium Iodide

  This coating was evaluated for removing ozone to minimize the oxidation of particulate matter collected on a filter downstream of this denuder. The reaction of ozone with potassium iodide has long been used as an analytical method for ozone determination. Potassium iodide-coated copper tubing previously has been used to remove ozone prior to collection of carbonyls on 2,4-dinitrophenyl hydrazine-coated sorbent tubes (Arnst and Tejada, 1989). Penetration efficiency was determined with a Monitor Labs model 8410 chemilumenescent ozone analyzer.

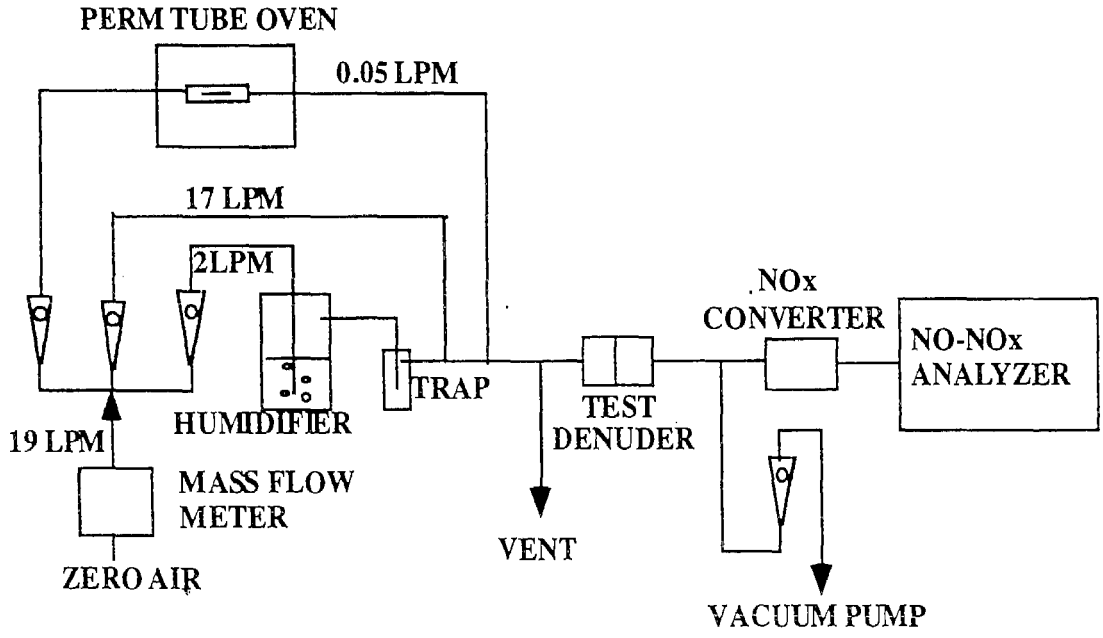
2.5 Overview of Testing Methods

- **Laboratory Evaluation**

Denuders were evaluated in the laboratory by passing known concentrations of nitric acid (HNO_3), nitrous acid (HNO_2), peroxyacetyl nitrate (PAN), formic and acetic acid, ozone, and ammonia (NH_3) through them at various temperatures and humidities. Denuder efficiencies were then calculated by the methods described in Section 2.2 depending on the measurement method used and the number and type of denuders test in series.

Figure 2-1 is a schematic drawing of the equipment used to expose the denuders to nitric acid for penetration efficiency testing. All plumbing components consisted of perfluoro alkoxy (PFA) Teflon tubing, fittings, and filter holders, while the permeation tube holder, trap, and humidifier were constructed of borosilicate glass. Gas mixtures in the range of 10-40 ppb were generated by adding the species of interest to purified air (using diffusion or permeation tubes or other appropriate sources). Concentration measurements, used to determine penetration, were made before and after the denuder using either collection substrates (coated filters) and/or real time analyzers by sampling through Teflon "T" tube fittings. The analyzer approach, when possible, allowed greater time resolution and nearly immediate feedback of results. This allowed us to rapidly evaluate denuder collection efficiency as a function of flow rate so an optimum range could be determined. To validate methods for ambient air monitoring, experiments were performed at two temperatures (20° and 40°C) and relative humidities (20% and 80%). Potential interferents also were tested. The background concentrations from extracted denuders were determined for each phase of testing by loading them into denuder cassettes and immediately unloading them into petri dishes. Denuder substrates were sent to Global Geochemistry for ion analysis as appropriate (ion chromatography for sulfate, nitrate, and nitrate; automated wet chemical for ammonium). For quality control, the laboratory reported duplicate analyses performed as a component of its standard operating procedures. Appendix A provides details of analysis methods.

Figure 2-1. Denuder test schematic for nitric acid



The following describes methods of generating pollutant gases for laboratory evaluations:

Pollution-Free Air

Pollution-free air was generated with an Aadco model 727 pure air generator.

Nitric Acid

Nitric acid vapor was generated by flowing dry air past a permeation tube containing liquid nitric acid.

Nitrous Acid

Nitrous acid by the sublimation of ammonia nitrite was used.

Ammonia, Sulfur Dioxide, and Organic Acids

These species were generated using commercial permeation tubes with specified emission rates.

Ozone

Ozone was generated using a low-pressure mercury lamp ozonator.

PAN

Peroxyacetyl nitrate (PAN) was prepared by the photolysis of ethyl nitrite (Stephens et al., 1965).

- **Ambient Denuder Evaluations**

To determine the denuder performance for particulate penetration and nitric acid collection under actual ambient conditions, samples were collected in Riverside, CA, on the roof of the CE-CERT laboratory. Samples were taken with multiple denuders, with a Teflon filter before the filters in one case, and behind them in the second case. The sampling substrates were extracted in a carbonate buffer and analyzed for nitrate and sulfate by ion chromatography as described in Appendix A. Samples for blank determination were obtained by placing the substrate in the filter holder in the configuration used for sampling, turning on the sampler for approximately 5 seconds, and then removing the substrate. The blank substrates were all handled in the same manner as actual samples.

The nitrate measurements were used to determine denuder efficiency by Method 1 described in Section 2.2. In addition, sulfate measurements were used to determine the amount of particulate nitrate that may be expected to be collected by the denuder. Since sulfate is a non-volatile particulate species, the amount of sulfate collected by each denuder compared to the sulfate on the Teflon front filter (or the sum of the sulfate on the back Teflon filter plus all of the preceding denuders) provides a measure of the penetration of fine particulate matter through the denuder. This assumes that nitrate and sulfate have a similar size distribution. Many studies have shown that this is the case, especially in

southern California (Lawson, 1990, Kim et al., 1996), but others have noted a large size mode greater than 2.5 μm aerodynamic diameter (Wall et al., 1988). Presumably this large size mode originates with sea salt and therefore normally is found where a marine influence is common. The use of sulfate as a nitrate particle surrogate also assumes that the NaCl-coated denuders do not collect gaseous SO_2 as sulfate. This has been verified previously (Perrino et al., 1990) and again by us during the laboratory evaluation; in addition, we have also found that SO_2 concentrations in Riverside are generally less than 1 ppb. The nitrate collected by each denuder, corrected for the penetration of particulate nitrate (assuming that nitrate and sulfate are in a similar size distribution) provides a measure of the efficiency of collection nitric acid by using Method 2.

This assumes that all remaining nitrate originates from nitric acid and not other gas phase species. Our laboratory experiments (see Section 3.1.2) showed insignificant nitrate collection from PAN and nitrous acid.

- **Ambient Comparison Studies with Other Methods**

The primary comparison study with other measurement methods was conducted in Claremont, CA. Collocated measurements were acquired from August 28 to September 26, 1995, in the parking lot of an unused automobile repair shop at 555 W. First Street. Table 2-2 summarizes the types of measurements made, along with their estimated detection limits and uncertainties. For this study a number of denuder configurations were tested in order to determine denuder efficiency and particulate penetration at 2 and 10 L/min for various gaseous pollutants. This was done to determine the feasibility of the method for both short and long-term collection periods. The 2 L/min samples were collected for seven days while 10 L/min samples were collected for nominal periods of 8 hours during the daytime and 16 hours overnight. Samples were analyzed by the methods described during the Riverside ambient evaluations.

Table 2-2. Measurements during the Claremont Comparison Study and estimated detection limits ($\mu g/m^3$)

Species	CE-CERT Weekly Denuder	CE-CERT 2/day Denuder	CADMP 2/day Sampler	SCAQMD Denuder	TDLAS	FTIR
Ammonia	0.05		0.05	0.1		1
Nitric Acid	0.05	0.1	0.05	0.1	2	5
Formic Acid	0.10			0.1		2
Nitrate	0.05	0.1	0.05	0.1		
Sulfate	0.05	0.1	0.05	0.1		
Formate	0.05					
Ammonium	0.05	0.1	0.05	0.1		

Figure 2-2 shows the site layout. This was a dead-end street with little traffic in an area of residential housing, light commercial and manufacturing. The area to the west of the site, the prominent direction from which air pollutants are transported in the afternoon, consisted of primarily residential housing for several miles. The particulate sample collectors were mounted on stands so the inlets were a half meter above the six-foot-high block wall fence located on the western side of the property. This location was chosen in part to minimize the noise of the particulate sampling pumps and other site activities, due to the presence of an apartment housing for elderly people bordering the northern boundary of the site.

Real time spectroscopic measurements of nitric acid were made using both a tunable diode laser absorption spectrometer (TDLAS) and a long path length Fourier transform infrared spectrometer (FTIR). The TDLAS has greater sensitivity than the FTIR (sub-ppb compared to approximately 5 ppb) and was able to provide around-the-clock measurements. Unlike the FTIR, the TDLAS was more subject to sampling artifacts since it needed to sample ambient air through a Teflon filter into a cell at 20 torr pressure. The FTIR, which measured nitric acid directly in the air, was therefore considered the ultimate reference method for nitric acid. The FTIR was also capable of measuring formic acid and ammonia. Since the FTIR could only measure relatively high concentrations of nitric acid, a nominal sampling interval for collection-based measurements was from 1100 to 1700 hours PDT, when the nitric acid was typically above the FTIR detection limit. This could not be readily accomplished for the weekly denuder samplers; the results were therefore compared to the TDLAS alone.

The 1995 Integrated Monitoring Study (IMS95) was a multi-sponsor study to measure particulate matter and precursors in the San Joaquin Valley during the winter of 1995-96. Table 2-3 summarizes the measurements that were made at the Bakersfield monitoring site. Ammonia was the primary gaseous pollutant of interest for this study. Samples were collected from December 5, 1995, to January 5, 1996. Based on PM mass measurements, eight days were chosen to perform full chemical speciation. A prototype sampler based on the denuder technology being evaluated in this study was installed at the Bakersfield monitoring site. A prototype sampler based on the denuder technology being evaluated in this study was installed at the Bakersfield monitoring site. Figure 2-3 shows the substrates used in the three sampling cassettes for this sampler arrangement. The sampler was designed to make the following measurements:

Table 2-3. Measurements conducted during the IMS95 Winter Field Program (December 9, 1995-January 6, 1996, at Bakersfield

Measurement (Sampler:Species)	Contractor	Temporal Scale
Particulate PM10		
DICHOT PM10 Mass	ARB	24 hour
DICHOT PM10 Elements	ARB	24 hour
Hivol SSI PM10 Mass	ARB	24 hour
Hivol SSI PM10 Ammonium	ARB	24 hour
Hivol SSI PM10 Sulfate	ARB	24 hour
Hivol SSI PM10 Nitrate	ARB	24 hour
Hivol SSI PM10 Total Carbon (TC)	ARB	24 hour
Hivol SSI PM10 Mass	ARB	24 hour
Hivol SSI PM10 Nitrate	ARB	24 hour
Hivol SSI PM10 Sulfate	ARB	24 hour
Hivol SSI PM10 Ammonium	ARB	24 hour
Hivol SSI PM10 TC	ARB	24 hour
Hivol Total Suspended Particulate Matter	ARB	24 hour
Portable PM10 Mass @ Saturation Sites	DRI/STI	24 hour
Portable PM10 Elements	DRI/STI	24 hour
Portable PM10 OC/EC	DRI/STI	24 hour
Portable PM10 Anions (SO4, NO3, Cl)	DRI/STI	24 hour
Portable PM10 Ammonium	DRI/STI	24 hour
Portable PM10 H2O Soluable K	DRI/STI	24 hour
Portable PM10 Babs	DRI/STI	24 hour
SFS PM10 Mass	DRI/STI	3 hour
SFS PM10 Elements	DRI/STI	3 hour
SFS PM10 OC/EC	DRI/STI	3 hour
SFS PM10 Anions (SO4, NO3, Cl)	DRI/STI	3 hour
SFS PM10 Ammonium	DRI/STI	3 hour
SFS PM10 H20 Soluable K	DRI/STI	3 hour
SFS PM10 Volatilized Nitrate	DRI/STI	3 hour
SFS PM10 Babs	DRI/STI	24 hour
Particulate PM2.5		
DICHOT PM2.5 Mass	ARB	24 hour
DICHOT PM2.5 Elements	ARB	24 hour
SFS PM2.5 Mass	DRI/STI	3 hour
SFS PM2.5 Elements	DRI/STI	3 hour
SFS PM2.5 OC/EC	DRI/STI	3 hour
SFS PM2.5 Anions (SO4, NO3, Cl)	DRI/STI	3 hour
SFS PM2.5 Ammonium	DRI/STI	3 hour
SFS PM2.5 H20 Soluable K	DRI/STI	3 hour
SFS PM2.5 Babs	DRI/STI	3 hour
SFS PM2.5 Volatilized Nitrate	DRI/STI	3 hour
SFS PM2.5 Artifact OC	DRI/STI	3 hour
Continued next page		

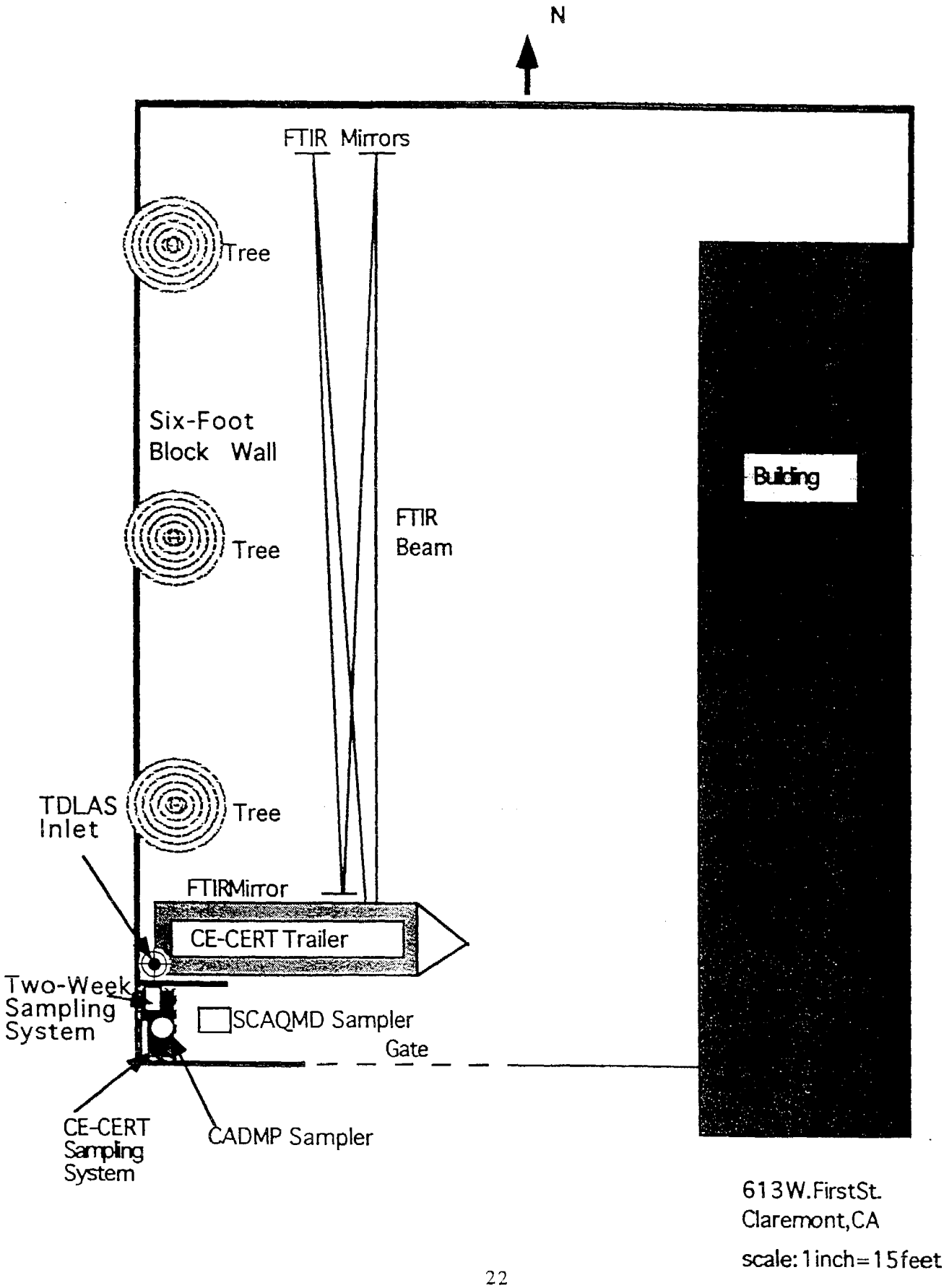
Table 2-3 (continued)

Measurement (Sampler:Species)	Contractor	Temporal Scale
Special Studies for PM and Visibility		
CADMP PM10 Mass	ARB	24 hour
CADMP PM10 Ca, Mg, Na, K,	ARB	24 hour
CADMP PM10 NH4	ARB	24 hour
CADMP PM10 SO4, NO3, Cl	ARB	24 hour
CADMP PM10 HNO3	ARB	24 hour
CADMP PM10 HNO2	ARB	24 hour
CADMP PM10 NH3	ARB	24 hour
CADMP PM10 SO2	ARB	24 hour
CADMP PM2.5 Mass	ARB	24 hour
CADMP PM2.5 Ca, Mg, Na, K,	ARB	24 hour
CADMP PM2.5 NH4	ARB	24 hour
CADMP PM2.5 SO4, NO3, Cl	ARB	24 hour
CADMP PM2.5 HNO3	ARB	24 hour
CADMP PM2.5 HNO2	ARB	24 hour
CADMP PM2.5 NH3	ARB	24 hour
CADMP PM2.5 SO2	ARB	24 hour
CE-CERT PM2.5 Acid Deposition (AD) Sampler	ARB	24 hour
CE-CERT AD PM2.5 Mass	ARB	24 hour
CE-CERT AD NO2-, NO3-, SO4=	ARB	24 hour
CE-CERT AD NH4+	ARB	24 hour
CE-CERT AD HNO3	ARB	24 hour
CE-CERT AD HNO2	ARB	24 hour
CE-CERT AD NH3	ARB	24 hour
HVDVI for Organic Aerosol Species	Caltech	24 hour
MOUDI and Chemistry (Event Based)	DRI/STI	6 hour
Versatile Air Pollution Sampler (VAPS)	ARB/EPA	24 hour
VAPS PM10 Mass	ARB/EPA	24 hour
VAPS PM10 sulfate	ARB/EPA	24 hour
VAPS PM10 nitrate	ARB/EPA	24 hour
VAPS PM10 elements	ARB/EPA	24 hour
Nephelometer (Bscat)	ARB	1 hour
Nephelometer (Bscat)	DRI/STI	1 hour
COH	ARB	2 hour
Filter Based Gaseous		
SFS Ammonia	DRI/STI	3 hour
SFS Nitric Acid	DRI/STI	3 hour
Portable Ammonia	DRI/STI	24 hour
Portable Nitric Acid	DRI/STI	24 hour
Continued next page		

Table 2-3 (continued)

Measurement (Sampler:Species)	Contractor	Temporal Scale
Continuous Gaseous		
CO	ARB	1 hour
NO/NO2/NOx	ARB	1 hour
O3	ARB	1 hour
S02	ARB	1 hour
Hydrocarbons (canisters [C2-C12)	OGI/STI	3 hour
Hydrocarbons (cartridges [C10-C20)	OGI/STI	3 hour
Carbonyls (cartridges [C2-C7)	AtmAA/STI	3 hour
Total Hydrocarbons (8202)	ARB	1 hour
Toxic Compounds (Xontech 910)	ARB	1 hour
Ammonia (NH3)/NO/NO2/NOx	STI/TEI	1 hour
Fog (Event Based)		
CASCC2/CHRCC Water Content (Bulk Fog Sampler)	CSU	20 min
CASCC2/CHRCC pH	CSU	20 min
CASCC2/CHRCC Nitrate	CSU	20 min
CASCC2/CHRCC Sulfate	CSU	20 min
CASCC2/CHRCC Ammonium	CSU	20 min
CASCC2/CHRCC Cl	CSU	20 min
CASCC2/CHRCC Na, K, Ca, Mg	CSU	20 min
CASCC2/CHRCC Fe & Mn	CSU	20 min
CASCC2/CHRCC Total Organic Carbon (TOC)	CSU	20 min
CASCC2/CHRCC Dissolved Organic Carbon (DOC)	CSU	20 min
CASCC2/CHRCC Organic Acids	CSU	20 min
CASCC2/CHRCC Hydroperoxides (H2O2 & Organics)	CSU	20 min
CASCC2/CHRCC Total S(IV)	CSU	20 min
CASCC2/CHRCC HMS	CSU	20 min
CASCC2/CHRCC Formaldehyde	CSU	20 min
ETH Cloud Impactor Water Content	CSU	1 hour
ETH Cloud Impactor pH	CSU	1 hour
ETH Cloud Impactor Ammonia	CSU	1 hour
ETH Cloud Impactor Nitric Acid	CSU	1 hour
ETH Cloud Impactor major ions	CSU	1 hour
Hydrogen Peroxide (gas phase, continuous)	NCAR/CSU	10 min
Surface and Upper Air Meteorology		
Rawinsonde (WS, WD, T, RH, P)	STI	15-20 min
WS/WD (Standard Anemometer) (Surface)	ARB	1 hour
Temperature (Surface)	ARB	1 hour
RH (Surface)	ARB	1 hour
Solar Radiation	ARB	1 hour

Figure 2-2. Layout of the sampling equipment at Claremont



- Acids Sampler

  The uncoated denuder estimates particle loss. The coated denuders will collect nitric and nitrous acid and the NaCl-coated quartz substrate will filter particulate ions and retain nitric acid that would otherwise volatilize.

- Bases Sampler

  The uncoated denuder will again be used to estimate particle penetration. The coated denuder will collect ammonia and the citric acid-coated quartz filters will collect particulate ions and retain ammonium that would otherwise volatilize.

- Fine Particulate Sampler

  This denuder/filter stack follows a CADMP cyclone and plenum to obtain a 2.5 μm size-cut. Gas phase nitric acid and ammonia are collected by the denuders, the Teflon filter collects particulate matter for mass and ion analysis, and the coated quartz filters collect volatilized ammonium nitrate (equal molar quantities of ammonia and nitrate are expected to be collected by each substrate). The nitric acid measurement provides an indication of losses and gains through the CADMP inlet system.

Each denuder/filter stack sampled for 24 hours, starting at midnight. The nominal flow rate through each one was 5 L/min. A fourth stack was configured as a base, acid, or fine particulate sampler. The sampler consisted of two sets of cassettes so sampling could be switched automatically at midnight. Appendix C contains the Standard Operating Procedure (SOP) for the sampler. This SOP describes the sampler in detail and provides operator instructions.

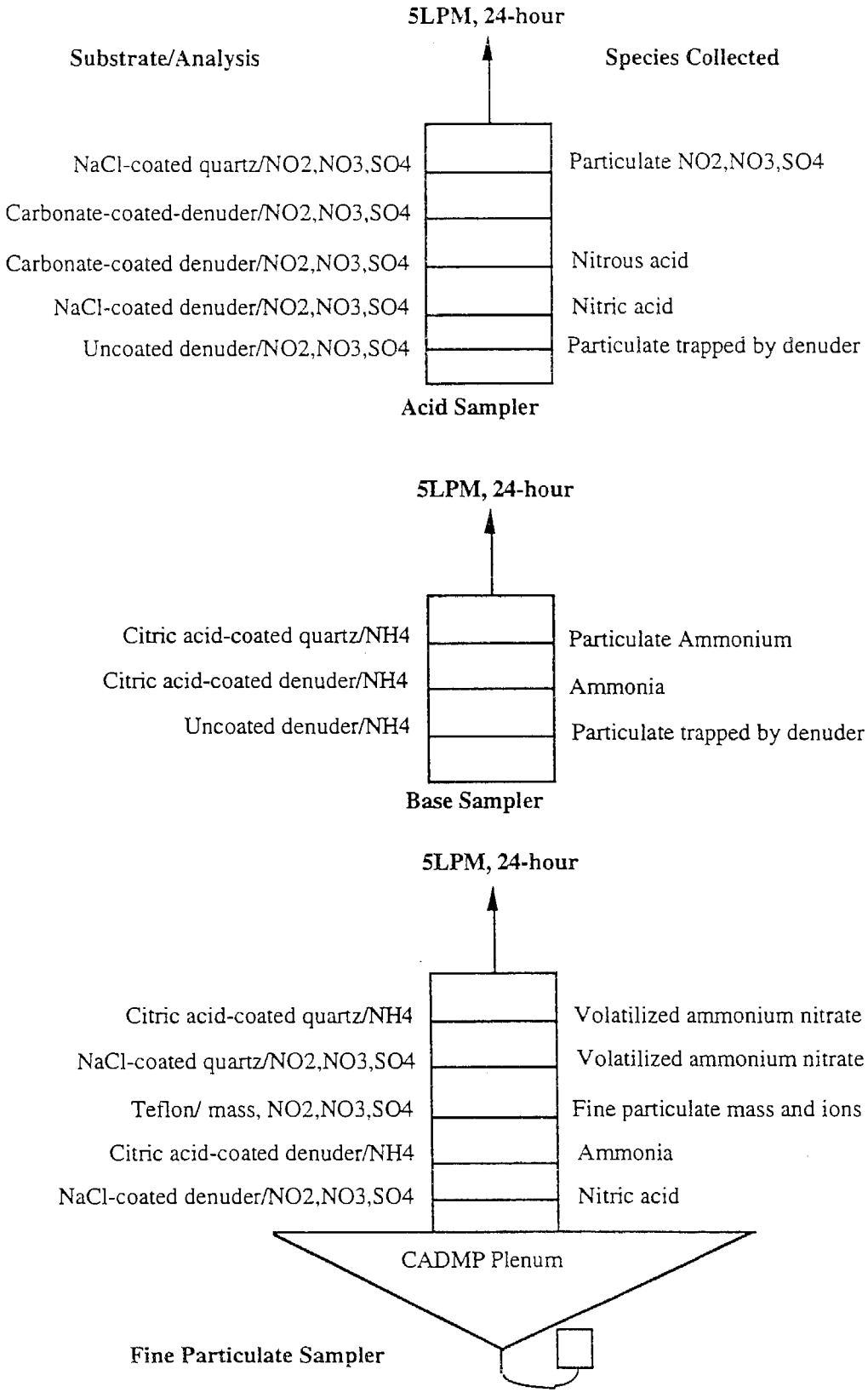
The data collected by the prototype CE-CERT sampler were compared with those of the following samplers which made the same measurements over the same time interval:

CADMP: $PM_{2.5}$ mass, nitrate, sulfate, ammonium, nitric acid

EPA-WINS $PM_{2.5}$ Reference Sampler: $PM_{2.5}$

TEI Continuous Ammonia Analyzer: Ammonia

Figure 2-3. CE-CERT sampler configuration for IMS95 at Bakersfield
(These were operated in parallel)



3.0 LABORATORY EVALUATION OF DENUDERS

Denuders were evaluated in the laboratory by passing known concentrations of nitric acid (HNO_3), nitrous acid (HNO_2), peroxyacetyl nitrate (PAN), formic and acetic acid, ozone, and ammonia (NH_3) through them at various temperatures and humidities. The basic schematic drawing of the exposure system was shown in Figure 2-1. Ammonia and sulfur dioxide also used permeation tubes, while for nitrous acid a sublimation tubes was used. An ultraviolet lamp was used to generate ozone. Gas mixtures in the range of 10-40 ppb were generated at relative humidities of 10-80%. Concentration measurements, used to determine penetration, were made before and after the denuder using either collection substrates (coated filters) and/or when possible, a real time analyzer by sampling through Teflon "T" tube fittings.

The following describes methods of generating pollutant gases for laboratory evaluations:

Pollution-Free Air

Pollution-free air was generated with an Aadco model 727 pure air generator that effectively reduces the concentrations of gases such as sulfur dioxide, nitric acid, and ammonia to less than one ppb. The pure air was humidified by splitting the flow, bubbling one fraction through deionized water, and then recombining the dry air with the water-saturated air as shown in Figure 2-1. All air flows were measured with rotameters and a mass flow meter, and controlled with needle valves. The rotameters and the mass flow meter were calibrated against a certified dry gas meter. Concentrations were estimated from permeation tube emission rates and clean air dilution volumes and then verified, when possible, by direct measurement.

Nitric Acid

Nitric acid vapor was generated by flowing dry air past a permeation tube containing liquid nitric acid. Nitric acid reduces to nitric oxide in the thermal converter of commercial NO-NO_X analyzers (Winer et al., 1974). A single Thermoenvironmental Model 42 NO-NO_X analyzer was therefore used to determine nitric acid concentrations before and after the denuders by sequentially inserting the inlet through the filter sampling ports. The instrument was calibrated and maintained in accordance with EPA PSD guidelines (US EPA, 1984, 1987). Zero and span checks were made before and after each day of measurements. The NO-NO_X analyzer was operated in the manual mode with the converter removed from the instrument case and placed as close to the sample point as possible to minimize nitric acid losses through the sampling inlet (after passing through the converter, the nitric acid has been converted to the much more stable nitric oxide).

Nitrous Acid

The approach demonstrated by Vecera and Dasgupta (1990) of generating nitrous acid by the sublimation of ammonia nitrite was used. In our case a six-inch section of $^1/_4$-inch diameter PFA Teflon tubing was packed with ammonium nitrite and maintained in a refrigerator at 4°C. The tube was purged with "prepure" grade nitrogen (Matheson) at a nominal flow rate of 10 ml/min and introduced into the exposure apparatus where the permeation tube line was normally connected. Penetration through the denuder was again determined by sampling with the Thermoenvironmental NO-NO_x analyzer calibrated against NO span gas. Nitrous acid was also quantified by collection on a quartz fiber filter (Pallflex QAT-UP) coated with a 2% (w/w) solution of potassium carbonate.

Ammonia, Sulfur Dioxide, and Organic Acids

These species were generated using commercial permeation tubes with specified emission rates. The permeation rate of the ammonia tube was determined gravimetrically. Manufacturer-specified permeation rates were used for sulfur dioxide, formic acid, and acetic acid permeation tubes. The test gas concentrations were calculated from the permeation rates and the dilution air flow rates. The concentration of ammonia was monitored by passing the sample through a CD Nova model CDN-101 Thermal Oxidizer equipped with a stainless steel converter and then to a Thermoenvironmental model 42 NO-NO_x analyzer calibrated against NO (also passed through the thermal oxidizer). The thermal oxidizer consists of a 1-foot-long, $^1/_4$-inch O.D. stainless steel tube maintained at a constant high temperature between 800°C to 950°C (temperature was periodically adjusted until no further conversion was observe. Sulfur dioxide concentrations were monitored using a Meloy 285 flame photometric analyzer. The sulfur analyzer was calibrated with the permeation tube used for the exposure studies using the stated emission rate. Concentrations were adjusted by varying the amount of diluent air. This was adequate for the test purposes because the ratio of SO_2 concentrations before and after the denuder were sought rather than the absolute SO_2 concentrations.

Ozone

Ozone was generated using a Monitor Labs Model 8600R gas calibrator equipped with a low-pressure mercury lamp ozonator. A Columbia Scientific Model 1600 analyzer was used to determine ozone concentrations before and after the denuders.

PAN

Peroxyacetyl nitrate (PAN) was prepared by the photolysis of ethyl nitrite (Stephens et al., 1965). The PAN was purified by preparative gas chromatography and then introduced into a 30-liter stainless steel tank. The tank was then pressurized with nitrogen to a PAN concentration of approximately 500 ppm at 50 psig. This concentration and purity was verified by IR analysis in a

10 cm gas cell. The PAN mixture was metered into the output of the pure air system (Aadco model 737) to produce a concentration of 10-50 ppb.

PAN concentrations were measured at the inlet and outlet of the denuder to be tested by using the Thermoenvironmental NO-NO_x analyzer. The IR analysis showed less than 5% of other nitrogenous species in the PAN tank and PAN has been shown to be reduced to nitric oxide in commercial NO-NO_x analyzer converters (Winer et al. 1974). The PAN concentrations were also verified by analyzing 50 ml aliquots with a gas chromatograph equipped with an electron capture detector. Tests at temperatures higher than that of the laboratory (20-24°C) were not conducted since the PAN would likely decompose in the sampling system prior to detection.

Table 3-1 shows the sets of conditions for which denuders were evaluated. Initially, nitric acid was used for extensive denuder testing and development.

While the nitric acid generating and measurement system performed adequately to evaluate denuder penetration, there were several aspects which contributed to greater measurement imprecision and effort than originally anticipated. These include the following:

- The pure air system did not provide a stable background source of NO_x at the ppb level. A fluctuation of ± one ppb was typical during a 24-hour period. The diurnal pattern appeared to reflect ambient pollutant concentrations rather than instrument drift. Replacing the purification unit did not alleviate this problem.

- The Thermoenvironmental model 42 NO-NO_x analyzer showed a sporadic zero drift of ± one to two ppb over a period of hours to days, although there was no long-term (monthly) direction to this drift. While this was within the instrument's stated specifications, it caused significant uncertainty in determining the penetration of nitric acid at low penetrations since the outlet concentrations would be near the zero of the instrument. Thus, if the zero uncertainty is 2 ppb and the nitric acid at the inlet is 40 ppb, then there is constant a 5% uncertainty regardless of the level of penetration calculated. If all nitric acid is removed, then the penetration is calculated as 0 ± 5%.

Table 3-1. Denuders tested and laboratory exposure conditions
(Coating solutions contained 2% glycerol by volume)

Test Gas	Nominal Conc. ppb	Temp °C	RH %	Duration (days)	Flow rate (L/min)	Denuder/ Coating	Coating Solution % by weight
HNO_3	40	21	10	<1	2-20	NaCl	2&9
HNO_3	10	21	10	<1	2-20	NaCl	2&9
HONO	35	22	70	1	2	NaCl, Na_2CO_3	9, 2
HONO	35	37	23	1	2	NaCl, Na_2CO_3	9, 2
HONO	35	20	25	3	2	NaCl, Na_2CO_3	9, 2
PAN	25	20	80	1	2	NaCl, Na_2CO_3	9, 2
PAN	25	20	20	3	2	NaCl, Na_2CO_3	9, 2
SO_2	30	20	80	1	2	NaCl, Na_2CO_3	9, 2
SO_2	30	40	20	1	2	NaCl, Na_2CO_3	9, 2
SO_2	30	20	20	4	2	NaCl, Na_2CO_3	9, 2
formic + acetic acid	34, + 56	23	19	3	2	NaCl. Na_2CO_3	9, 2
formic + acetic acid	34, + 56	23	80	3	2	NaCl. Na_2CO_3	9,2
formic + acetic acid	34, + 56	40	25	3	2	NaCl. Na_2CO_3	9,2
O_3	100	23	15	<0.1	2	KI	2
O_3	100	23	15	<0.1	2	NaCl	9
NH_3	40	38	20	<0.1	2	NaCl	9
NH_3	40	38	20	<0.1	2	KI	2
NH_3	40	21	20	0.1	2	citric acid	2
NH_3	40	21	80	0.6	2	citric acid	2
NH_3	40	22	25	5	1	citric acid	2
NH_3	40	22	25	2	2	citric acid	2
NH_3	40	20	20	0.1	2	citric acid	9
NH_3	40	21	17	0.9	2	phosphoric acid	2
NH_3	40	20	20	1.8	2	phosphoric acid	9
NH_3	13	21	20	1.1	2	phosphoric acid	9
NH_3	13	21	80	7.0	2	phosphoric acid	9
NH_3	13	38	22	4.9	2	phosphoric acid	9
NH_3	40	38	20	2.7	2	phosphoric acid	9

- Long lag times, typically several hours, to reach 95% of the final value occurred after step changes in the nitric acid concentrations. This has been observed previously in this laboratory (Fitz and Hering, 1996) and may be due to adsorption/desorption processes on the PFA Teflon tubing (used to introduce the nitric acid to the denuder and provide an inlet to the analyzer) or in the NO_X converter.

- Small changes in NO_X response (0.5 ppb) were observed for zero air when the humidity was increased from 0 to 50%, and larger changes were seen (up to two ppb) when additional water was added to the humidifier. The latter were not reproducible, and the zero returned to its approximate initial value within several hours. (Since the zero would drift for other reasons, this response was difficult to quantify.)

- The exposure system was set up with the NO-NO_X analyzer in a large storage room next to a dynamometer facility. Vehicles were occasionally operated briefly in this room, causing high NO_X concentrations. While no leaks could be found in the exposure or sampling system, upward drifts of up to several ppb were observed in the NO_X measurements when some of these emission activities occurred. This was most noticeable when sampling zero air but obviously would have a similar effect regardless of the sampling mode. We believe that the NO_X from these activities permeated the PFA sample line to the NO-NO_X analyzer. Room concentrations were measured several times during these vehicle start-up events and found to be from 0.5 ppm to offscale (greater than 10 ppm). At these concentrations, very little permeation would cause ppb-level responses in the NO-NO_X level.

The combination of the five phenomena above made the measurement uncertainty difficult to estimate. For example, while one is waiting for the concentration to stabilize after a step change, several ppb of drift may occur. This is especially critical when determining the collection efficiency since one ppb change at zero concentration causes an apparent 5% change in efficiency when 20 ppb of nitric acid is used for the exposure. The NO-NO_X analyzer data should therefore be thought of in most cases as qualitative at low levels of penetration. The one exception is when the denuder is removing most of the nitric acid and the analyzer has not been exposed to nitric acid for several hours. However, for these requirements, it must be assumed that the nitric acid at the inlet of the denuder remains unchanged (since it cannot be measured without requiring several hours to reach the final concentration, depending on the humidity, and several more hours to reach a stable zero). In the course of obtaining such a measurement, zero drift of the instrument may have occurred, although it would not be quantifiable.

3.1 Denuder Substrate Material Evaluation for Nitric Acid

Denuders coated with sodium chloride and sodium carbonate were used for the initial laboratory evaluation of denuder performance. This study was conducted in two phases, the first to validate the approach and the second to optimize it for nitric acid.

Phase I

A variety of cloth materials was obtained at a fabric store. The materials were chosen for open weave (ones with greater porosity) which should allow maximum particle penetration. The store could provide little information as to the composition of the fabrics other than all cotton or containing synthetic components (determined by a char test using a match). The bolts contained no information other than the manufacturer, and sometimes this information was not present. The initial fabric chosen (Material 1) was coated by immersing in a 50/50 (v/v) solution of methanol/water containing 2% (w/w) sodium chloride or sodium carbonate and 1% (w/w) glycerol and then removing the fabric and allowing it to air dry on aluminum foil. The denuder was exposed to a nominal 30 ppb of nitric acid using the system described in section 2. The nitric acid was measured with a NO-NO_X analyzer before and after the denuder. All exposures were conducted at room temperature (20 ± 1°C) at a nominal relative humidity of 10%. The nitric acid concentration and relative humidities were chosen to provide the most difficult ambient conditions for a coated substrate to collect this species.

Table 3-2 summarizes the results in chronological order. Method 2 was used to calculate denuder efficiency since a continuous analyzer was used to measure concentrations before and after the denuder; denuders themselves were not analyzed. Sodium chloride was the first coating mixture evaluated. This coating mixture is preferred because it does not efficiently remove other nitrogenous species such as nitrous acid (HONO) or peroxyacetyl nitrate (PAN). Sodium carbonate would remove these species as nitrite rather than nitrate, but nitrite is easily oxidized to nitrate when exposed to ambient concentrations of ozone. With the 2% sodium chloride coating on Material 1, the collection efficiency was never better than 89% even at a flow rate as low as 0.6 L/min and would not stabilize.

The experiments were repeated with a sodium carbonate coating on Material 1. Nitric acid was found to be collected nearly quantitatively at flow rates up to 5 L/min, although the efficiency dropped to 83% after four hours of sampling. Figure 3-1 shows the efficiency (after stabilization) of removing 33 ppb of nitric acid in dry air for a variety of flow rates. At 10 L/min the efficiency was 93%, which is in good agreement with the theoretical value of 98% (see Section 2-1). We expected the measured efficiency to be lower than the theoretical since theory assumes that each molecule of nitric acid contacting the fiber was removed, which may not be the case. Two such denuders in series at 19 L/min were found to be as quantitative in retaining nitric acid as a Nylasorb filter sampling at 15 L/min (a higher flow rate could not be obtained due to the pressure drop through the Nylasorb filter).

Table 3-2. Summary of results in chronological order

Date (95	Denuder Material	Coating** Material	Coating Conc (%	RH %	HNO3 In, ppb	0.6 L/min HNO3 out,ppb	0.6 L/min % Effic	5 L/min HNO3 out,ppb	5 L/min % Effic	10 L/min HNO3 out,ppb	10 L/min % Effic.	15 L/min HNO3 out,ppb	15 L/min % Effic.	19 L/min HNO3 out,ppb	19 L/min % Effic.	Comments
10-Nov	1	NaCl	2	10	32.6	6.7	79	6.1	81	7.9	76	8.8	73			at 15 L/min efficiency dropped to 21% after 17 hours
11-Nov	1*	NaCl	2	10	32.6	19.3	41	20.5	37	25.3	22	25.8	21			at 0.6 L/min efficiency rose to 65% after 3 hours
14-Nov	1*	NaCl	2	10	29.2	3.1	89	17.8	39							
14-Nov	1*	NaCl	2	10	29.2	12.0	59									at 0.6 L/min efficiency rose to 68% in 1 hour
14-Nov	1	Na2CO3	2	10	29.2	1.1	96	0.5	98	0.8	97	2.1	93			at 15 L/min efficiency dropped to 57% over 16 hours
15-Nov	1*	Na2CO3	2	10	33.4	0.0	100	3.0	91							at 5 L/min efficiency dropped to 83% in 4 hours and stabilized
16-Nov	1	Na2CO3	2	10	33.4	0.0	100	0.0	100	0.5	99	1.2	96	2.1	94	
16-Nov	1*	Na2CO3	2	10	33.4	0.0	100	0.0	100	1.3	96	2.0	94	2.1	94	
17-Nov	1*	Na2CO3	2	10	33.4	0.0	100	0.9	97	3.1	91	4.5	87			
17-Nov	1*	Na2CO3	2	10	33.4	0.0	100	0.4	99	0.3	99	0.3	99			at 10 L/min eficiency dropped to 72% in 15 hours
18-Nov	1	None	0	10	39.3					39.3	0					
18-Nov	2	Na2CO3	2	10	32.2	2.1	93	2.6	92							#2 material not as good as #1
21-Nov	2*	Na2CO3	2	10	32.2	0.8	98	8.7	73	15.4	52		100		100	#2 material saturating
22-Nov	1/1	Na2CO3	2	10	33.8	1.3	96	0.4	99	0.0	100	0.2	99	0.4	99	Series denuders very efficient
23-Nov	1*/1*	Na2CO3	2	10	32.6	0.6	98							0.6	98	
23-Nov	nylon filter			10	33.5							0.8	98			
23-Nov	1*/1*	Na2CO3	2	10	33.5									0.4	99	
23-Nov	removed/1*	Na2CO3	2	10	33.5									0.5	99	efficiency down to 87% in 100 min;adding 2nd denuder restored it
24-Nov	1*/1*	Na2CO3	2	10	33.5									21.2	37	after sampling @ 19L/min for 22 hours
28-Nov	1*/1*	Na2CO3	2	10	33.5	1.3	96									after sampling @ 0.6 L/min for 90 hours
28-Nov	1*/1*	Na2CO3	2	10	33.5			4.2	87							at 5 L/min efficiency dropped to 73% after 3 hours
28-Nov	1	Na2CO3	9	10	33.5	2.2	93							4.2	87	at 19 L/min efficiency dropped to 68% in four hours
29-Nov	1*	Na2CO3	9	10	33.5									14.5	57	additional 17 hours of sampling; 9% not solution
29-Nov	1	NaCl	9	10	33.5	1.4	96							8.4	75	at 19 L/min efficeiency dropped to 61% in 4hours
30-Nov	1*	NaCl	9	10	33.5									15.0	55	stable at this efficiency
30-Nov	1	NaOH	9	10	33.5	1.2	96							0.6	98	at 19 L/min efficiency dropped to 42% in 25 hours
1-Dec	1/1	NaCl	9	10	33.5	2.2	93							1.1	97	at 19 L/min efficiency dropped to 69% in 16 hours
2-Dec	1*1*	NaCl	9	10	33.5	2.2	93	5.5	84							at 5 L/min efficiency dropped to 41% after 72 hours
8-Dec	3	NaCl	9	10	33.5			1.0	97							at 5 L/min efficiency dropped to 68% in 48 mins; 55% in 16 hours
8-Dec	4	NaOH	9	10	33.5	1.2	96	2.0								at 5 L/min efficiency dropped to 72% in 20min; to 63% in 4hours
8-Dec	4*	NaCl	9	10	33.5					13.1	61	18.1	46			
9-Dec	1/1	NaCO3	2	10	33.5	0.6	98	5.5	84	0.0	100	0.0	100	0.0	100	at 5 L/min efficiency dropped to 69% after 62 hours

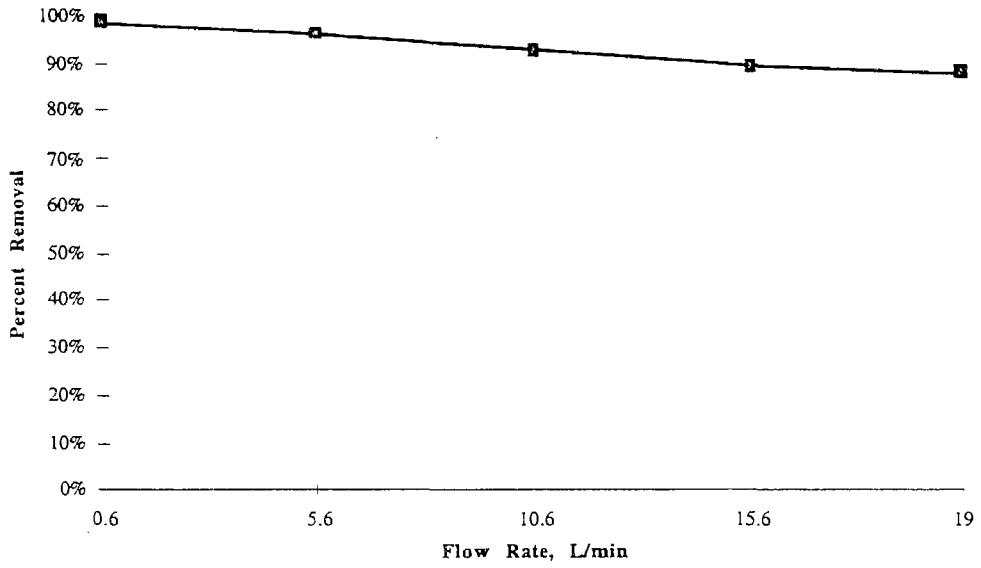
* Same denuder as previous experiment

** All denuders were coated using a solution of 50/50 v/v of water/methanol to which 1% (w/w) glycerol was added

Material 2 was coated with sodium carbonate and was found to have lower sampling efficiency for nitric acid and to be more easily saturated. Increasing the percentage of sodium carbonate or chloride in the coating mixture 2 to 9% did not cause a significant improvement in either the initial retention efficiency or reduce the saturation effect. This material was therefore not considered further.

Materials 3 and 4 displayed poorer retention of nitric acid than 1 or 2, particularly with respect to saturation. Since they appeared to be 100% synthetic fabrics, it is likely that the amount of coating material they adsorbed was low. When fabric 4 was coated with potassium hydroxide, the initial retention efficiency was over 90% but dropped rapidly in tens of minutes. This further confirmed that it was difficult to obtain a sufficient amount of coating on these synthetic materials.

Figure 3-1. Nitric acid removal efficiency (35 ppb) sodium carbonate coated denuder



Phase II

The goal of Phase II of the laboratory evaluation of sodium chloride-coated denuders was to determine the most effective denuder material and coating mixture for removing nitric acid. As in the first phase, the tests were conducted at room temperature and a nominal relative humidity of 10%. Nitric acid concentrations ranged from 10-25 ppb. These concentrations are more typical of ambient episodes in the South Coast Air Basin than the 30-35 ppb used during Phase I. The tests were also conducted at a design flow rate of 10 L/min, to allow sufficient sensitivity for extraction and analysis of 12-hour samples.

Table 3-3 presents the results in chronological order. Method 2 was again used to calculate denuder efficiency from the continuous analyzer data. We started with Material 5, which is an all-cotton, loosely woven fabric. The collection efficiency was too low to be useful as a sampling substrate (<35%) and we proceeded to test a number of other materials. These included a loosely woven rayon, nylon of the type used for women's hosiery with and without a coating (since nylon filters remove nitric acid, we hypothesized that hosiery nylon might also), a fine bronze mesh with a coating, an aluminum window screen (again we hypothesized that aluminum may not need to be coated since it is used as a nitric acid denuder sorbent surface), and a coated fiberglass window screen. The best performance was obtained by soaking rayon in a saturated solution of sodium chloride. The performance, however deteriorated rapidly, most likely due to a light coating because of the limited ability of the solution to be adsorbed. Three uncoated nylon denuders in series produced 90% collection efficiency, but this also deteriorated with time. Additionally, we felt that three (or more) denuders in series would not meet the sampler objectives and such multiple denuders probably would result in significant particle losses.

We then retested Material 1 with a 9% sodium chloride coating (the glycerol concentration was increased to 2% (v/v) for all coating mixtures at this sodium chloride concentration). While denuder efficiency was initially near 90%, it dropped to 45% after 14 hours of sampling. Denuder Material 5 was then evaluated with a carbonate coating. The collection efficiency was less than 40%; this material therefore did not work as well as Material 1. We then performed a series of experiments on Material 5 by adjusting the NaCl coating procedure to improve the performance. The best performance, 76% efficiency, was achieved with three denuders in series that had been soaked in a saturated NaCl solution in boiling water in an attempt to produce a pure sodium chloride surface on the denuder. This efficiency would require three or more denuders in series which might lead to significant particulate loss; its performance to remove nitric acid also deteriorated to 63% after 14 hours of sampling. During this testing, we found that a higher efficiency would be obtained if a three-inch-long spacer was installed in the front of the denuder holder. This apparently reduced the jetting effect

Table 3-3. Summary of the phase II laboratory evaluation of the nitric acid removal efficiency by sodium chloride coated denuder substrate. (Unless otherwise indicated, all tests at room temperature 20±2°C and flow rate of 10 L/min through the denuder.)

Material	NaCl* Coating	RH Percent	HNO3 In ppb	HNO3 Out ppb	Percent Removal	Comments
5	2%	0%	18.0	13.3	26%	
5	2%	13%	18.0	11.9	34%	
Rayon	2%	12%	21.9	6.5	70%	
Rayon	sat	12%	20.8	5.5	74%	
Rayon	sat	12%	20.8	18.1	13%	After running denuder 14 hours
Nylon	none	12%	24.6	16.0	35%	
Nylon	none	12%	24.6	9.4	62%	Two denuders in series
Nylon	none	12%	24.6	2.8	89%	Three denuders in series
Nylon	none	12%	24.6	15.1	39%	Three denuders in series after running 14 hours
Nylon	sat	12%	24.6	21.0	15%	
Screen	sat	12%	24.6	17.6	28%	Bronze 200 mesh screen
Screen	none	12%	24.6	20.3	17%	Aluminum 20 mesh screen
Screen	sat	12%	24.6	18.7	24%	Fiberglass 20 mesh screen
1	9%	12%	24.6	3.0	88%	
1	9%	12%	24.6	13.6	45%	After running denuder 14 hours
5	2%†	12%	23.8	15.1	37%	Long spacer installed permanently in front of denuders
5	2%†	12%	23.8	10.0	58%	Three denuders in series
5	sup sat	12%	23.8	19.8	17%	After 15 hours of sampling
5	sup sat	12%	23.8	9.1	62%	Glycerol pretreatment
5	sup sat	12%	23.8	5.7	76%	5 % Glycerol, cooled in super sat soln, 3 series denuders
5	sup sat	12%	23.8	8.7	63%	Same after 14 hours
7	9%	11%	22.6	9.5	58%	New Flow system, 1 l/min?
7	9%	21%	22.6	5.6	75%	1 L/min?
7	9%	11%	11.7	8.1	31%	1 L/min?
8	9%	11%	11.7	2.3	80%	1 L/min? efficiency dropped to 63% over 3 hours
9	9%	11%	11.7	3.8	68%	1 L/min? efficiency dropped to 24% over 3 hours
10	9%	11%	11.7	8.0	32%	1 L/min? efficiency dropped to 11% over 3 hours
11	9%	11%	11.7	3.2	73%	1 L/min?
11	9%	11%	11.7	10.7	9%	1 L/min? after sampling 16 hours
12	9%	11%	11.7	5.6	52%	1 L/min? efficiency the same for 3 hours
5	9%	11%	11.7	2.6	78%	1 L/min, stable over 3 hours
7	9%	11%	11.7	2.2	81%	1 L/min
7	9%	11%	11.7	2.1	82%	Back to 10 L/min
8	9%	11%	11.7	1.4	88%	Stable 1 hour
5	9%	11%	11.7	2.2	81%	
7	9%	11%	14.4	4.4	69%	Efficiency dropped to 32% over 2 hours
8	9%	11%	14.4	5.5	62%	
14	9%	11%	14.4	4.2	71%	Efficiency dropped to 44% in 90 minutes
15	9%	11%	14.4	6.7	53%	Efficiency dropped to 38% in one hour
16	9%	11%	14.4	5.2	64%	Efficiency dropped to 49% in one hour
17	9%	11%	14.4	4.5	69%	Efficiency dropped to 42% in two hours

Continued next page

Table 3-3 continued

Material	Coating	Percent	ppb	ppb	Removal	Comments
8	9%	10%	9.9	2.5	75%	Stable 30 minutes
7	9%	10%	9.9	3.6	64%	Stable one hour
9	9%	10%	9.9	2.2	78%	Stable two hours
8	9%	10%	9.9	2.1	79%	Stable two hours
20	9%	15%	9.9	2.9	71%	
19	9%	15%	9.9	3.5	65%	
1	9%	15%	9.9	2.0	80%	
8	9%	15%	9.9	1.2	88%	6 L/min
5	9%	15%	9.9	1.8	82%	2 L/min, stable two hours
5	9%	15%	9.9	7.2	27%	5 L/min; after 14 hours of sampling
5	9%	15%	9.9	5.3	46%	1.5 L/min after 14 hours of 5 l/min sampling

* All coating mixtures contain 2% v/v glycerol
† Sodium carbonate coating

of the 10 L/min of air used to expose the denuders. This jet would cause only the center part of the denuder to be exposed to significant amounts of nitric acid. This jetting effect would be reduced under ambient sampling since an open-face holder would be used. (A closed-face holder was necessary in the laboratory to direct the synthetically-produced nitric acid stream to the denuder.)

Twelve additional materials were then evaluated using a 9% sodium chloride coating solution. Materials 1 and 5 were also retested with the now adopted spacer on the front of the holder. Materials 1, 5, 7, and 8 showed over 80% initial collection efficiency, but this efficiency invariably dropped with continued sampling.

3.2 Interference Testing of Sodium Chloride Coating (Denuder Material 5, 9% Coating Mixture)

The sodium chloride denuders were also tested for penetration of HONO, PAN, SO_2, formic acid and acetic acid during evaluation of sodium carbonate denuders for collection of these species (see section 3.3), and for penetration of NH_3 during evaluation of the phosphoric acid-coated denuders (see section 3.5). The collection of HONO, PAN, formic acid, acetic acid, and NH_3 on the sodium chloride denuders was below detection limits; penetration efficiencies were better than 99.5%. The collection of SO_2 on the sodium chloride denuders was less than 1% at 20% RH, and approximately 3% for the test conducted at 80% to 90% RH.

3.3 Sodium Carbonate Coating (Denuder Material 5)

Sodium carbonate denuders were tested for collection of HONO, PAN, SO_2, formic acid and acetic acid. The collection efficiency of individual sodium carbonate denuders was tested in parallel with the collection efficiency of the overall denuder stack. The denuder stack consisted of one sodium chloride denuder followed by two sodium carbonate denuders in series (the denuder substrates were

separated by spacers in the Savillex holders). This array was chosen since an ambient sampler would require a sodium chloride-coated denuder to remove nitric acid prior to the removal of other acidic species. The single sodium carbonate denuder and the sodium chloride/sodium carbonate denuder stack sampled simultaneously in parallel from the test gas system at flow rates of 2 L/min. The concentrations of the test gas upstream and downstream of the single denuder were alternately monitored with a continuous analyzer. After exposure, the single denuder and the denuders in the denuder stack were extracted and analyzed for nitrite, nitrate, sulfate, and chloride or for formate and acetate.

We did not have a continuous analyzer for formic and acetic acid. Therefore, two denuder stacks were sampled in parallel, rather than one denuder stack and one single denuder. The denuders were exposed to both gases at once by including both formic acid and acetic acid permeation tubes in the permeation system at the same time. Three pairs of denuder stacks were sampled under conditions shown in 3-1, but only two stacks were extracted and analyzed: one at 23°C and 19% RH, and one at 23°C and 80% RH. The duplicate stacks sampled at these conditions, and both stacks sampled at 40°C and 25% RH are archived at CE-CERT.

The results for HONO, PAN, SO_2, formic acid, and acetic acid collection on sodium chloride and sodium carbonate denuders and are shown in Table 3-4. The method used to calculate denuder efficiency depended on whether the denuder was in a stack or not, and whether is was the first denuder in a stack. For Method 2 denuder efficiencies were calculated at hourly intervals from the continuous analyzer and the average over the sampling period was reported. The collection efficiencies shown for all three methods in Table 3-4 are expressed in terms of efficiency for a single denuder. The efficiency of a denuder stack consisting of two like denuders in series, assuming equal collection efficiency for each denuder, may be calculated as follows:

$$E_2 = 1 - (1-E_1)*(1-E_1) \qquad (5)$$

where:

E_1 = collection efficiency of a single denuder

E_2 = collection efficiency of two denuders in series

Thus for example, the denuder efficiency of 86% reported for a 3-day exposure to 35 ppb HONO at 25% RH produces an overall collection efficiency of 98% for the denuder stack.

Table 3-4. Results for laboratory testing of NaCl and Na_2CO_3 coated denuders

Test gas	Nominal Concentration ppb	Temp C	RH %	Duration days	Collection efficiency of each gas for a single denuder (%)		
					Method 3 NaCl(1st)-coated of stack	Method 1 Na_2CO_3-coated of stack	Method 2 Na_2CO_3-coated-single
HONO	35	22	70	1	<1	98	95
HONO	35	37	23	1	<1	96	92
HONO	35	20	25	3	<1	86	77
PAN	25	20	80	1	<1	-	0
PAN	25	40	20	-	-	-	-
PAN	25	20	20	3	<1	-	0
SO2	30	20	80	1	<4	>99	93
SO2	30	40	20	1	<1	>99	75
SO2	30	20	20	4	<1	<50	40
formic + acetic acid	34 + 56	23	80	3	<1, <1	97, 57	
formic + acetic acid	34 + 56	23	19	3	<1, <1	62, <50	

For HONO under humid conditions, the collection efficiency for the carbonate coated denuder was observed to remain constant at about 95% for 20 hours. At high temperature and dry conditions, the initial collection efficiency was about 96% and dropped steadily to about 88% after 24 hours, averaging 92%. For dry conditions at room temperature, collection efficiency dropped steadily from 96% to 60% after 90 hours, averaging 77%. The efficiencies determined by Method 1 for the first carbonate coated denuder of the stack for these three test conditions were 98%, 96%, and 86% respectively. Based on these results, two sodium carbonate denuders in series at 2 L/min are adequate for quantitative collection of HONO at loadings up to about 100 ppb-days.

The gas chromatograph showed that during the course of the project, the PAN gradually decomposed. The PAN concentration determined by the GC was approximately 60% of the nitrate response measured by the NO_X analyzer. The decomposition products were visible on the GC trace as a peak eluting well before the PAN peak. The partial decomposition of PAN did not affect the assessment of denuder efficiencies for PAN collection because the PAN and its decomposition products were passed with 100% efficiency by both the single carbonate coated denuder and the denuder stack: NO_X analyzer-measurable nitrate was not reduced by the denuders, and no measurable quantities of NO_2^- or NO_3^- ion were measured in the denuder extracts. For PAN at room temperature

under both humid and dry conditions, the collection efficiency of the sodium carbonate denuder was less than 2% based on the ion analyses, and undetectable based on the continuous analyzer. Based on these results, PAN does not pose an interference for collection of nitric acid and HONO with this denuder stack.

For SO_2, the results by Method 1 for the first carbonate coated denuder of the stack indicate collection efficiencies of >99% for the one-day tests. However, the chart trace from Method 2 for the single denuder shows steadily decreasing efficiency over the course of 24 hours, averaging 93% for humid conditions at room temperature, and 75% for hot, dry conditions. The loading collected on the single denuder was nearly twice that collected on the front denuder of the denuder stack. The reason for these discrepancies could not be determined, but apparently the single denuder received a much higher input concentration or a much higher flow rate than the denuder stack; thus the single denuder accumulated a much larger load. As a result, the collection efficiency of the single denuder was less than 100% and declined steadily with time as indicated by the chart trace from Method 2. These data indicate that collection efficiency or collection capacity for SO_2 using carbonate coated denuders is sensitive to increases in flow rate and/or concentration. This is borne out by the results for the four-day test at room temperature and dry conditions. Both the single and stacked denuders showed substantial breakthrough. Thus we do not recommend using the current denuder stack for sampling of SO_2 without further study to determine its capacity.

For formic acid and acetic acid, Table 3-4 shows the results for room temperature at 19% RH and 80% RH. Results could only be calculated by Method 1 since we did not have a continuous analyzer. For the NaCl coated denuder the lower limit collection efficiency was estimated using the concentration of acid calculated from the stated permeation rate of the source tube. The data show that substantial breakthrough occurred under the conditions of the experiments except for formic acid at high relative humidity. For formic acid at 80% RH, the collection efficiency was 97%. For both 80% and 20% RH, the collection efficiency for formic acid was much better than the collection efficiency for acetic acid; this is consistent with formic acid being the stronger of the two acids. Also, for both acids, the collection efficiency was much better at 80% RH than at 20% RH, which is also consistent with behavior for other species.

The data are sufficient to show that sodium carbonate denuders are not highly efficient collectors for organic acids, but that they do collect substantial amounts of organic acid. The observed breakthrough may be due in part to the high exposure levels. The combined concentration of formic and acetic acid was 90 ppb for a cumulative exposure of 270 ppb-days. An average concentration of 10 ppb collected for seven days would produce a cumulative exposure of only 70 ppb-days. At this loading and for moderate humidities, the sampler might be effective for organic acids, particularly formic acid. This is especially true when two denuders in series are used for collecting organic acids.

A denuder stack (NaCl, Na2CO3, Na2CO3) for the collection organic acids would require a substantial test program to characterize its performance. It needs testing at lower concentrations of organic acids individually, in combination with each other, and in combination with stronger acid gases such as HONO that will pass the sodium chloride denuder and compete for active sites on the carbonate denuder. It is possible that collected acetic acid is driven off the denuder by subsequent exposure to stronger acids.

3.4 Citric Acid Coating (Material 5)

Denuders coated with 2% citric acid and with 9% citric acid were tested for collection of ammonia. The TECO model 42 NO_X analyzer equipped with a high temperature (900°C) stainless steel converter was used to monitor ammonia concentrations upstream and downstream of either a single denuder or a pair of denuders in series. During each test, either a single denuder or a pair of denuders in series was exposed. The denuders were then extracted and analyzed for ammonium. When two denuders in series are monitored, the denuder efficiency of both is calculated when using the continuous data (since we cannot sample between the two denuders). Assuming that the collection efficiencies of each denuder are constant and equal, then the efficiency of a single denuder is calculated by rearranging equation (5) to yield:

$$E_1 = 1 - \text{sqrt}(1-E_2) \qquad (6)$$

where:

E_1 = collection efficiency of a single denuder

E_2 = overall collection efficiency of two denuders in series

This method of calculating single denuder efficiencies will be referred to as Method 2b.

The results of citric acid denuder testing are shown in Table 3-5.

The first four tests shown in this table for 2% citric acid actually constitute a single test. A single 2% citric acid coated denuder was subjected to 40 ppb ammonia at 20% RH and 21°C. Initial efficiency was 73% and dropped to 68% after 2 hours, averaging 70%. Humidity was then raised to 80%. The collection efficiency rose to 74% and dropped steadily to 62% after an additional 15 hours, averaging 67%. Humidity was then lowered to 20%. Collection efficiency dropped to about 40%. Flow rate was then reduced to 1 L/min. Collection efficiency rose to 50% and continued to drop steadily. This denuder was not analyzed.

Table 3-5. Results for laboratory testing of citric acid denuders.

Test gas	Nominal Conc. ppb	Temp C	RH %	Duration days	Flow rate L/min	Denuder	Collection efficiency for a single denuder (%)		
							Method 1	Method 2	Method 2b
NH_3	40	38	20	<0.1	2	2% NaCl		0	
NH_3	40	38	20	<0.1	2	2% KI		0	
NH_3	40	21	20	0.1	2	2% citric acid		70	
NH_3	40	21	80	0.6	2	2% citric acid		67	
NH_3	40	21	20	0.1	2	2% citric acid		40	
NH_3	40	21	20	0.1	1	2% citric acid		50	
NH_3	40	22	25	5	1	2% cit. ac. pair	44	(65 for pair)	41
NH_3	40	22	25	2	2	2% cit. ac. pair	13	(60 for pair)	37
NH_3	40	20	20	0.1	2	9% citric acid		85	

Next, a pair of 2% citric acid denuders in series was exposed to 40 ppb ammonia at 25% RH and 22°C for about 5 days at 1 L/min. The initial efficiency of the pair was 98% and dropped steadily to 43% after 118 hours, averaging 65% by Method 2. An efficiency of 65% for a pair of denuders corresponds to an efficiency of 41% for a single denuder. Method 1 gives a single denuder efficiency of 44%.

Another pair of 2% citric acid denuders in series was exposed to the same conditions as above, but at a flow rate of 2 L/min for 2 days. The initial efficiency of the pair was 100% and dropped steadily to 32% after 48 hours, averaging 60% by Method 2. An efficiency of 60% for a pair of denuders corresponds to an efficiency of 37% for a single denuder. Method 1 gives a single denuder efficiency of 13% (the assumptions of constant and equal efficiency were probably violated, resulting in an underestimate).

The laboratory collection efficiency of 2% citric acid was not adequate to meet sampling needs. We tried boosting collection efficiency by using a 9% citric acid coating. A single denuder coated with 9% citric acid was exposed to 40 ppb ammonia at 20% RH and 20°C at a flow rate of 2 L/min. The initial collection efficiency was 94% but dropped steadily to 78% after 3 hours, and the test was terminated. This denuder was not analyzed.

These results clearly show that the citric acid denuders are not highly efficient collectors of ammonia in otherwise pure humidified laboratory air. This result is interesting because ambient experience with these denuders and with citric acid coated filters indicate good collection efficiencies. In fact, even uncoated denuder substrates appear to be highly efficient for ammonia in field tests, but a test of an uncoated denuder in the laboratory test system showed 0% collection efficiency for ammonia. There appears to be an interaction with ambient pollutants that results in retention of ammonia on uncoated and citric acid coated denuders. This situation is analogous to the results for nitric acid, which demonstrate that uncoated denuders are efficient collectors of nitric acid in ambient air, but poor collectors of nitric acid in laboratory tests. These issues are discussed later in the analysis of field study results.

3.5 Phosphoric Acid Coating (Material 5)

Denuders coated with 2% phosphoric acid and with 9% phosphoric acid were tested for collection of ammonia. The NO_X analyzer was used to monitor concentrations upstream and downstream of a single denuder. The denuders were then extracted and analyzed for ammonium. Collection efficiencies were calculated using Method 2. The results of testing phosphoric acid coated denuders are shown in Table 3-6.

Table 3-6. Results for laboratory testing of phosphoric acid denuders

Test gas	Nominal Conc. ppb	Temp C	RH %	Duration days	Flow rate L/min	Denuder Coating (w/w)	Collection efficiency (%) (Method 2)
NH_3	38	21	17	0.9	2	2% phosphoric	66
NH_3	38	20	20	1.8	2	9% phosphoric	90
NH_3	40	38	20	2.7	2	9% phosphoric	95
NH_3	15	21	20	1.1	2	9% phosphoric	100
NH_3	15	21	80	7.0	2	9% phosphoric	100
NH_3	13	38	22	4.9	2	9% phosphoric	100

The 2% phosphoric acid denuder was tested for collection efficiency with a nominal 40 ppb ammonia, 17% RH, and 21°C at a flow rate of 2 L/min. The initial collection efficiency was 93% and fell steadily to 47% after 22 hours, averaging 66%.

The 9% phosphoric acid denuders were tested at nominal concentrations of 40 and 15 ppb, 20°C and 40°C, 20% RH and 80% RH at a flow rate of 2 L/min. Average collection efficiencies indicated by Method 2 were 90-95% at 40 ppb for tests of two to three days duration. At 15 ppb, Method 2 did not detect any breakthrough for tests of one to seven days duration. The reported values of 100% collection efficiency by Method 2 have an uncertainty of approximately ±7% (1 ppb out of 15 ppb). Experiments with these concentrations of ammonia proved difficult due to several complications: the variable amount of time (typically several hours) required for ammonia concentrations, based on the thermal oxidizer-NO-NO_X analyzer approach, to stabilize throughout the sampling system was several hours; the thermal oxidizer degraded during this time and was replaced; and a temporary failure in the zero air supply system allowed low ppb levels of NOx into the zero air.

Overall, the collection efficiency of a single 9% phosphoric acid denuder is better than 90%, and two denuders used in series would have better than 99% collection. This denuder is therefore suitable for field sampling of ambient ammonia.

3.6 Potassium Iodide Coating (Material 5)

Denuders coated with 2% KI and 1% glycerol were tested for removal of ozone. The denuder sampling at 2.1 L/min was first tested at 102 ppb in bone dry (dew point ~ -40°C) calibration gas at room temperature using Method 2. The initial collection efficiency was 30% and dropped to less than

5% within one hour and the experiment was terminated. This denuder was then tested at 2 L/min, room temperature, relative humidity of 15%, and a concentration of 90 ppb ozone. The initial efficiency was 22% and remained at that level for 0.5 hours, at which point the experiment was terminated.

The conclusion is that 2% potassium iodide denuders are not adequate to remove ozone at flow rates of 2 L/min.

3.7 Conclusions from Laboratory Testing

The laboratory testing showed that Materials 1, 5 , 7 and 8 coated with NaCl resulted in denuders that were more than 80% effective in removing nitric acid, although the efficiency dropped with continued exposure. Material 5 was considered to have the highest potential for both effectively removing gases and passing particles. It was tested for removal of a variety of gases using different coating materials. The conclusions are that:

- Sodium chloride coatings did not remove measurable amounts of HONO, PAN, SO_2, formic acid or acetic acid.
- Sodium carbonate coating effectively removed HNO_3, HONO and SO_2, partially removed formic and acetic acid, and did not remove PAN.
- Citric acid coatings were partially effective at removing ammonia and therefore not a good candidate for quantifying this species.
- Phosphoric acid coatings effectively removed ammonia and could be used for quantification.
- Potassium iodide coatings were not effective in removing ozone and therefore could not be used to reduce the oxidation of particulate matter collected on filters downstream.
- The denuders show sufficient potential to perform evaluations using ambient air.

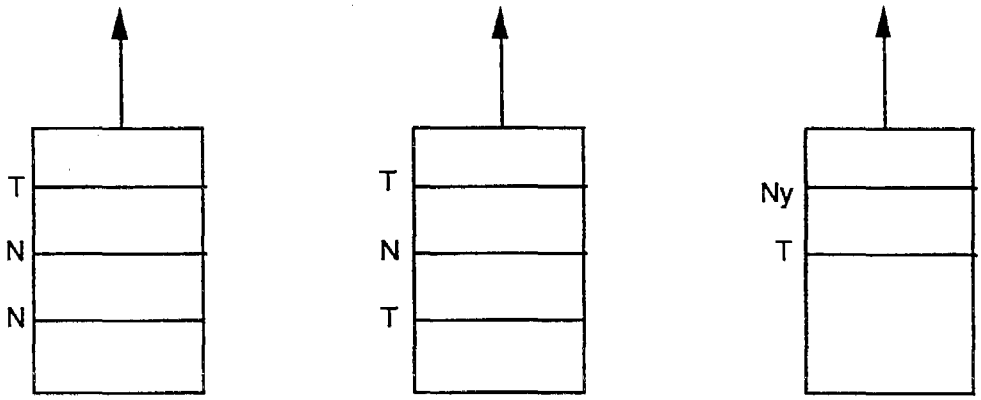
4. RIVERSIDE AMBIENT AIR DENUDER TESTING

4.1 First Evaluation

The first ambient air evaluation of the fabric denuder was conducted from January 31 to February 3, 1995. While ambient pollutant concentrations were expected to be approximately an order of magnitude lower this time of year compared with summer (resulting in greater measurement error), we felt it necessary to determine how the denuder functioned on ambient air before proceeding with the laboratory evaluation. Figure 4-1 shows the sampling configuration used for this evaluation. Sodium chloride (2% (w/w) with 1% (v/v) added glycerol) coated denuders (test Material 1) were used to sample both upstream and downstream of Zefluor Teflon filters. Nitric acid was also measured by the filter pack approach of collecting nitric acid on a nylon filter downstream of a Teflon filter. Samples were collected on 47 mm substrates at 5 L/min for 24 hours starting at 1300 hours PST.

Figure 4-1. Sampling configuration for the first ambient evaluation of denuders (Material 1)

5 L/min-24hr



N = Sodium chloride coated (2%) denuder material #1

T = Gelman 2μm pore Zefluor Teflon filter

Ny - Gelman 1 μm pore Nylasorb filter

Table 4-1 shows the results of nitrate and sulfate analyses. The blank correction (four dynamic blanks) for the denuder substrates were 0.89 ± 0.13 μg/filter for nitrate and 1.89 ± 0.27 μg/filter for sulfate. At the nominal flow rate of 5 L/min for 24 hours, the uncertainty of the measurements depending on the blank variability, was 0. 05 $\mu g/m^3$ for nitrate and 0.08 $\mu g/m^3$ for sulfate with a flow

uncertainty of an estimated 5%. For these experiments, the uncertainty due to blank variability was dominant, ranging from 7%-167% for nitrate and from 35%-67% for sulfate, depending on the concentration.

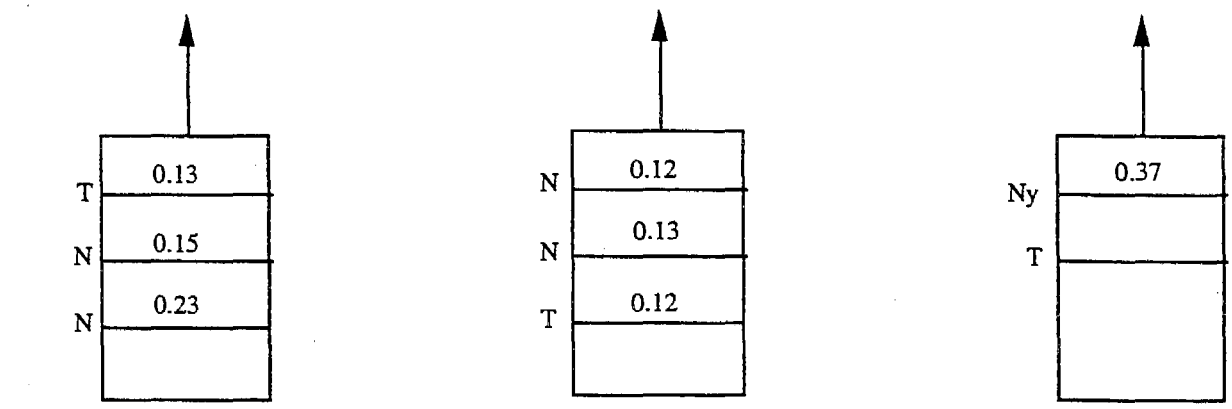
Table 4-1. Summary of first ambient air evaluation of denuders (2% NaCl on Material 1, sample collection periods were started and stopped between 1500 and 1600 hours PST)

Start Date	Substrate	Blank-corrected Concentration	
		NO3, µg/m3	SO4, µg/m3
1/31/95	NaCl Denuder 1	0.86	0.32
1/31/95	NaCl Denuder 2	0.08	0.21
1/31/95	Back Teflon	0.20	0.18
2/1/95	NaCl Denuder 1	0.59	0.15
2/1/95	NaCl Denuder 2	0.06	0.15
2/1/95	Back Teflon	0.18	0.15
2/2/95	NaCl Denuder 1	0.81	0.29
2/2/95	NaCl Denuder 2	0.02	0.09
2/2/95	Back Teflon	0.11	0.07
2/3/95	NaCl Denuder 1	0.57	0.18
2/3/95	NaCl Denuder 2	-0.03	0.17
2/3/95	Back Teflon		
	Mean Denuder Front	**0.71**	**0.23**
	Mean Denuder, Back	**0.03**	**0.15**
	Mean Teflon, Back	**0.17**	**0.13**
1/31/95	Front Teflon	0.21	0.11
1/31/95	NaCl Denuder 1	0.57	0.18
1/31/95	NaCl Denuder 2	-0.03	0.17
2/1/95	Front Teflon	0.24	0.14
2/1/95	NaCl Denuder 1	0.41	0.16
2/1/95	NaCl Denuder 2	-0.01	0.10
2/2/95	Front Teflon	0.17	0.09
2/2/95	NaCl Denuder 1	0.58	0.10
2/2/95	NaCl Denuder 2	-0.06	0.07
2/3/95	Front Teflon		
2/3/95	NaCl Denuder 1	0.47	0.08
2/3/95	NaCl Denuder 2	-0.03	0.15
	Mean Denuder Front	**0.51**	**0.13**
	Mean Denuder, Back	**-0.03**	**0.12**
	Mean Teflon, Front	**0.20**	**0.12**
1/31/95	Nylon Back	0.90	0.49
2/1/95	Nylon Back	0.76	0.30
2/2/95	Nylon Back	0.87	0.33
2/3/95	Nylon Back	0.78	0.35
	Mean Nylon	**0.83**	**0.37**

Mean denuder blank (4) nitrate = .89µg±0.37;
0.13 ± 0.05 µg/m3 @ 5 L/min
Mean denuder blank (4) sulfate =1.89 ±0.59µg;
0.27 ± 0.08 µg/m3 @ 5 L/min

Figure 4-2 summarizes the sulfate results. It appeared that gaseous sulfur was retained by the sodium chloride-coated denuders as sulfate since denuders which followed the Teflon filter contained nearly as much sulfate as the denuders which sampled directly. While the concentrations were close to the uncertainty of the measurement, there was no difference in sulfate collected by the Teflon filters whether preceded by two denuders or not. This is an indication that the denuders did not remove a measurable amount of particulate matter. The nylon filter showed an even greater amount of sulfate collection of a gaseous sulfur-containing species. This phenomenon has been previously reported (Japar et al., 1984).

Figure 4-2. Blank-corrected mean sulfate measurements (μg/m3) for the first ambient evaluation of denuders (Material 1, sodium chloride coating) at 5L/min (January 31-February 3, 1995)



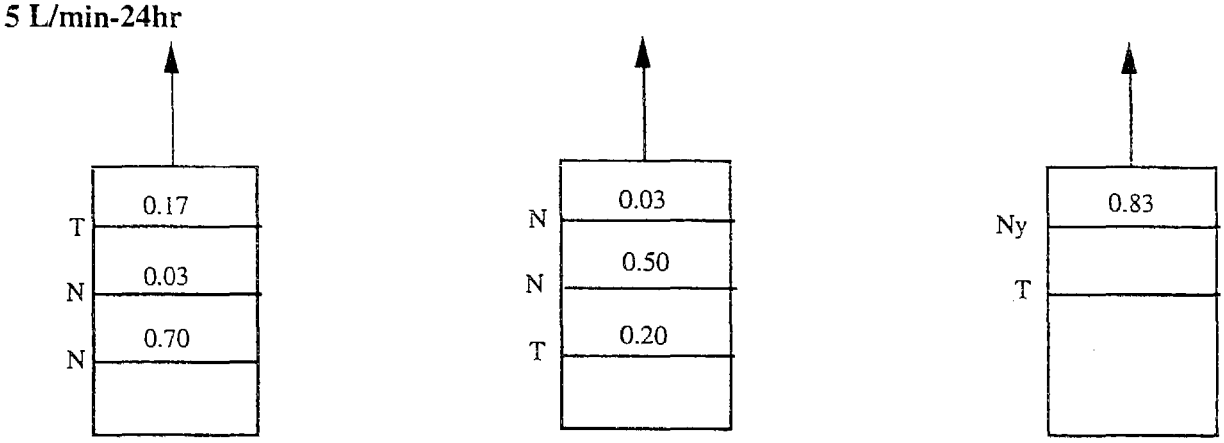
N = Sodium chloride coated (2%) denuder Material #1

T = Gelman 2μm pore Zefluor Teflon filter

Ny = Gelman 1μm pore Nylasorb filter

Figure 4-3 summarizes the nitrate results. All values were corrected by the mean concentration of dynamic blanks Average total nitrate concentrations were all below 1 $\mu g/m^3$, and due to potential measurement errors at this level, conclusions should be considered qualitative. The concentration on the second denuder was nearly zero within the measurement uncertainty. This indicated high denuder efficiency, approximately 95%. The sum of nitrate for the denuders sampling below a Teflon filter was similar to the nitrate determined by the nylon filter below a Teflon filter (0.73 $\mu g/m^3$ compared with 0.83 $\mu g/m^3$). This is another indication that the denuders are effectively and selectively removing nitric acid.

Figure 4-3. Blank-corrected mean (four days) nitrate measurements (μg/m3) for the first ambient evaluation of denuders (Material 1, sodium chloride coating), January 31-February 3, 1995



N = Sodium chloride coated (2%) denuder Material #1

T = Gelman 2μm pore Zefluor Teflon filter

Ny - Gelman 1 μm pore Nylasorb filter

4.2 Second Evaluation

The second ambient evaluation was similar to the first, except under conditions where the pollutant concentrations were higher, so that the results would be more definitive. While the same denuder material and coating were used (Material 1 with a 2% sodium chloride coating mixture), the flow rate was raised to 10 L/min since the results from the first ambient evaluation indicated that this was feasible. The tests were conducted in two phases, each having four sampling intervals, although the sampling periods varied from 24 to 72 hours. Samplers were started and stopped between 1500 and 1600 hours. The first phase evaluated particle penetration alone, while the second also evaluated nitric acid penetration through the denuders. The primary source of uncertainty at the higher concentrations encountered during this sampling was that due to flow rate and measurement precision, estimated at 5% each. Thus, the total uncertainty was approximately 7%. Blank uncertainties for 24-hour samples were 0.02 $\mu g/m^3$ and 0.11 $\mu g/m^3$ for sulfate and nitrate respectively.

Table 4-2 shows the results for nitrate and sulfate concentration measurements. Figure 4-4 illustrates the mean results of particle penetration as measured by particulate sulfate. In the first phase, 11% more sulfate was collected on the Teflon filter without two denuders preceding it, while in the second phase 19% more sulfate was collected. The overall particle penetration, therefore, ranged from 80%

to 90% for two denuders in series. The sodium chloride-coated denuders are again observed to collect gaseous sulfur, as shown by the concentrations downstream of the Teflon filter. If we subtract this sulfate from that of the denuders upstream of the Teflon filter, then 10% of the particulate sulfate was trapped by the first denuder and 2% by the second. This indicates a loss of 7% of the sulfate by other than the denuders (the PFA filter holder and support grid).

Figure 4-4. Blank-corrected mean sulfate measurements (μg/m3) for the second ambient evaluation of denuders (Material 1, sodium chloride coating) at 10 L/min

Figure 4-4a. Sulfate measurements during the particle penetration tests (4/26/95-5/2/95)

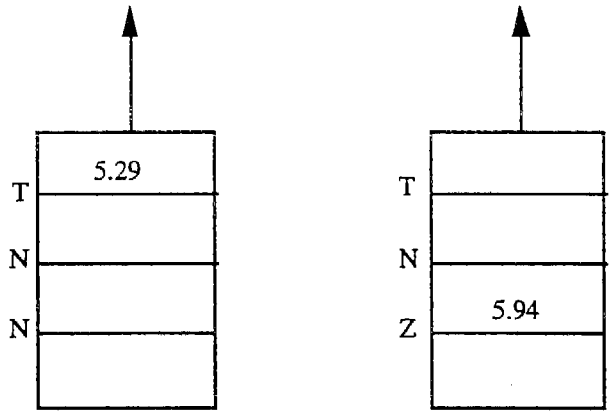
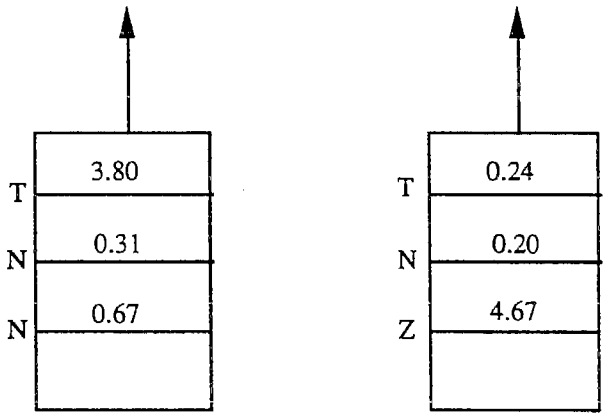


Figure 4-4b. Sulfate measured during the nitric acid penetration tests (5/10/95 - 5/19/95)



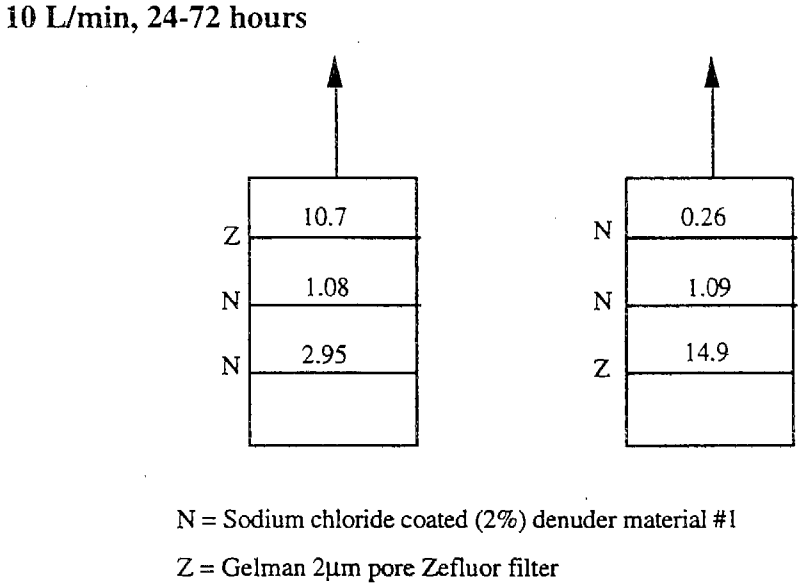
N = Sodium chloride coated (2%) denuder material #1

T = Gelman 2μm pore Zefluor Teflon filter

Table 4-2. Summary of second ambient air evaluation of denuders (2% NaCl on Material 1)

Start Date	Hours Sampled	Substrate	Blank-corrected Concentration NO3, µg/m3	SO4, µg/m3
3-7a. Particle Penetration Tests				
4/26/95	24	Teflon Back	16.02	5.73
4/27/95	24	Teflon Back	16.40	8.14
4/28/95	72	Teflon Back	10.24	4.00
5/2/95	48	Teflon Back	9.66	3.29
		Mean Teflon, Back	**13.08**	**5.29**
4/26/95	24	Zefluor Front	21.73	6.90
4/27/95	24	Zefluor Front	18.85	8.43
4/28/95	72	Zefluor Front	11.91	4.42
5/2/95	48	Zefluor Front	13.26	4.01
		Mean Teflon, Front	**16.44**	**5.94**
3-7b. NaCl-Coated Denuders				
5/10/95	24	NaCl Denuder 1	4.58	0.86
5/10/95	24	NaCl Denuder 2	1.76	0.40
5/10/95	24	Back Teflon	18.92	5.83
5/11/95	24	NaCl Denuder 1	4.09	0.89
5/11/95	24	NaCl Denuder 2	1.38	0.38
5/11/95	24	Back Teflon	15.26	6.15
5/12/95	72	NaCl Denuder 1	0.82	0.33
5/12/95	72	NaCl Denuder 2	0.39	0.19
5/12/95	72	Back Teflon	1.11	1.02
5/15/95	72	NaCl Denuder 1	2.30	0.59
5/15/95	72	NaCl Denuder 2	0.78	0.27
5/15/95	72	Back Teflon	7.57	2.19
		Mean Denuder 1	**2.95**	**0.67**
		Mean Denuder 2	**1.08**	**0.31**
		Mean Teflon, Back	**10.71**	**3.80**
5/10/95	24	Front Teflon	23.83	6.44
5/10/95	24	NaCl Denuder 1	1.42	0.28
5/10/95	24	NaCl Denuder 2	0.63	0.62
5/11/95	24	Front Teflon	22.58	7.85
5/11/95	24	NaCl Denuder 1	0.90	0.16
5/11/95	24	NaCl Denuder 2	0.18	0.11
5/12/95	24	Front Teflon	2.18	1.47
5/12/95	72	NaCl Denuder 1	0.98	0.12
5/12/95	72	NaCl Denuder 2	0.12	0.10
5/15/95	72	Front Teflon	10.80	2.91
5/15/95	72	NaCl Denuder 1	1.07	0.25
5/15/95	72	NaCl Denuder 2	0.11	0.14
		Mean Denuder 1	**1.09**	**0.20**
		Mean Denuder 2	**0.26**	**0.24**
		Mean Teflon, Front	**18.65**	**6.20**
		Mean denuder blank (4) nitrate = 0.83µg/filter Mean denuder blank (4) sulfate = 1.62 µg/filter Mean Teflon blank (2) nitrate = 1.49 µg/filter Mean Teflon blank (2) sulfate = 0.61 µg/filter		

Figure 4-5. Blank-corrected mean (four days) nitrate measurements (μg/m3) for the second ambient evaluation of denuders (Material 1, sodium chloride coating) conducted at 10 L/min



N = Sodium chloride coated (2%) denuder material #1

Z = Gelman 2μm pore Zefluor filter

Figure 4-5 illustrates the mean nitrate concentrations obtained. The Teflon filter following the denuders contained less nitrate relative to the front filter, as expected, since greater volatilization of particulate nitrate is likely when nitric acid has been removed from the air stream. In addition, nitric acid may have been adsorbed by the Zefluor filter (most likely due to particulate material collected on this filter, not the Teflon itself which is inert to nitric acid) preceding the denuders. Based on the nitrate on the denuders used with the Teflon prefilter, the collection efficiency for nitric acid was 76% calculated by equation (2). The nitrate on the denuders without the Teflon front filter was over twice as high as those denuders with a front filter, and the apparent denuder efficiency was 63%. These results may be due to particle collection on the denuder since during this phase the sulfate indicated that 19% of the particulate sulfate was lost passing through the two denuders. Without knowing the concentration of true particulate nitrate it is difficult to estimate the amount of nitrate on the denuders that is expected from particulate nitrate, assuming that both nitrate and sulfate particles are collected with equal efficiency. We can assume, based on sulfate collection, that 10% and 2% of the nitrate on the Teflon filter preceding the denuders (which itself is subject to a volatilization and adsorption artifacts) is collected on the first and second denuders without a Teflon prefilter (which should not be subject to a volatilization artifact since the nitrate should be stabilized by the sodium chloride). This results in 1.49 $\mu g/m^3$ nitrate particulate collected by the first and 0.27 $\mu g/m^3$ collected by the second denuder. This undercorrects for the for both denuders upstream of the Teflon filter compared with denuders downstream of the Teflon filter. A possible explanation is that nitrate particles are not retained with the same efficiency as the sulfate due to a different size distribution. We concluded that

under these conditions, denuder Material 1 coated with sodium chloride may have a positive bias when sampling at 10 L/min to measure the concentration of nitric acid.

4.3 Third Evaluation

A field evaluation of denuder Materials 5, 8, and 9 was conducted in Riverside during August of 1995. Denuder coatings were 9% (w/w)NaCl and 2% glycerol (v/v). Three flow rates were used: 1, 5, and 10 L/min. The 1 L/min sampling rate was evaluated to determine the applicability system for one-week sampling periods. This lower flow rate should also provide the highest nitric acid removal efficiency. Based on our previous ambient air evaluations, 5 L/min appeared to be an optimum compromise for high particle penetration and nitric acid removal when 12-hour sampling periods are desired. The 10 L/min rate was evaluated to determine whether these denuders could be useful for even shorter sampling periods. The 1 L/min samples operated for a five-day period, while samples were changed daily for the other samples. The 1 L/min samplers were turned off while substrates in the other samplers were changed. Thus the five one-day samples were collected over the same interval as the five-day samples. All daily samples were changed between 0800 and 0830 hours each day.

Figure 4-6 shows a schematic of the experimental system. Overall particulate matter penetration was again evaluated by comparing the sulfate on the Teflon filter preceded by three denuders with that collected by the Teflon filter without denuder upstream. Particulate matter retention by each denuder was estimated by comparing the sulfate on each denuder without a Teflon prefilter to the sulfate on the Teflon filter without denuders upstream. The sulfate on each denuder is expected to be an upper limit of sulfate particle retention, as we have previously observed that sodium chloride-coated denuders may retain some gaseous sulfur compounds as sulfate. Sulfate was used to estimate particulate matter penetration since it is not volatile and generally not subject to sample collection artifacts on Teflon filters; it is also found in generally the same size particles as nitrate.

As shown in 4-6, except for the control, of the other sampling cassettes consisted of three sodium chloride coated denuders followed by a Zefluor Teflon filter. The laboratory evaluation had shown that denuder Materials 1, 7 and 8 had the greatest potential for high nitric acid removal efficiency. These denuders were all coated with a 9% (w/w) solution of sodium chloride to which 1% (v/v) glycerol had been added. Denuder Material 5 was not tested at 10 L/min since it was shown in the laboratory to have the lowest nitric acid collection efficiency. This material was considered appropriate for testing since it appeared to have a looser weave, and was therefore likely to allow a greater percentage of particle to penetrate the material.

Figure 4-6. Sampling configuration for the third ambient evaluation of the denuders (T= Gelman Zefluor Teflon filter, N= NaCl coated denuder)

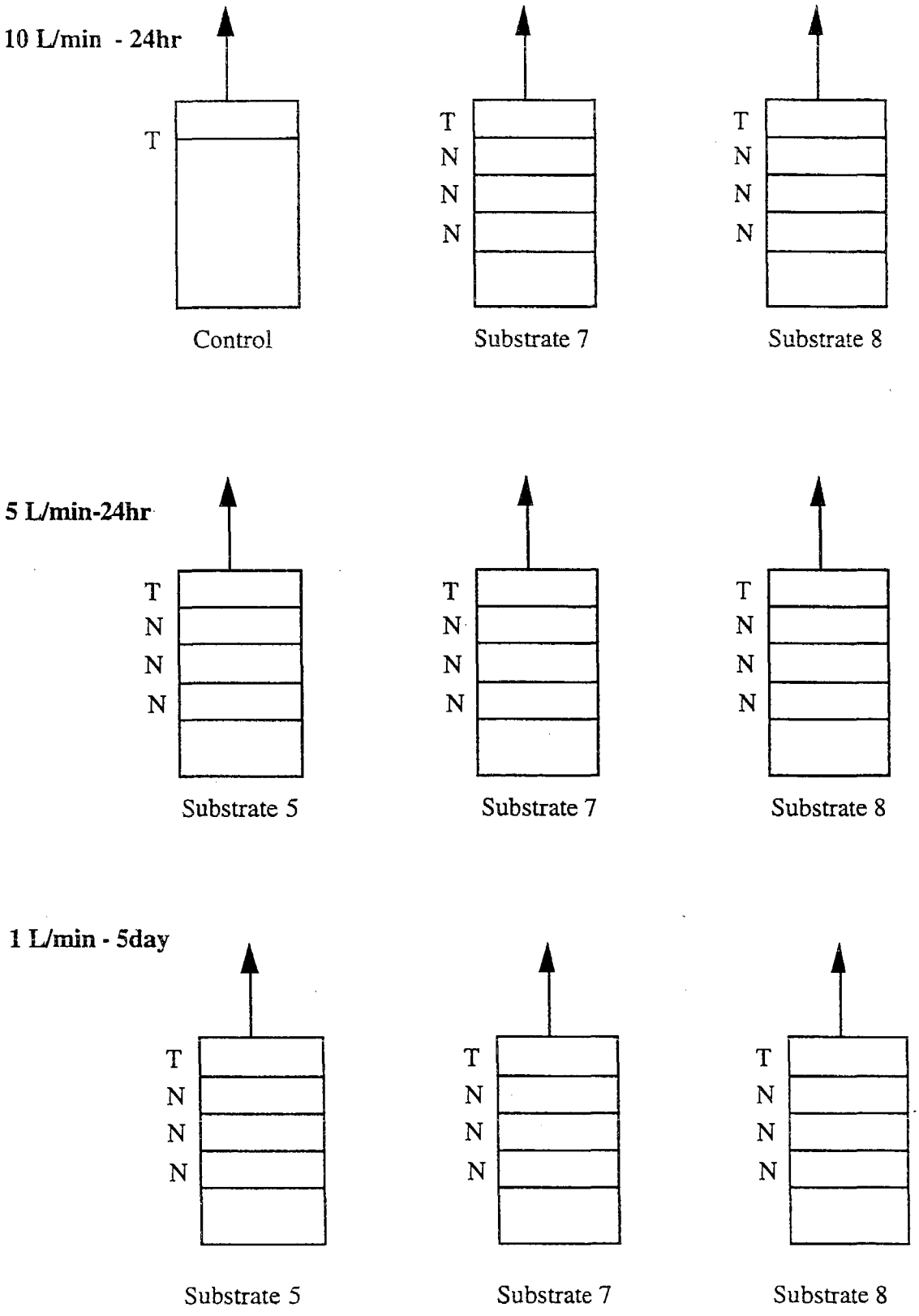


Table 4-3 presents a summary of the results of sulfate and nitrate measurements. The values for 5 and 10 L/min sampling represent the mean of five daily determinations. Figure 4-7 shows the average sulfate on each sample stage. Except for Materials 5 and 8 at the 1 L/min flow rate, the sum of sulfate for each cassette is within 10% of the non-denuded Teflon filter alone. This indicates good measurement precision and little retention of sulfur dioxide or particulate sulfate. Material 5 appeared to pass the highest percentage of sulfate particles, followed by Material 7 and then 8. Figure 3-7 shows that decreasing flow rates resulted in lowered particulate penetration. This may indicate that greater losses are due to diffusion, since the particle retention increased as the denuder face velocity decreased. While not predicted by the calculations in Section 2, this may be caused by fine fibers protruding from the primary thread of the material (later inspection with a magnifying glass did not reveal any obvious such fibers). Since little gas phase sulfur appeared to be retained, we can estimate the efficiency of each stage based on the total particulate sulfate retained by individual substrates. These results are shown in Table 3-8 as the ratio to the remaining sulfate. For example, for the first denuder in the air stream of sampler 1, the ratio is 0.11 or 11% (0.40/3.65) while for the next denuder it is 0.08 or 8% (0.25/(3.65-0.40)).

Figure 4-8 illustrates the particle penetration calculated this way for each denuder. Based on the sulfate data, Material 5 appears to have the highest particulate penetration of the three, although laboratory tests showed it possessed the lowest collection efficiency for nitric acid.

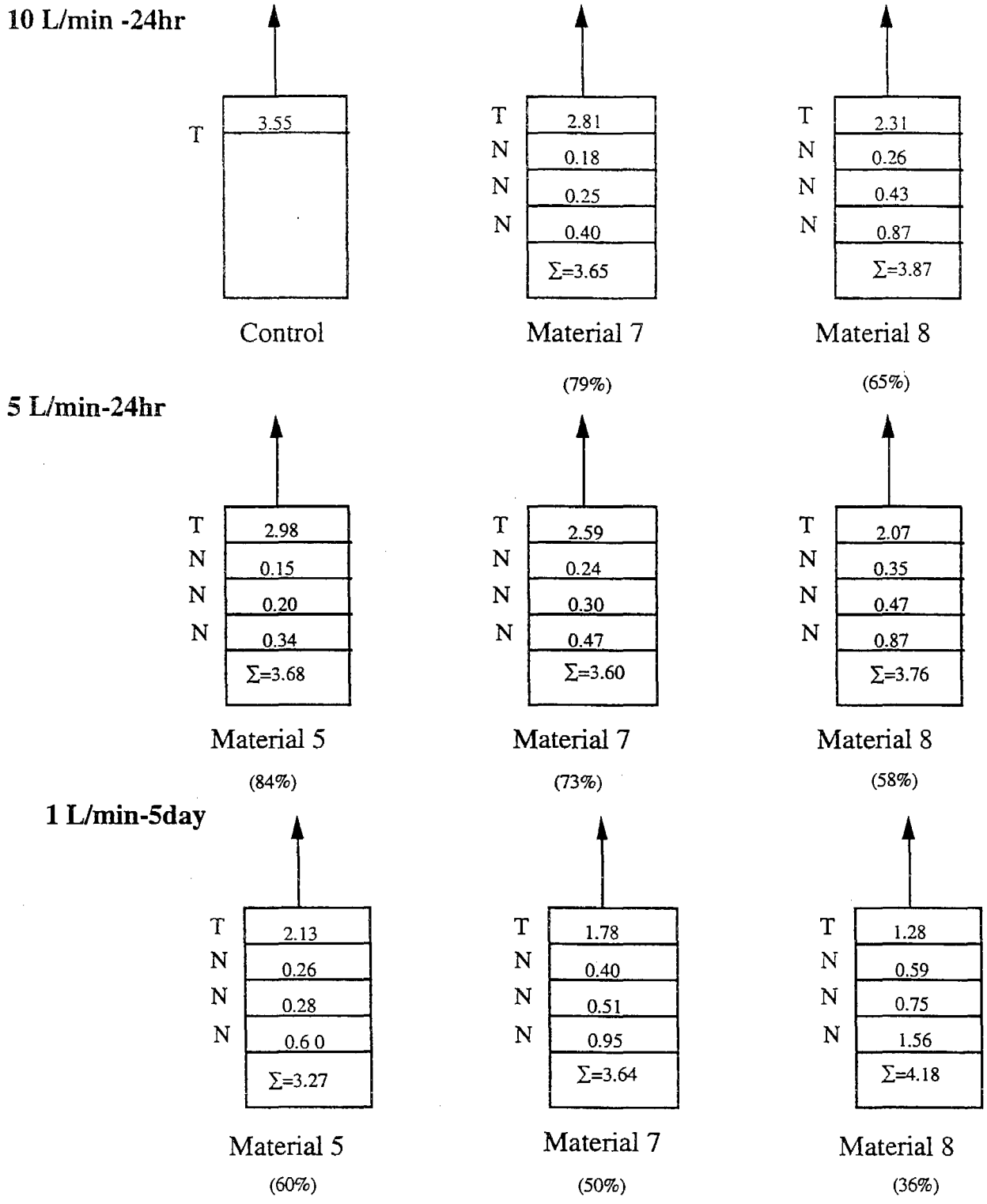
Figure 4-9 summarizes the mean nitrate concentrations observed. The nitrate concentrations obtained from denuder Material 8 were consistently higher than the other two, consistent with it having the lowest particulate penetration of the three. This substrate therefore appears to be collecting a substantial amount of particulate nitrate, resulting in a high bias for measuring nitric acid. The last two columns of Table 4-3 show the nitric acid denuder efficiency calculated using equation (2) with and without a correction for particulate nitrate collected. This correction was made by subtracting the product of the denuder particle penetration based on sulfate measurements ("sulfate ratio to remaining") by the 10.61 $\mu g/m^3$ of particulate nitrate collected by the Teflon filter without a denuder from the nitrate collected by each denuder. This correction should be considered approximate since the particulate sulfate may have a different size distribution than nitrate and the particulate nitrate on the Teflon filter was subject to potential volatilization and adsorption artifacts during collection. Figure 4-10 summarizes the denuder collection efficiency both with and without this correction applied. The average nitric acid collection efficiency of the first denuder ranged from 70% to 99% with this correction.

Table 4-3. Summary of results of third ambient air evaluation (Average of 5 collection periods)

Sampler Number	Material	Flow Rate L/min	Substrate Number	Blank-corrected Nitrate, µg/m3	Blank-corrected Sulfate, µg/m3	Ratio to Remaining	Denuder Collection Efficiency %	Corrected Denuder Collection Efficiency %
1	7	10	D1 Avg.	5.40	0.40	0.11	71 (64-75)	84 (78-91)
	7		D2 Avg.	1.58	0.25	0.08	40 (23-56)	56 (25-75)
	7		D3 Avg.	0.89	0.18	0.06		
	T		T1 Avg.	5.57	2.81			
Sum of Stages				13.43	3.65			
2	8	10	D1 Avg.	8.32	0.87	0.22	73 (66-81)	99 (78-162)
	8		D2 Avg.	2.21	0.44	0.15	53 (43-57)	72 (2-107)
	8		D3 Avg.	1.01	0.26	0.10		
	T		T1 Avg.	2.72	2.30			
Sum of Stages				14.25	3.87			
3	T		T1 Avg.	10.61	3.55			
4	5		D1 Avg.	5.70	0.34	0.09	81 (71-88)	96 (83-120)
	5		D2 Avg.	0.98	0.21	0.06	20 (-2-35)	36 (-15-65)
	5		D3 Avg.	0.74	0.15	0.05		
	T		T1 Avg.	7.24	2.98			
Sum of Stages				14.66	3.68			
5	7	5	D1 Avg.	5.73	0.47	0.13	78 (71-83)	82 (73-91)
	7		D2 Avg.	1.23	0.30	0.10	28 (19-45)	34 (13-49)
	7		D3 Avg.	0.89	0.24	0.09		
	T		T1 Avg.	5.77	2.59			
Sum of Stages				13.62	3.60			
6	8	5	D1 Avg.	7.32	0.87	0.23	74 (61-82)	70 (-77-116)
	8		D2 Avg.	1.82	0.48	0.17	35 (27-45)	66 (-208-131)
	8		D3 Avg.	1.16	0.35	0.14		
	T		T1 Avg.	3.41	2.07			
Sum of Stages				13.71	3.76			
7	5	1	D1	8.89	0.60	0.18	88	100
	5		D2	1.09	0.28	0.11	-16	502
	5		D3	1.27	0.26	0.11		
	T		T1	3.67	2.13			
Sum of Stages				14.92	3.27			
8	7	1	D1	8.97	0.95	0.26	82	107
	7		D2	1.62	0.51	0.19	19	-51
	7		D3	1.32	0.40	0.18		
	T		T1	3.05	1.78			
Sum of Stages				14.96	3.64			
9	8	1	D1	8.63	1.56	0.37	78	124
	8		D2	1.90	0.75	0.29	17	-54
	8		D3	1.58	0.59	0.31		
	T		T1	2.23	1.28			
Sum of Stages				14.34	4.18			

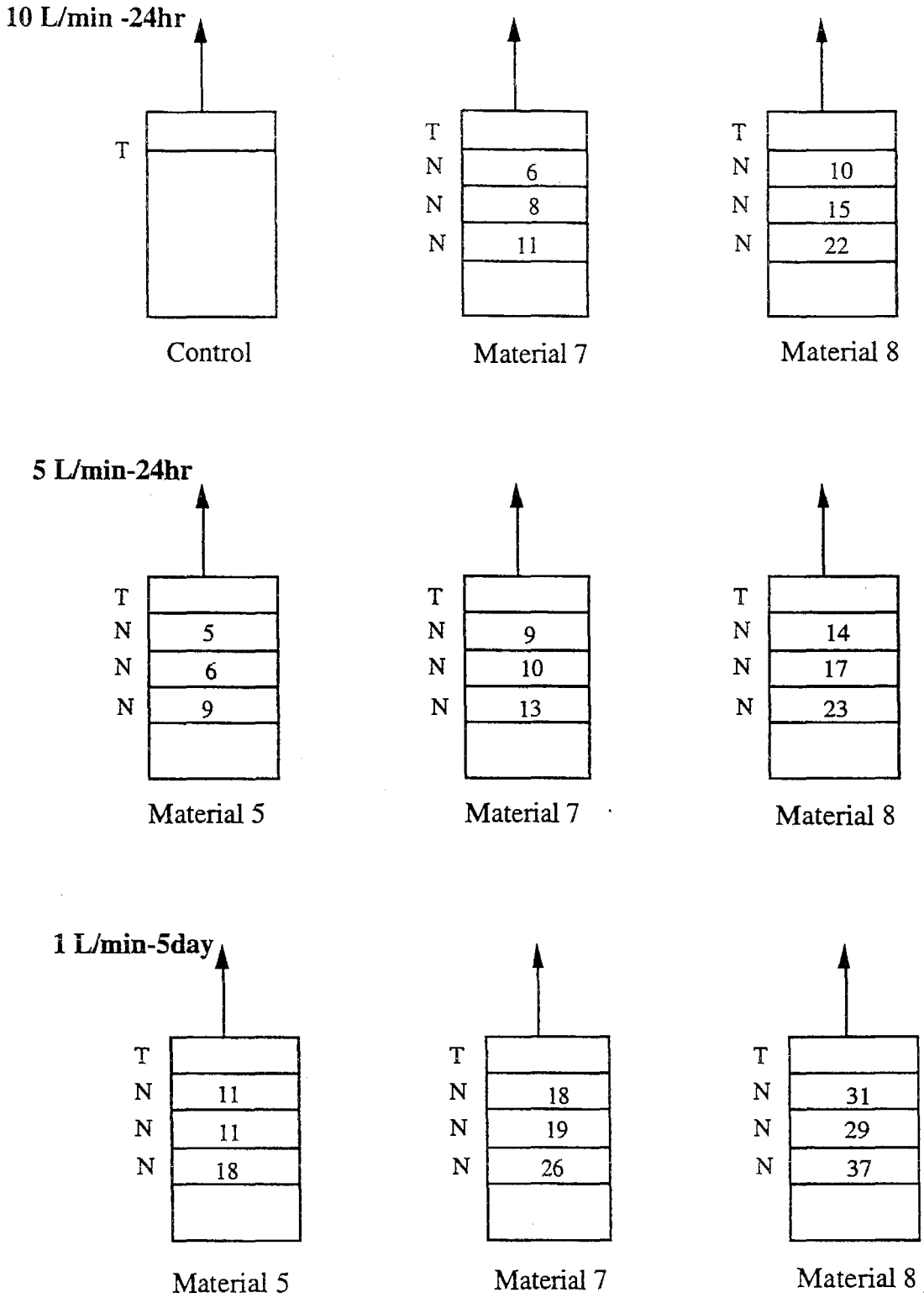
Substrate Number:
D=Denuder
T=Gelman Zefluor Teflon filter
1-3=Position in cassette; 1 is the first of the D or T series to contact the air stream, 2 the second, and 3 the third.

Figure 4-7. Blank-corrected sulfate data in μg/m3 for the third ambient evaluation of denuders (5-day study, 1-day collections were averaged. Total sulfate penetrations calculated by using the 3.55 μg/m3 obtained by the control as shown in parentheses.



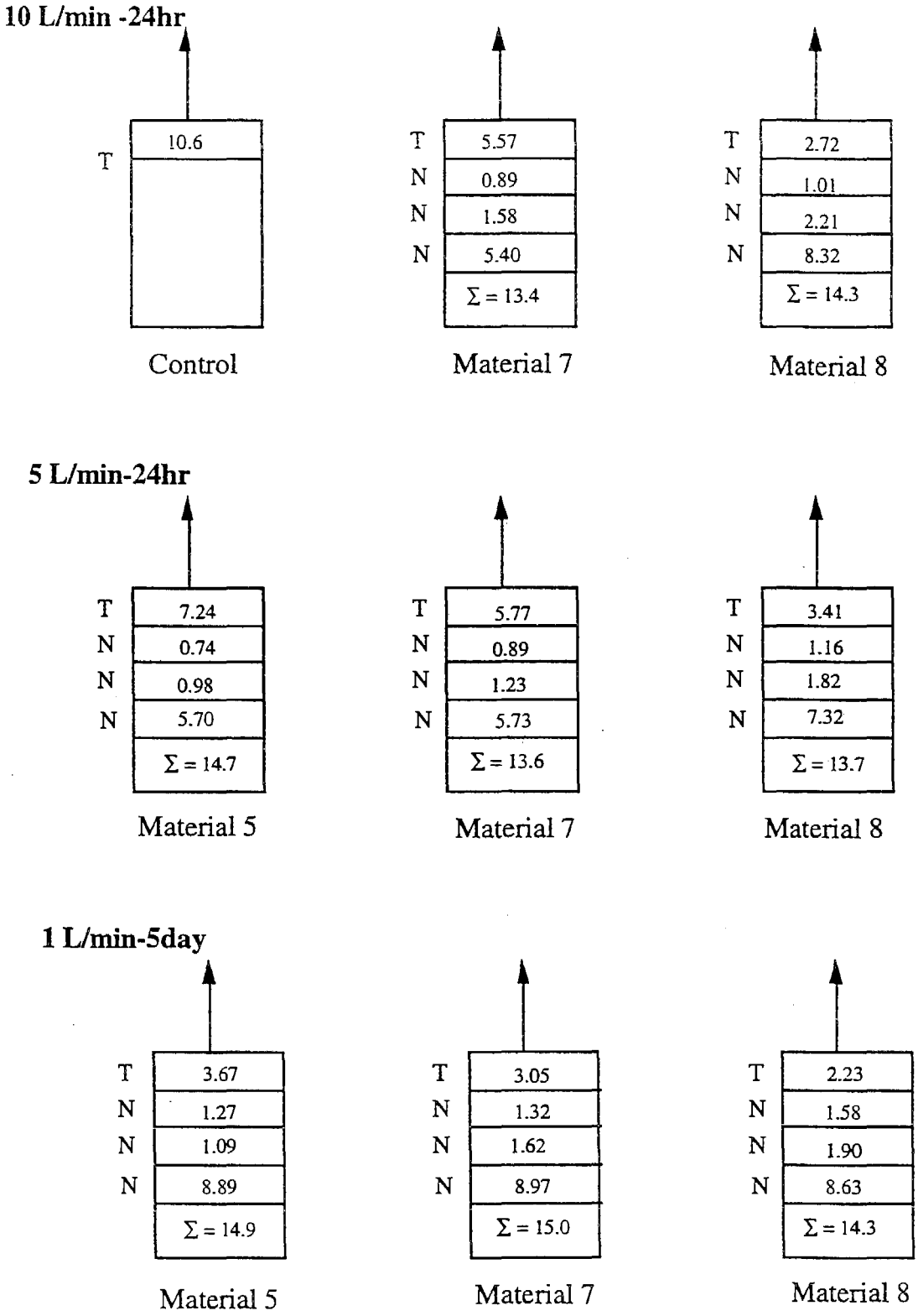
N = Sodium chloride coated (9%) denuder
T= Gelman 2μm pore Zefluor Tefon filter

Figure 4-8. Percent particulate sulfate collection by each denuder stage as a percentage of "remaining" for each sampler.



N = Sodium chloride coated (9%) denuder
T = Gelman 2μm pore Zefluor Teflon filter

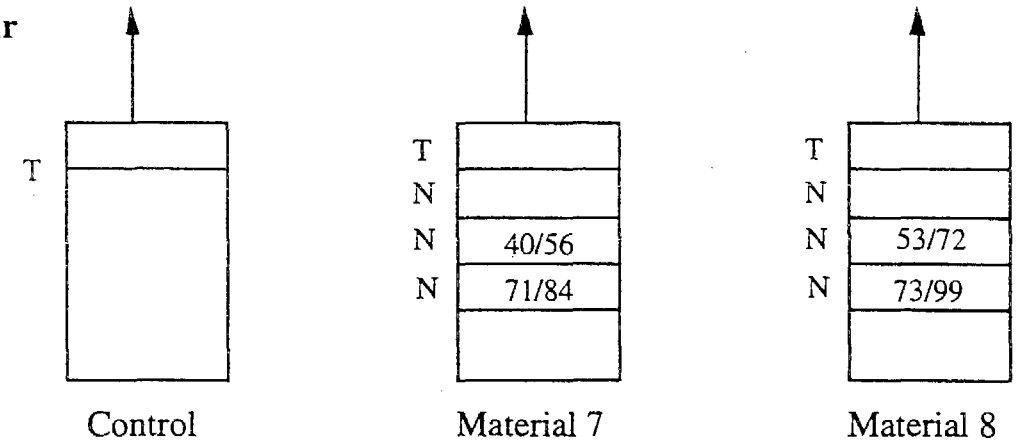
Figure 4-9. Summary of Blank-corrected nitrate measurements for the third ambient air evaluation (mg/m^3)



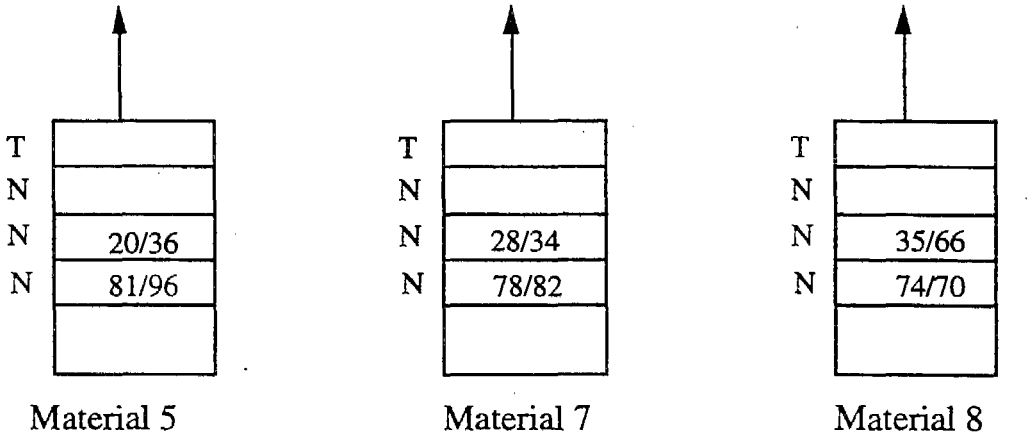
N = Sodium chloride coated (9%) denuder
T = Gelman 2µm pore Zefluor Teflon filter

Figure 4-10. Denuder nitric acid collection efficiency in percent (uncorrected/corrected)

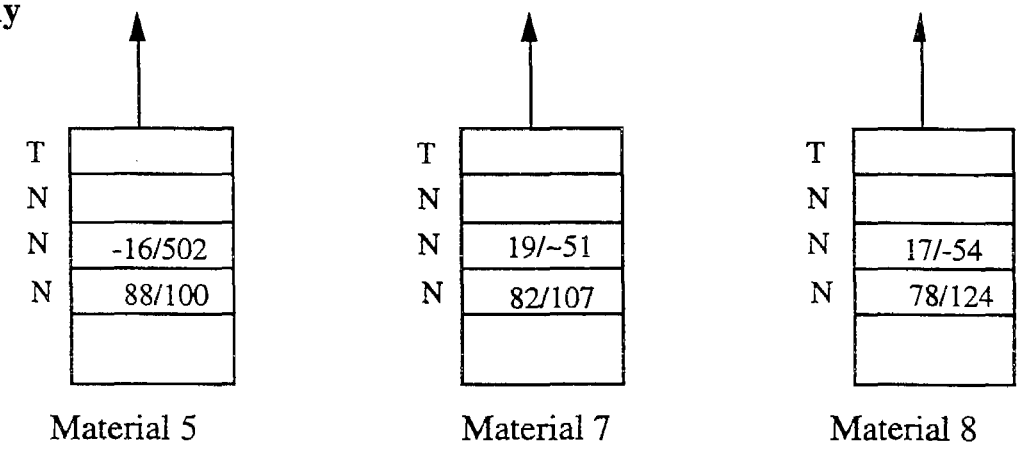
10 L/min -24hr



5 L/min-24hr



1 L/min-5day



The overall nitrate measurements show that most of the nitric acid was removed by the first denuder. Since the nitrate on the second and third denuders was low and nearly identical, a wide range of efficiencies were calculated for the second denuder. The origin of the nitrate on these denuders is mostly likely due to either the partial retention of particulate nitrate which could not be corrected for (either due to the lack of a measurement of "true particulate nitrate" or a nitrate particle size distribution different than that of sulfate) or other gas phase nitrogenous species.

We conclude that Material 5 represents the best compromise between high particle penetration and high denuder efficiency. This material, along with 1, 7, and 8, will therefore be evaluated by comparing with ambient collocated measurements using other techniques.

5. AMBIENT AIR COMPARISONS WITH OTHER METHODS

5.1 Claremont Comparison Study

A field evaluation was conducted in Claremont for a 28-day period starting on August 28, 1995. As described in section 2.5, this was primarily a methods comparison study for nitric acid measurements, although the FTIR also quantified ammonia and formic acid. In addition to the CE-CERT denuder sampling for measurement and method evaluation, nitric acid was determined with the FTIR, TDLAS, CADMP sampler and SCAQMD sampler.

The weather was initially very warm, with highs over 45°C and the daily nitric acid maxima typically over 30 ppb. This extreme heat and the need to locate both the FTIR and TDLAS in a single trailer caused one of the two air conditioners in the trailer to sporadically fail during the setup period. Until the air conditioner was working properly, on September 2, there was only a limited amount of FTIR data collected. None of the other measurements were affected.

In the following sections we will describe the measurements of each instrument and compare them with the FTIR, using it as the reference method. We will also intercompare measurements of the various other methods as appropriate.

5.1.1 FTIR

The kilometer-pathlength infrared spectroscopic system consists of a Mattson Instruments Sirius 100 FTIR spectrometer interfaced, via a set of transfer optics, to a 25-meter basepath, open multiple-reflection, and a gold-coated mirror system of the Horn-Pimentel-White design (White, 1942; Horn and Pimentel, 1971). The instrument in the present study is the same one employed during the ARB-sponsored 1985 Nitrogenous Species Measurement Comparison Study (Winer et al., 1986; Biermann et al., 1988) and the 1986 Carbonaceous species Methods Comparison study (Winer et al., 1987; Anlauf et al., 1991), but with an upgraded moving mirror for the interferometer, a new PC-based data system, and a current Mattson software package. Details concerning the optical systems components and design as well as the alignment procedure have been described in the above references.

The spectrometer and data system were housed in a trailer (Figure 2-2). A modular steel frame, constructed with legs extending through the trailer's floor, provided a vibration-isolated ground support for the spectrometer bench. The outdoor mirror assemblies which comprise the multiple-reflection optics were, likewise, each supported by a modular steel frame. (This is in contrast to the installations during the 1985 NSCMS and 1986 CSMCS, where the spectrometer and long path optics were all supported by massive concrete blocks.) The infrared beam originating from the spectrometer and the return beam from the multiple-reflection optics passed through holes in the trailer wall. The

optical path was along a south-north orientation, with the beam height above the sloping ground varying from approximately 3 m at the spectrometer (south end) to 2 m at the far mirror assembly.

Routine Monitoring

Spectra were recorded at a total pathlength of 1,150 meters and a full-width at half-height resolution of 0.13 cm^{-1} (unapodized). Fifty scans (interferograms) were co-added during a ~5.5 min period and transformed to a single beam spectrum (calculation time of ~15 sec). Each spectrum was truncated and only the 700-3,200 cm^{-1} segment was archived. With the above scan parameters, six to seven spectra per hour were collected. This rate of data collection allowed a cursory examination of the quality of the spectra being displayed on the monitor screen and periodic browsing of the spectra for signals due to the analytes of interest.

Calibration and Analysis of Spectra

Prior to the field study, reference spectra of HNO_3 and NH_3 at sub-ppm concentrations at a pathlength of 96 meters were recorded in the laboratory by the same spectrometer, using the same scan parameters as would be employed in the field, with air mixtures of the samples in a 4,000-liter Teflon chamber. The absorption coefficients for the infrared absorptions of HNO_3 and NH_3, as well as that of HCOOH, which are consistent with the spectral resolution employed in the present study, have been determined previously (Winer et al., 1986; Biermann et al., 1988; Tuazon, 1989; Tuazon et al., 1980). The two Q-branch absorption features of HNO_3 at 896.1 cm^{-1} and 885.4 cm^{-1}, with absorption coefficients (base 10) at 298 K and 740 torr of 5.2 ± 0.4 cm^{-1} atm^{-1} and 6.1 ± 0.5 cm^{-1} atm^{-1}, respectively, were those employed in the analysis of ambient air spectra. The narrow 885.4 cm^{-1} Q-branch is devoid of interferences and was useful in providing a quick estimate of the prevailing HNO_3 concentrations directly from the single beam spectra that were not affected by excessive noise. However, despite the inclusion of parameters during the calculation of spectra that added definition (e.g., interpolated points) to the contour of this absorption feature, the 885.4 cm^{-1} Q-branch was inadequately defined by the 0.13 cm^{-1} resolution limit of the spectrometer such that it was more susceptible to noise distortion than the weaker but broader Q-branch at 896.1 cm^{-1}. Hence, HNO_3 concentrations were based on the 896 cm^{-1} feature, by ratioing the sample spectra with a background spectrum to compensate for a minor interference by a very weak H_2O absorption. The criteria used to ensure that the selected background spectra contained HNO_3 at levels well below detection limits were low noise, clear absence of the 885.4 cm^{-1} absorption, and correspondence with low ozone levels (≤ 25 ppb) in the early morning or late evening hours. The FTIR detection limits for HNO_3 during this study were 4-6 ppb.

For NH_3, the vibration-rotation fine structure at 1103.4 cm^{-1}, which is well isolated from atmospheric H_2O and CO_2 absorptions and which has an absorption coefficient of 18.2 ± 0.9 cm^{-1} atm^{-1}, was

employed and enabled the straightforward analysis of NH_3 from the single beam spectra (no ratioing with background spectra were needed). The detection limit for NH_3 was 2 ppb.

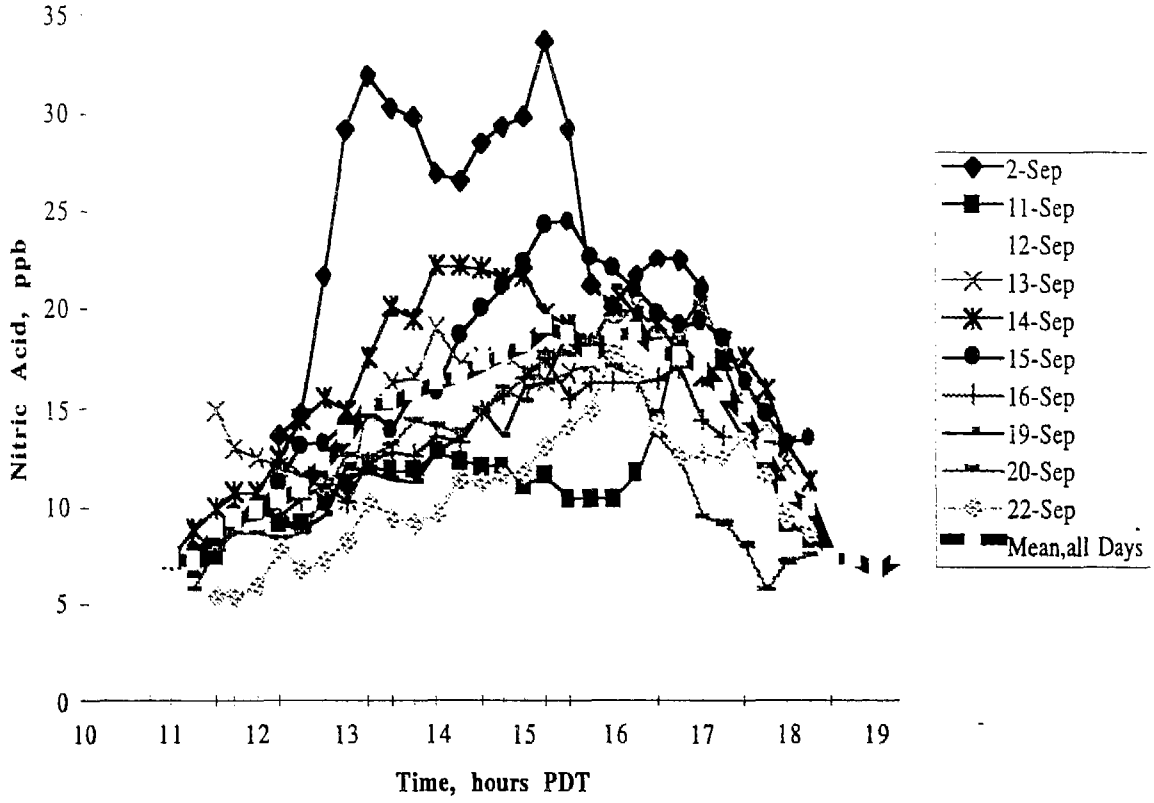
The Q-branch at 1,105.0 cm^{-1} was used to measure the HCOOH; this has an absorption coefficient of 30 ± 3 cm^{-1} atm^{-1}. Although this absorption resides on the shoulder of a strong H_2O band, the intensity of this Q-branch (hence, the concentration) was easily measured from the single beam spectrum. The detection limit for HCOOH was approximately 1 ppb.

The spectrometer was programmed for continuous data collection, but operation in this mode was often interrupted by the need to realign the external mirrors. This is because the present installation, which relied on the steel frames for support of the mirror assemblies, was found to be much more susceptible to optical misalignments than previous systems, which employed heavy concrete blocks. Data from FTIR spectrometer was therefore collected only in the daytime, coinciding with the hours of highest photochemical activity and including the daily nominal 1100 to 1700 PDT schedule for the various samplers.

• Nitric Acid

Nitric acid concentrations could be compared only with sampler data from the daytime collection periods if they were above the FTIR detection limit for the entire collection period. For ten days, FTIR data were available for the entire denuder/filter collection periods. Appendix E contains the complete data set for fifteen-minute intervals. Individual measurements were made at approximately seven-minute intervals. If more than one data point was collected during a fifteen-minute period, the average for the period was reported. Figure 5-1 is a plot of measurements as a function of time for all of the ten days. Also shown in the Figure is the mean nitric acid concentration plotted for each time of the day. The highest nitric acid concentration, over 35 ppb, was recorded on September 2, which was the first day that the instrument was fully operational. Other maxima were typically between 15 and 25 ppb.

Figure 5-1. Nitric acid measurements by FTIR in Claremont (ppb)



- **Ammonia**

Ammonia was above the detection limit on most of the days that the FTIR was operated. Figure 5-2 shows the mean and maximum for each of these measurement days (measurements were over a nominal period from 1100 to 1700 PDT corresponding to the period for which samples were collected on denuders and filters). Daily maxima were generally in the range between 2 and 20 ppb. Three days, September 2, 5, and 25, showed ammonia episodes where the maxima were over 40 ppb. While the maxima were much higher on these days, the means were in the typical range of 3-15 ppb because these episodes were of short duration. Figure 5-3 illustrates the time-concentration profile for September 5, 15, and 25. Large spikes in concentration with maxima of 72 and 68 ppb, respectively, for September 5 and 25 occurred from 1130 to 1230 hours, while for the rest of each day the concentrations were mostly below 10 ppb. These concentration spikes are likely due to transport from a local source, possibly the feedlots of Chino, approximately seven miles southeast.

Figure 5-2. FTIR ammonia means and peaks from daily measurements

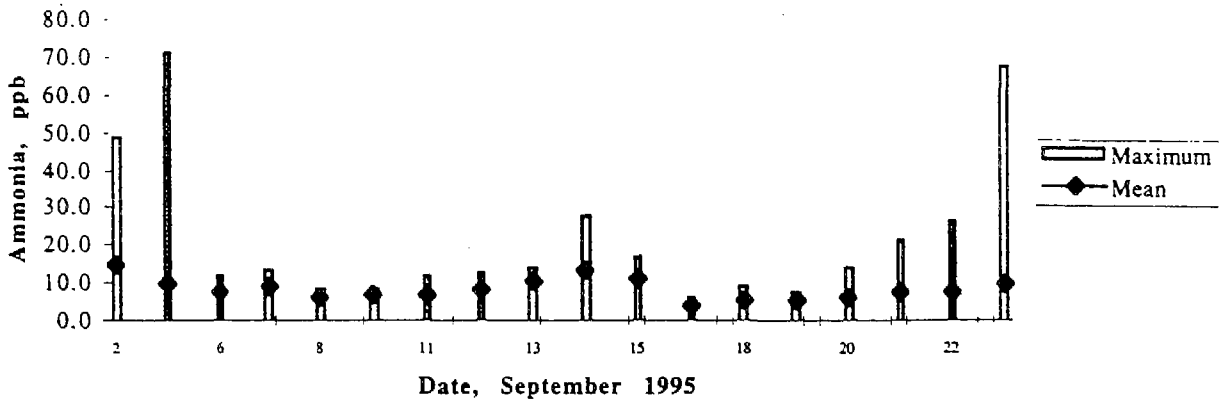
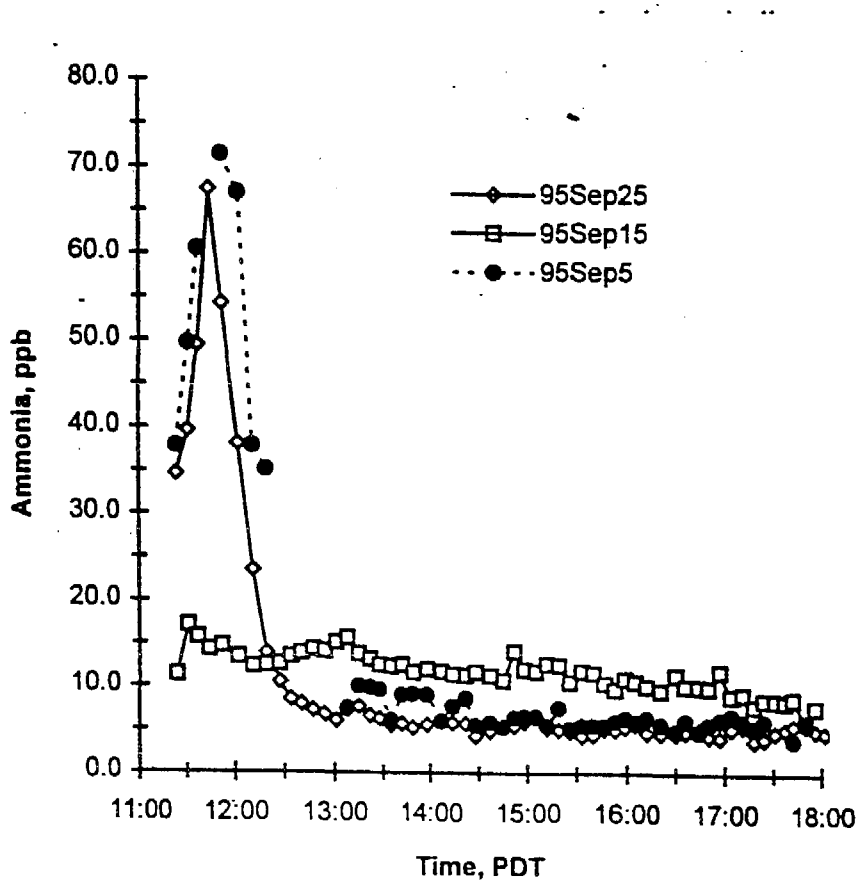


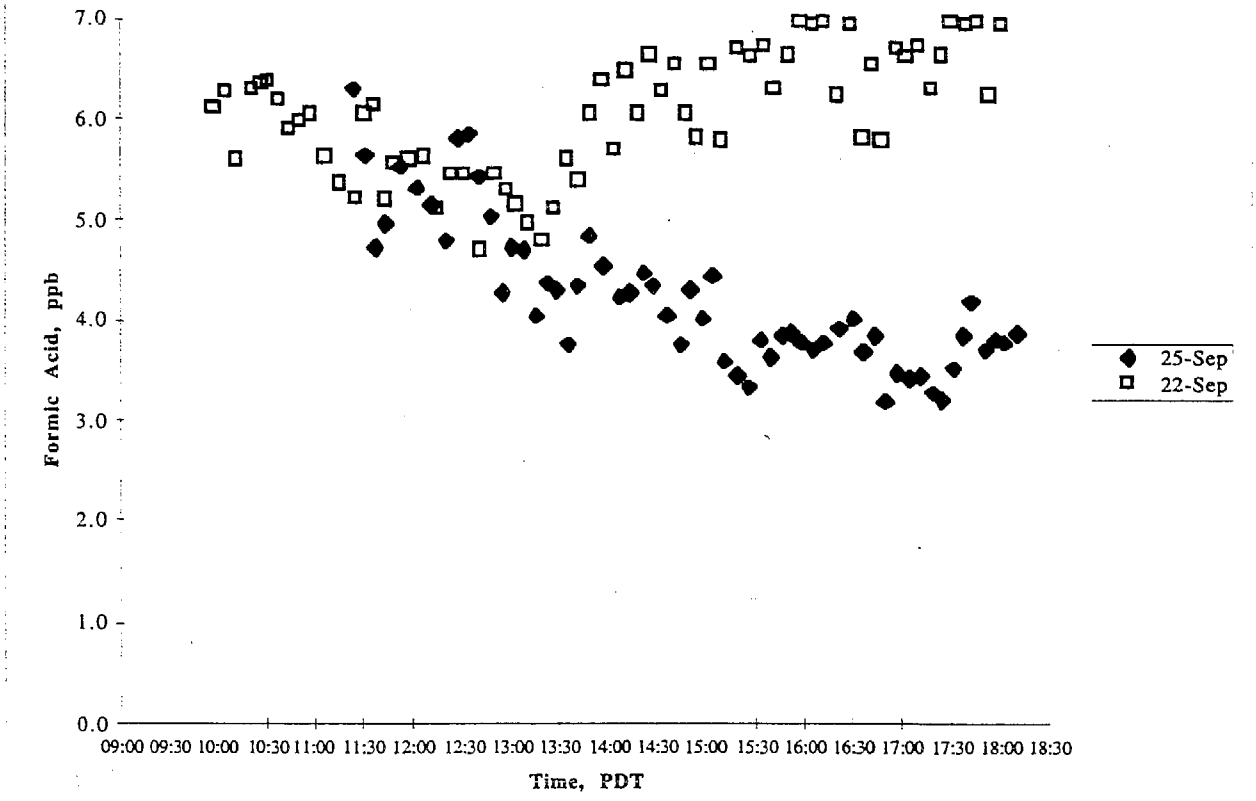
Figure 5-3. Ammonia time-concentration profile on September 25, 1995 in Claremont, CA



• **Formic Acid**

Formic acid was generally above the nominal 2 ppb detection limit for most of the days that the FTIR was operated. The objective was to compare the formic acid concentrations determined using the FTIR with the concentration determined using the CE-CERT denuder substrates coated with KOH. Since the FTIR could not be operated at night or for all days within a one-week denuder sampling period, it was not possible to make a direct comparison with the samples collected for one-week intervals. The comparison could be made for the four daytime samples collected at 10 L/min using the "sampler" configuration of coated denuder substrates (see Figure 5-18). Of these four days, a complete set of FTIR data were available on two days, September 22 and 25. Figure 5-4 is a time-concentration plot of this data for these two days. The concentration profiles, unlike ammonia or nitric acid, show little diurnal variation and range from 3-7 ppb.

Figure 5-4. Formic acid time-concentration profiles on September 22 and 25, 1995, in Claremont, CA.



5.1.2 TDLAS

A Unisearch Associates Inc. model TAMS-150 tunable diode laser absorption spectrometer (TDLAS) was used to measure nitric acid *in-situ*. This approach has been previously described (Hastie et al., 1983) and found to compare favorably with other methods of nitric acid measurement (Anlauf et al., 1988, 1991). With this instrument, particulate matter is removed with a Teflon filter and drawn into a Teflon-lined cell at 10 L/min and maintained at 25 torr pressure. The residence time in the cell is approximately four seconds. A laser-generated IR beam at 1720.3857 cm^{-1} is introduced into the cell, where white-cell optics with a 1.5 m basepath are used to reflect the beam multiple times to produce an effective beam length of 153 m. The IR beam is highly monochromatic and allows scanning of a single rotational-vibrational line in the mid-infrared. The result is a highly specific measurement of nitric acid with a detection limit typically less than one ppb. Calibration is performed by introducing nitric acid generated by a permeation tube maintained at constant temperature. The output rate of the permeation tube is measured by bubbling the effluent from the tube through a buffered aqueous solution and titrating with a standard solution of potassium hydroxide monitoring the change in pH with an electrode.

While the TDLAS method is sensitive and selective, the sampled air passes through a Teflon filter and is therefore subject to interferences from volatilization of nitric acid from ammonium nitrate particles deposited on the filter. While the response times did not indicate such artifacts, they may have a time scale similar to the several minutes for the analyzer (due to plumbing in the measurement system).

Appendix F presents the entire data set of nitric acid measurements made at Claremont. Figure 5-5 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 5-6 is a plot of 15-minute averaged nitric acid concentrations determined by the TDLAS compared with the FTIR. The TDLAS data were reported by Unisearch as 15-minute averages with averaging periods from 0000 to 0015, 0015 to 0030, 0030 to 0045, etc. The FTIR data were reported by SAPRC as instantaneous readings at approximately six-minute intervals. CE-CERT averaged these FTIR readings into the 15-minute time intervals reported for the TDLAS data. The number of instantaneous FTIR readings contributing to each 15-minute averaging period ranged from 0 to 3. The correlation coefficient for the regression forced through the origin is surprisingly low, $r^2 = 0.39$. We believe that there are two main reasons for the observed scatter: a time lag of approximately one hour in TDLAS response, and the higher detection limit of 5 ppb for the FTIR response. This is explained further after discussion of the observed diurnal patterns.

Figure 5-5. Nitric acid measured by TDLAS in Claremont, California, 1995

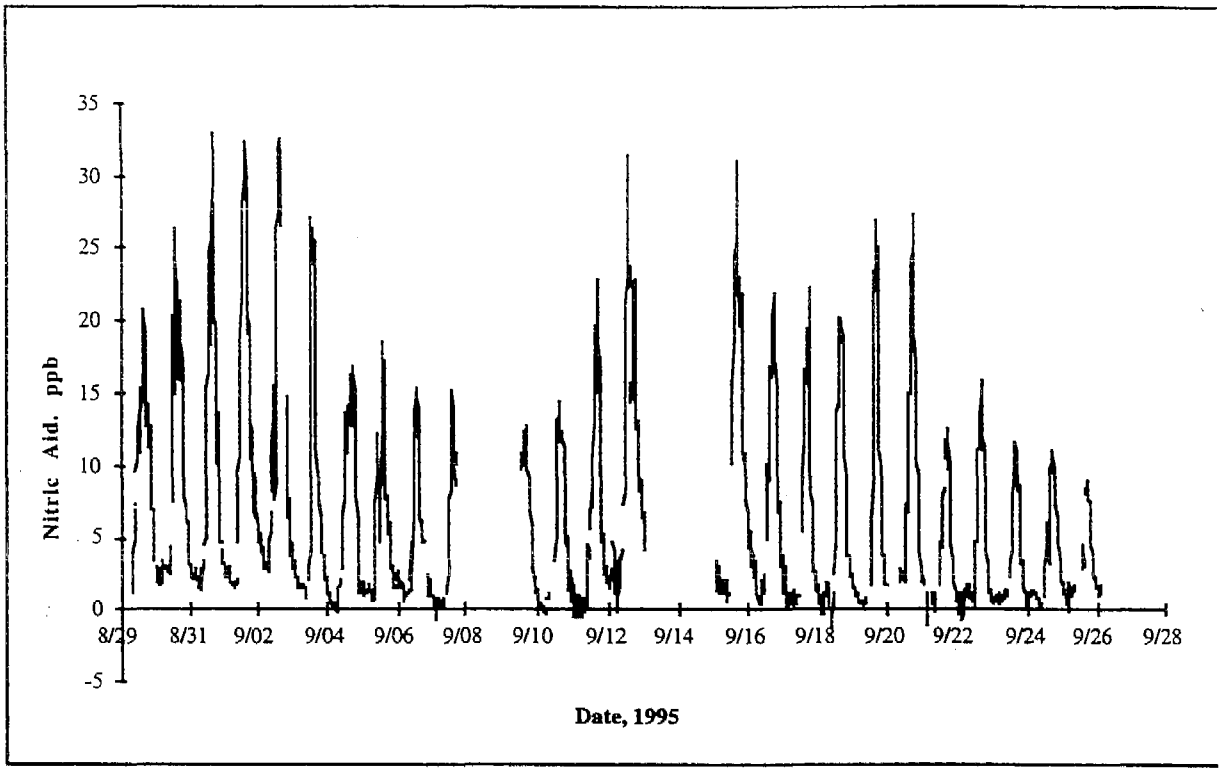


Figure 5-6. Nitric acid concentrations by FTIR and TDLAS

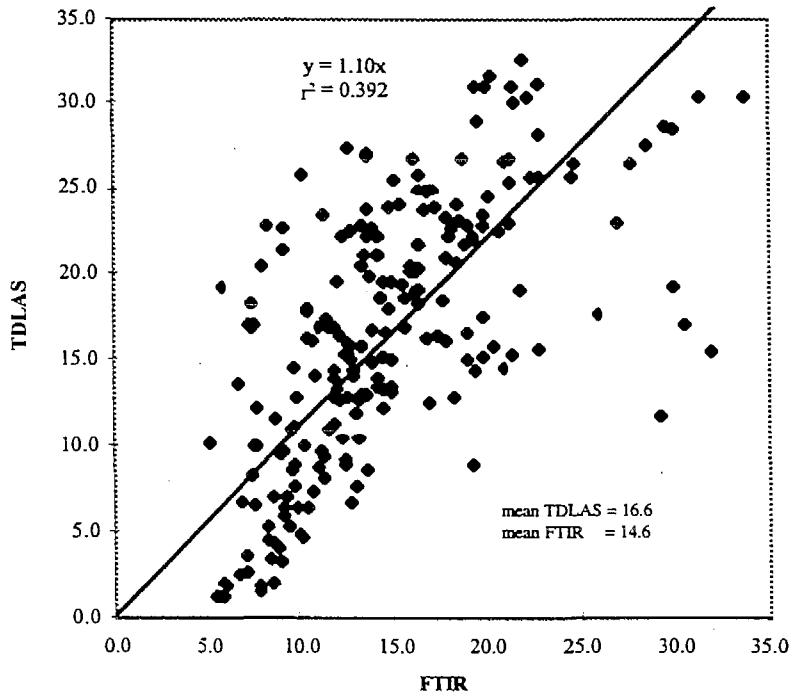


Figure 5-7 compares the two measurement approaches by using a composite diurnal profile of nitric acid for eight days when data from both spectroscopic methods were available. The chart maps only 15-minute periods for which at least five days' worth of data were collected. As shown in the Figure, TDLAS response rises later in the morning than the FTIR, and TDLAS response falls off later in the evening than the FTIR. A possible explanation for the lower TDLAS values in the morning may be the retention of nitric acid by the Teflon prefilter, while the higher values later in the day may be due to volatilization of nitric acid from this filter. Figure 5-8 shows a comparison of the nitric acid time-concentration profiles (15-minute averages) as measured by the TDLAS and FTIR with those of a Dasibi ozone monitor for September 11 and 15. The plots illustrate that the FTIR nitric acid profiles more closely track the progress of the smog episode, as indexed by the ozone levels, than the TDLAS data.

Since the differences in nitric acid concentration are likely to have been caused by environmental factors, the TDLAS data cannot be corrected to provide data equivalent to the FTIR reference data for the periods when FTIR data are not available. These data also show that straight-forward comparison of the two spectroscopic methods was not possible under these ambient conditions.

Figure 5-7. Comparison of FTIR and TDLAS nitric acid, daytime, Claremont using 15 minute periods averaged over eight days

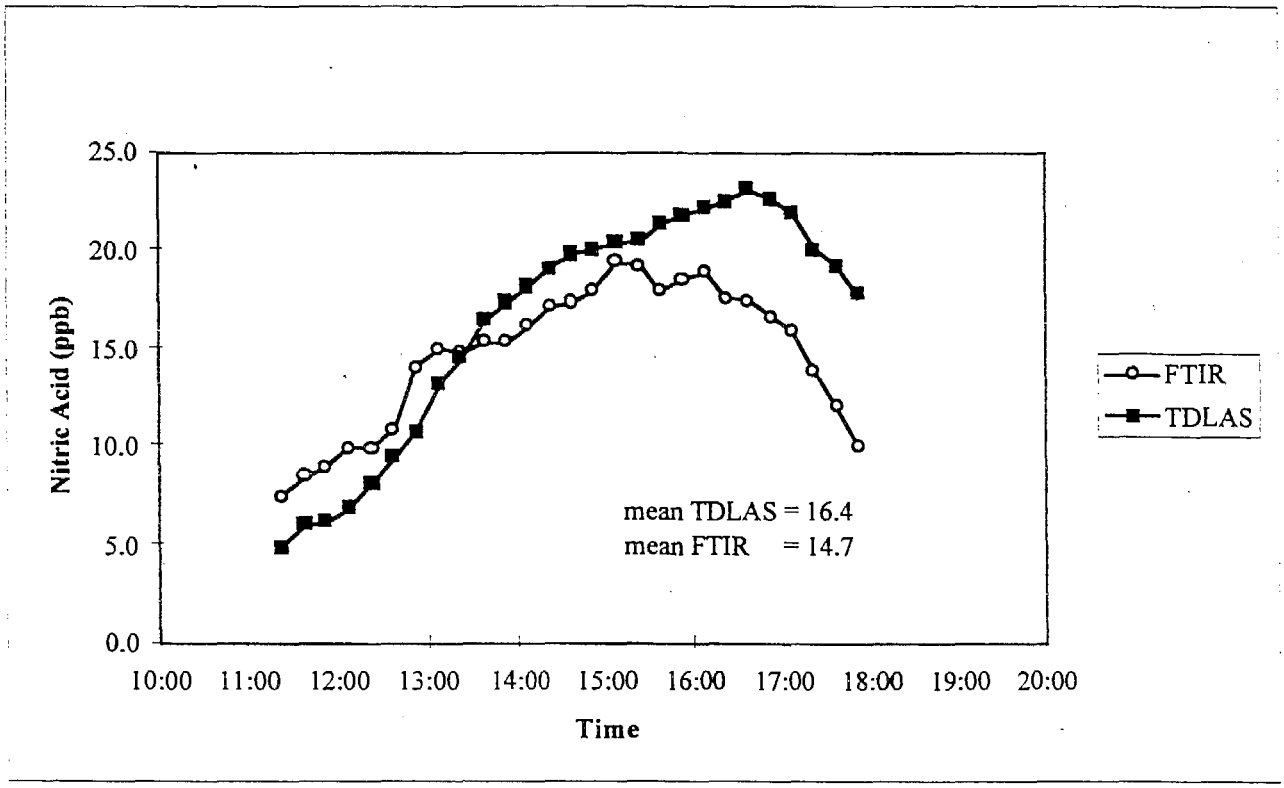
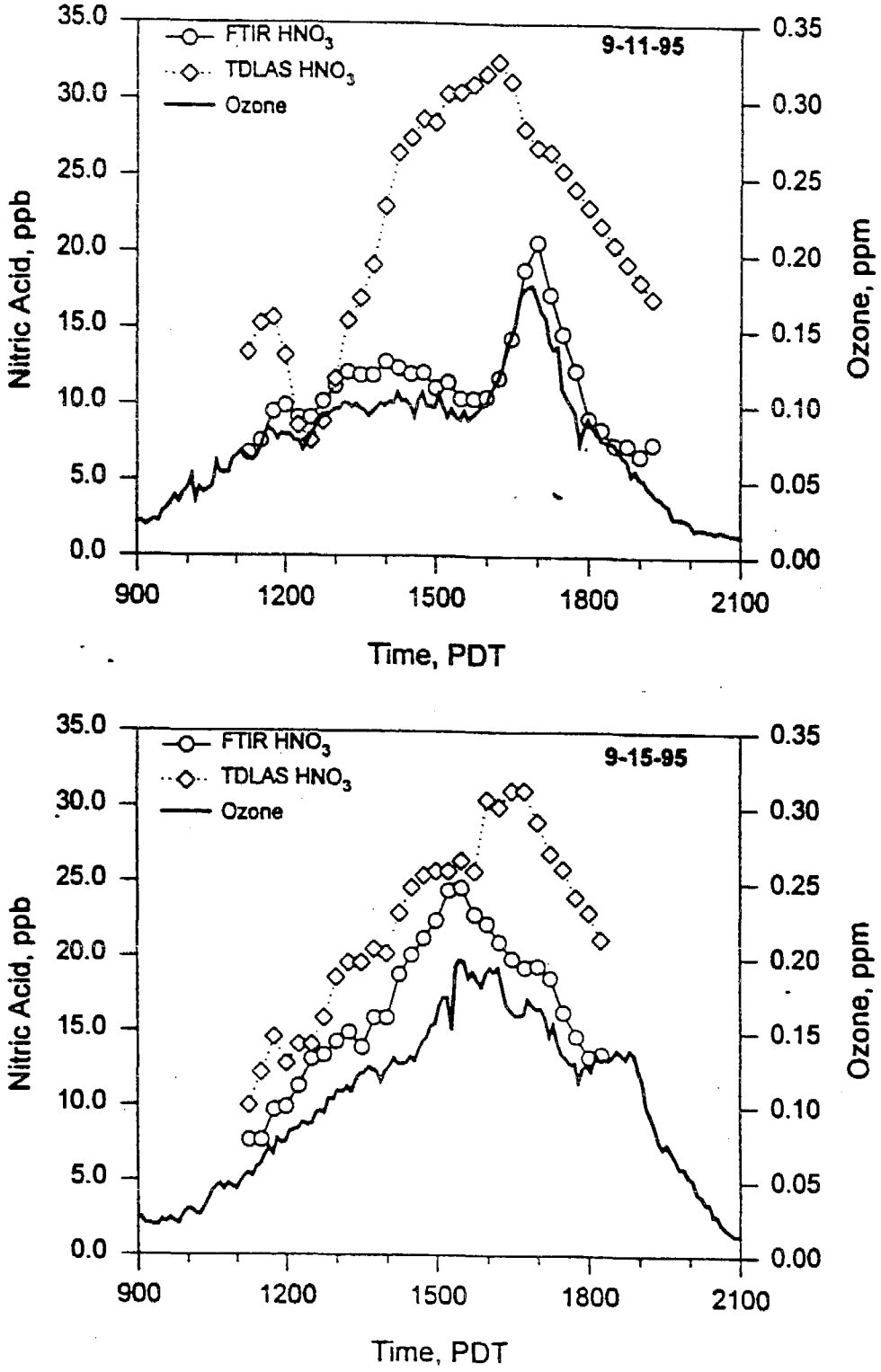


Figure 5-8. Nitric acid and ozone concentrations as a function of time.



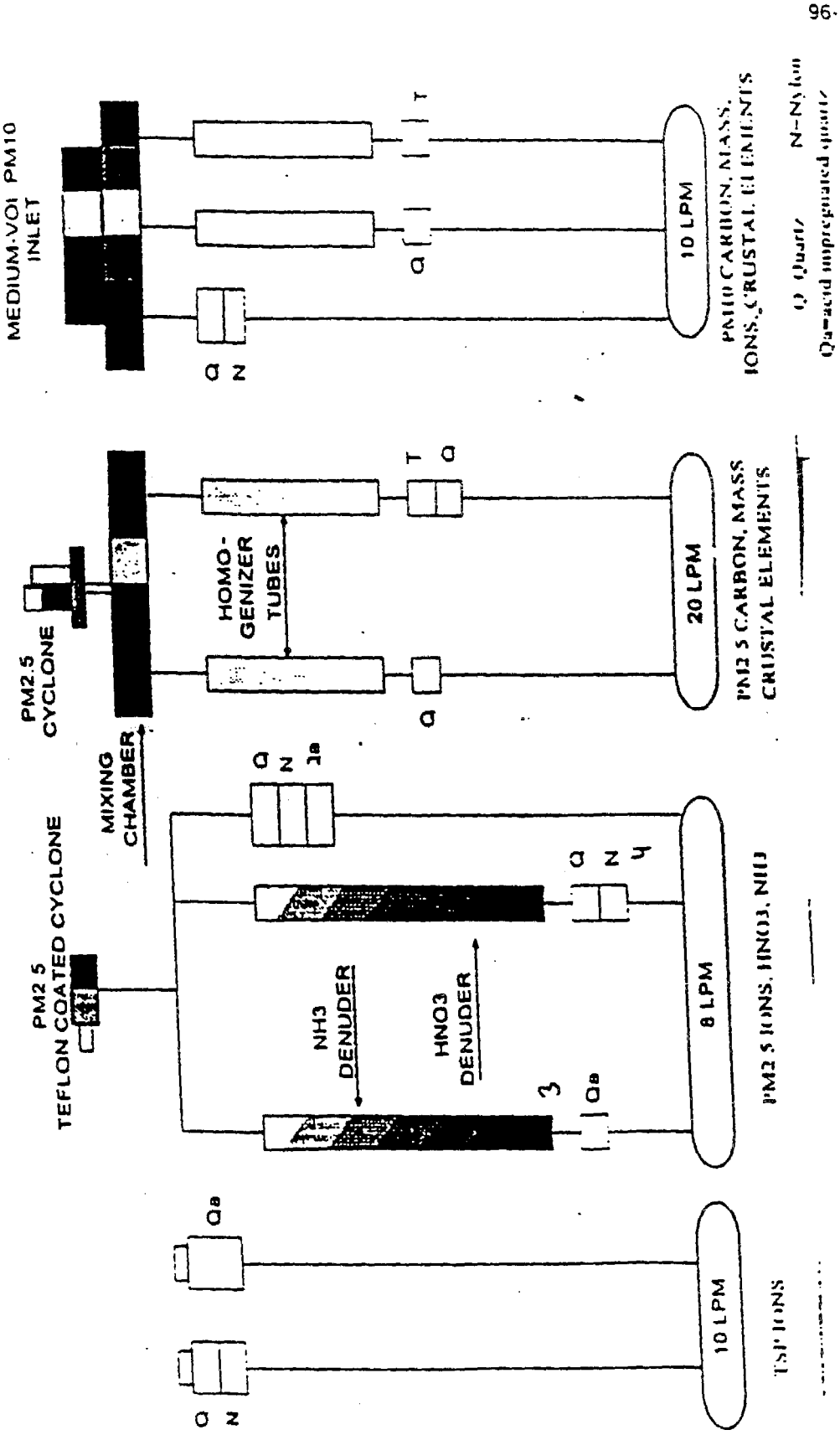
The effect of the time lag on the scatterplot (Figure 5-6) is that the early morning observations fall well below the TDLAS/FTIR regression line, and the late afternoon observations fall well above the regression line. This effect is exacerbated by the fact that the FTIR was used only during the daytime and has a high detection limit of 5 ppb. The effect of this censoring on the totality of the data can be seen in Figure 5-6. Because the nighttime data has been censored by the FTIR, a large cloud of observations for which the FTIR and TDLAS results would probably agree (that nitric acid levels were low) has been excluded from the scatterplot. This reduces the correlation coefficient and necessitates forcing the regression line through the origin. Further, the FTIR cuts off in the evening before the TDLAS has fully returned to low nitric acid levels. Thus, a cloud of early evening observations having moderate TDLAS and low FTIR response (which would balance the morning readings having low TDLAS and moderate FTIR response) is absent from the scatterplot.

In Figure 5-6, the mean TDLAS response is 12% higher than the mean FTIR response. In figure 5-7, the mean TDLAS response is 14% higher than the mean FTIR response. Due to the effect of censoring discussed above, a more complete FTIR data set would probably result in a larger positive bias for the TDLAS.

5.1.3 SCAQMD Sampler

The sampler developed by the South Coast Air Quality Management District (SCAQMD) for its Enhanced Fine Particulate Monitoring Program (PTEP) has four channels: one for total, two for $PM_{2.5}$ (one for nitric acid and ammonia sampling, the other for mass, carbon, and crustal elements) and one for PM_{10} (Teffera et al., 1996). Figure 5-9 is a schematic drawing of the sampler. The $PM_{2.5}$ component was set up at the Claremont site and operated on the same twice-per-day schedule as the denuder test samplers. This component consists of a PFA-Teflon coated cyclone (nominal flow of 27 L/min) to remove particles larger than 2.5 μm aerodynamic diameter. The air is then divided into three sampling pathways using PFA-coated metal plumbing components. Each stream samples at a nominal 9 L/min. In the first, ammonia is removed by a denuder consisting of sheets of quartz filters coated with citric acid, followed by a citric acid-coated filter to collect particles and volatilized ammonium. In the second path, nitric acid is removed by a denuder consisting of plates of anodized aluminum followed by quartz and nylon filters in series to collect particles and volatilized nitrate. In the third, a quartz filter is used to remove particulate matter, a nylon filter removes nitric acid and volatilized nitrate, and a citric-acid coated quartz filter removes ammonia and volatilized ammonium. Ammonia and nitric acid are quantified by subtracting the amount collected after the denuder from the total collected without a denuder. Note that the filter pack approach for quantifying nitric acid and ammonia is available from the sampling cassette without the denuder, although the front filter is quartz rather than the typical Teflon. Teflon filters are generally considered more inert than quartz and less likely to adsorb reactive gases.

Figure 5-9. Schematics of the South Coast AQMD Multi-Channel Fine Particulate Sampler



In laboratory testing (Teffera et al., 1996) at a nominal concentration of 60 ppb, the losses of nitric acid through PFA-Teflon coated tubing used in the system was shown to be approximately 5% by using a commercial NO-NO_X analyzer. In similar testing, the nitric acid denuder was found to remove over 95% of the nitric acid. The penetration of ammonia through the ammonia denuder was determined by using filtered ambient air as an ammonia source and sampling before and after the denuder with citric acid-coated quartz filters. The denuder averaged 93% efficiency over seven such tests.

Samples in Claremont were collected over the same twice-per-day intervals as those for the denuder evaluation (nominally 1100-1700 hours PDT and 1700-1100 hours PDT). The SCAQMD analyzed substrates by ion chromatography. The measurements of nitric acid and ammonia were then compared with the FTIR and TDLAS real time analyzers, and with the CADMP and denuder evaluation measurements.

All sampling substrates were provided and analyzed by the SCAQMD. Appendix G presents the results for the nitrate and ammonium analyses. None of these concentrations were corrected for blanks. Samples for ammonia analysis were not collected until September 8 as the substrates were not available. There is a gap in the data from September 12 to 20 due to missing substrates. The values for nitric acid and ammonia from the denuder difference approach are shown in Appendix G.

- **Nitric Acid**

Figure 5-10 is a plot of the daytime nitric acid determined from the denuder difference approach of the SCAQMD sampler compared to the TDLAS, FTIR and CE-CERT sampler. For the TDLAS, the square of the correlation coefficient was 0.21; the two data sets are therefore very poorly correlated. The correlation did not improve when the nitric acid determined by the SCAQMD filter pack was compared with the TDLAS data. We cannot explain the lack of correlation between the two methods in the daytime. The limited amount of data for comparison with the CE-CERT sampler and FTIR precluded a regression fit but also showed wide scatter. For daytime measurements of nitric acid none of the three methods are in agreement.

Figure 5-11 is a plot of the nighttime nitric acid determined from the denuder difference of the SCAQMD sampler compared with the TDLAS. One outlier was excluded from the regression analysis. These data are much better correlated with an r^2 of 0.88. The intercept is near the origin, at 1.38 $\mu g/m^3$, and the slope was 1.25. It is not clear why the agreement was so much better for nighttime sampling. Based on the means, the SCAQMD sampler measurements are 35% lower than the TDLAS during the nighttime.

Figure 5-10. Comparison of SCAQMD, TDLAS, FTIR and CE-CERT nitric acid, daytime, Claremont, CA

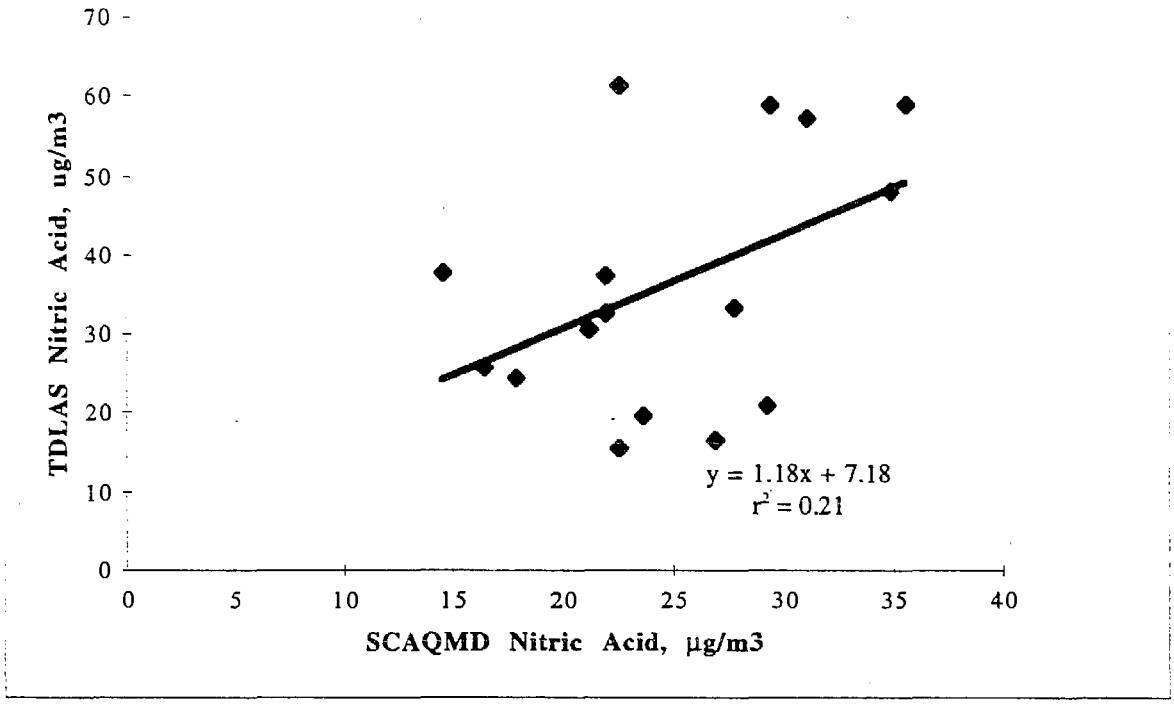
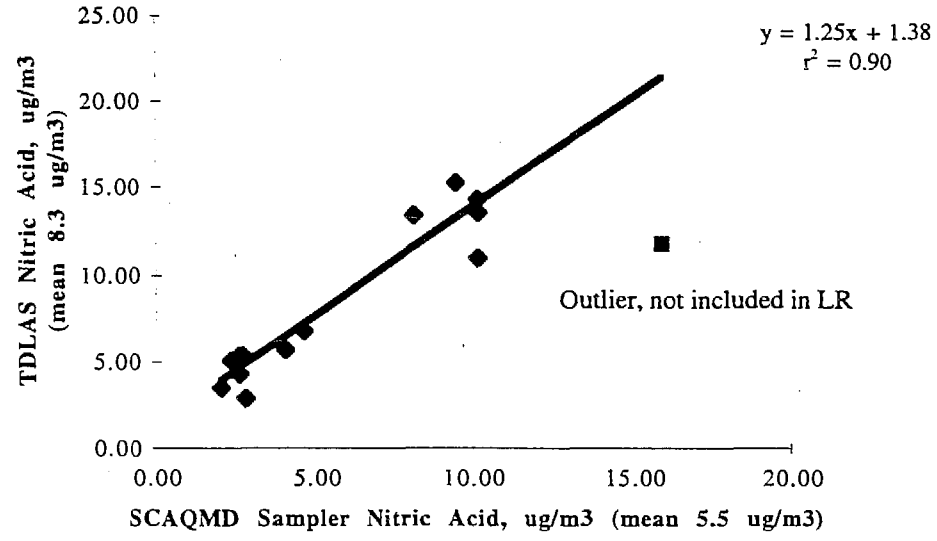


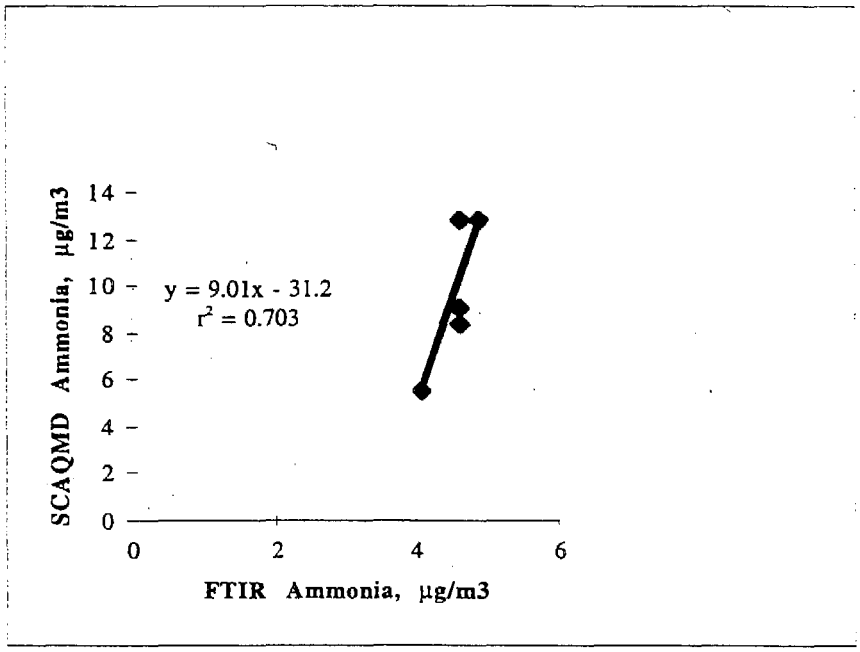
Figure 5-11. Comparison of FIPS and TDLAS nitric acid, nighttime, Claremont, CA



- **Ammonia**

Five data points were available to compare ammonia measurement made with the SCAQMD sampler with the FTIR. Figure 5-12 is a plot of these data. While the correlation coefficient squared of 0.70 indicated a relationship between the two data sets, the absolute value of the intercept was nearly three times the average ammonia measured by the SCAQMD. With this large of an intercept the data cannot be considered equivalent. It is possible that the large intercept may reflect contamination due to filter handling. Such contamination was not observed for the CE-CERT evaluation for ammonia sampling (see section 5.1.5.3). Thus, it is unlikely that it occurred while loading the cassettes in the on-site trailer.

Figure 5-12. Comparison of SCAQMD and FTIR ammonia measurements, daytime, Claremont, CA



5.1.4 CADMP

The CADMP sampler used was the primary unit at the Azusa site, using the pumps from the Azusa collocated sampler. This sampler was renovated in the fall of 1993 as part of a special study which compared the CADMP with a TDLAS (Motallebi and Ashbaugh, 1993). Renovation consisted of cleaning all of the sampler's interior surfaces followed by conditioning with a dilute aqueous solution of nitric acid. The nitric acid denuders were soaked in a solution of sodium hydroxide to remove the adsorbed nitrate.

Recent studies (Fitz and Hering, 1996) have shown that losses of nitric acid through the CADMP collocated Azusa sampler average 15% and that its anodized aluminum tube denuder removes an average of 90% of the nitric acid. The sampler evaluated was renovated prior to being collocated with the Azusa primary CADMP in the fall of 1993. These values therefore pertain to a sampler that had been used for over a year while sampling every sixth day.

The CADMP sampler was operated on the same daytime and nighttime schedule as that for the denuder evaluation samples collected twice per day. Samples were collected at a nominal 20 L/min. Nylon and Teflon substrates were provided by the ARB Monitoring and Laboratory Division, which also analyzed them after collection for nitrate. The nitric acid measurements, both by the filter pack and denuder difference methods, were then compared with the FTIR and TDLAS real time analyzers and with the SCAQMD and denuder evaluation measurements.

Figures 5-13 and 5-14 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 when TDLAS values were not available for at least 75% of the CADMP's sampling interval. 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 5-15 and 5-16 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.

Figure 5-13. CADMP vs. TDLAS nitric acid measurements, daytime, Claremont, CA

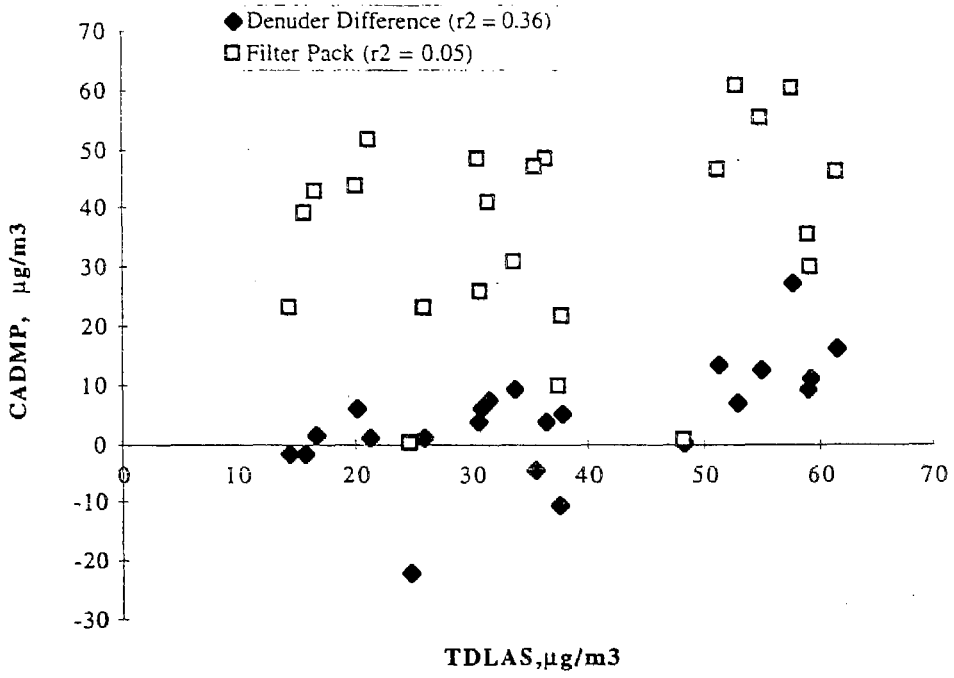


Figure 5-14. CADMP vs. TDLAS nitric acid measurements, nighttime, Claremont, CA

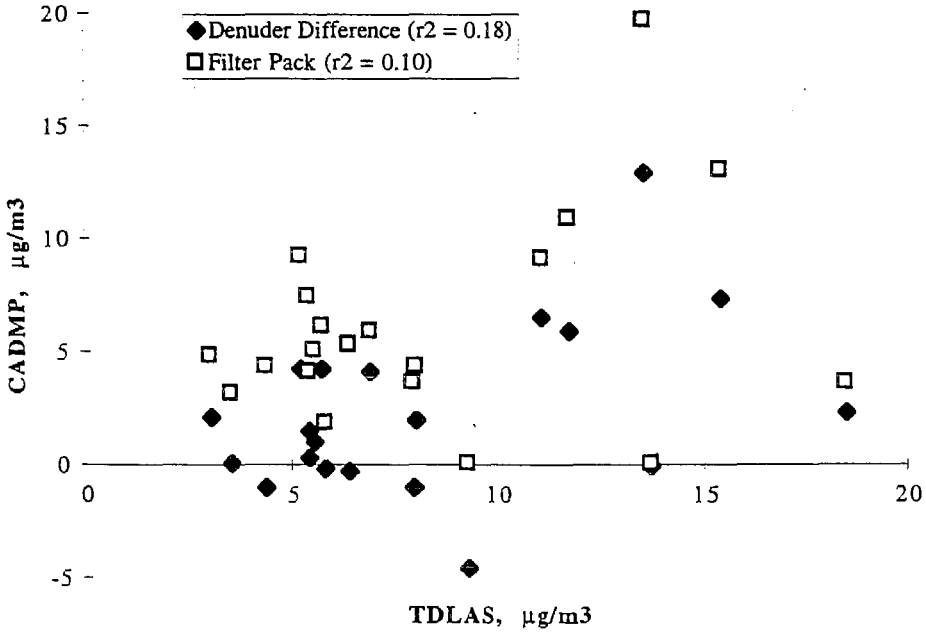


Figure 5-15. Time series plot of nitric acid by TDLAS, CADMP denuder difference and CADMP filter pack, daytime, Claremont, CA

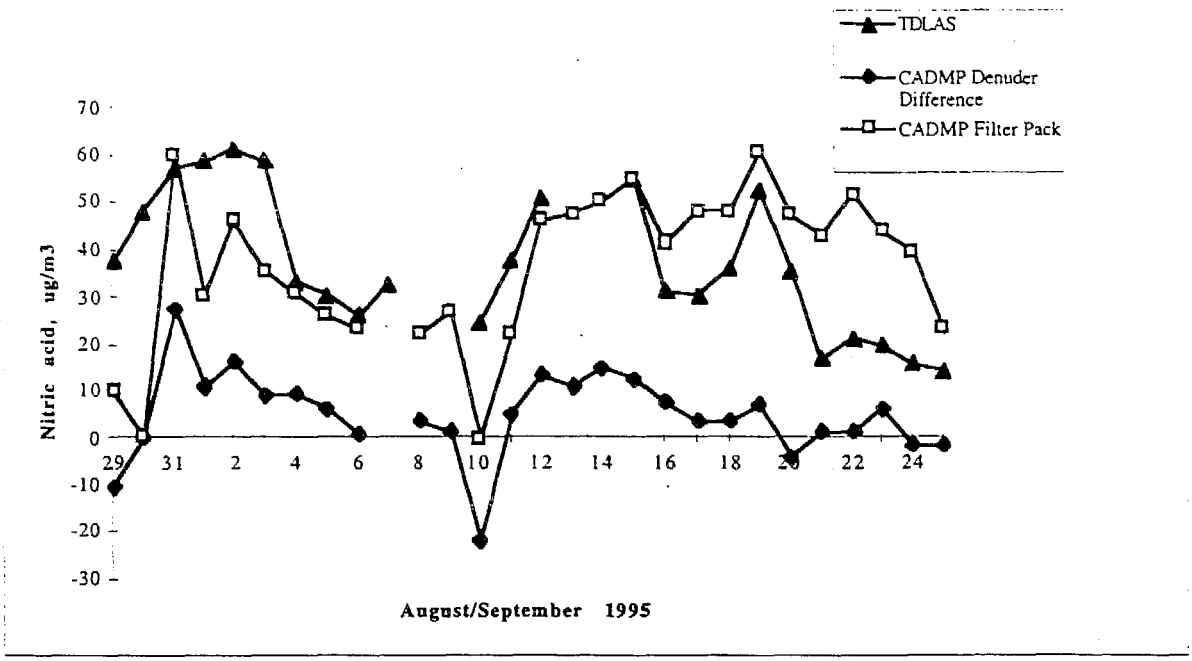
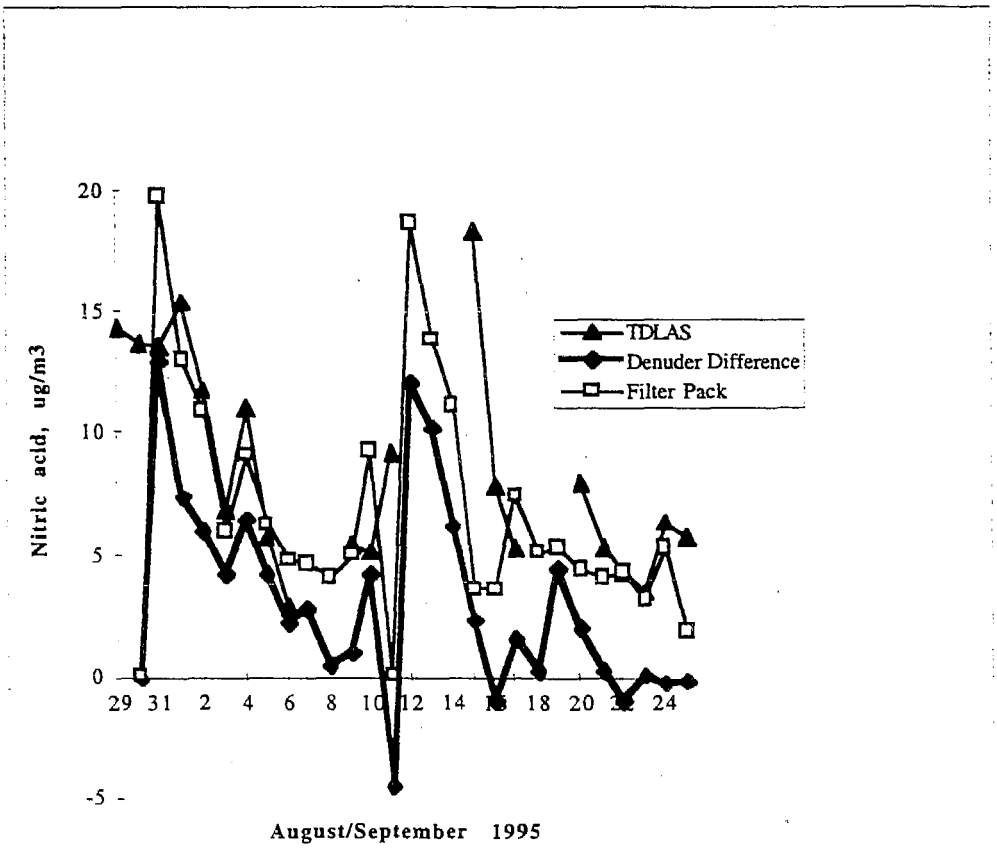


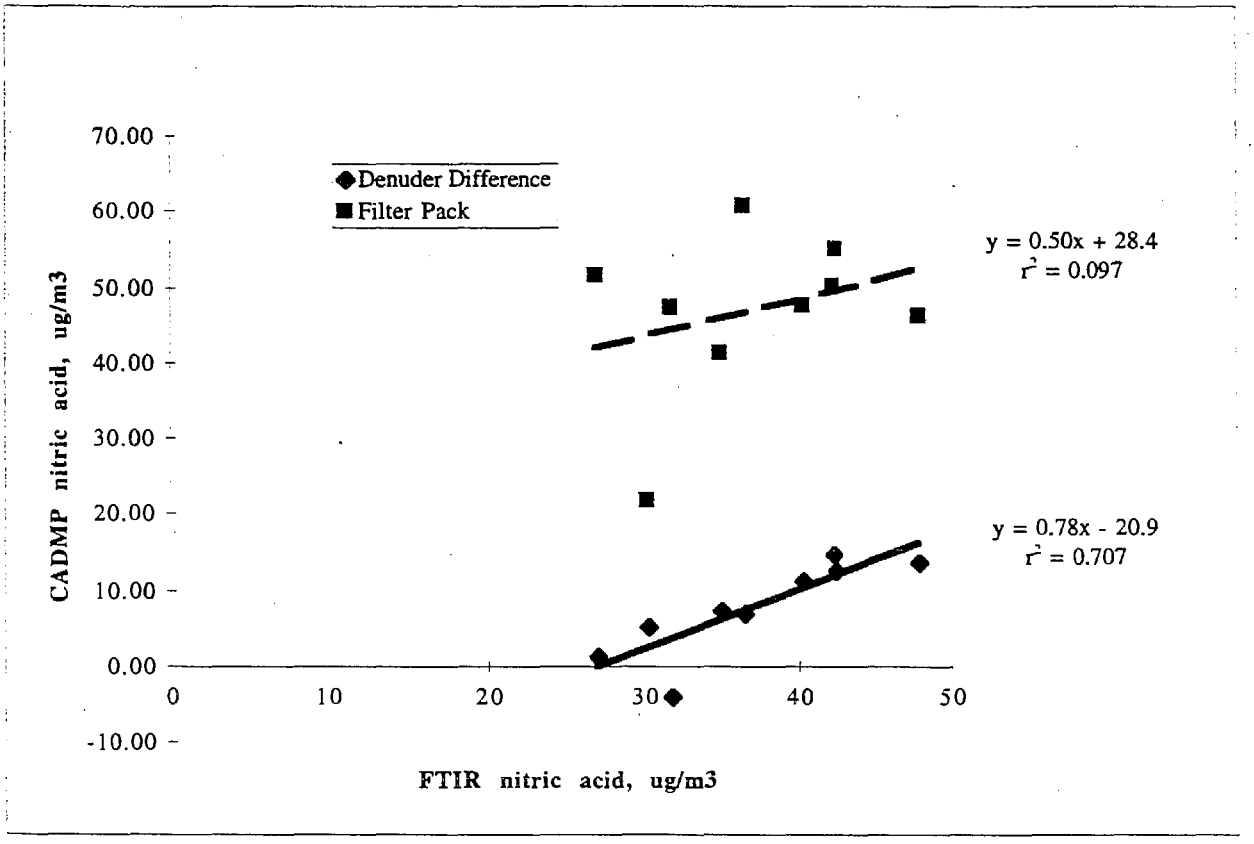
Figure 5-16. Time series plot of nitric acid measured by TDLAS, CADMP denuder difference, and CADMP filter pack, Nighttime, Claremont, California



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. It is not clear, however, why changing the laser would affect the measurement unless the calibration system was perturbed during the changeout period. Alternatively, the CADMP's surfaces may be conditioning to nitric acid and allowing greater penetration during the later part of the period.

Figure 5-17 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 mg/m^3 compared to 37.8 mg/m^3) and with a large intercept (- 20.9 mg/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.

Figure 5-17. CADMP vs. FTIR nitric acid measurements, Daytime, Claremont, CA



The scatter and generally low nitric acid measured by the CADMP compared to the TDLAS (mean of 4.6 ± 9.6 mg/m^3 versus 37.2 ± 15.4 mg/m^3) during the daytime indicated that this denuder (daytime

denuder) had poor nitric acid 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 mg/m^3 versus 8.4 ± 4.3 mg/m^3). This could be explained in part by the nighttime denuder being more efficient in removing nitric acid since it had not been exposed to as much in the preceding two years.

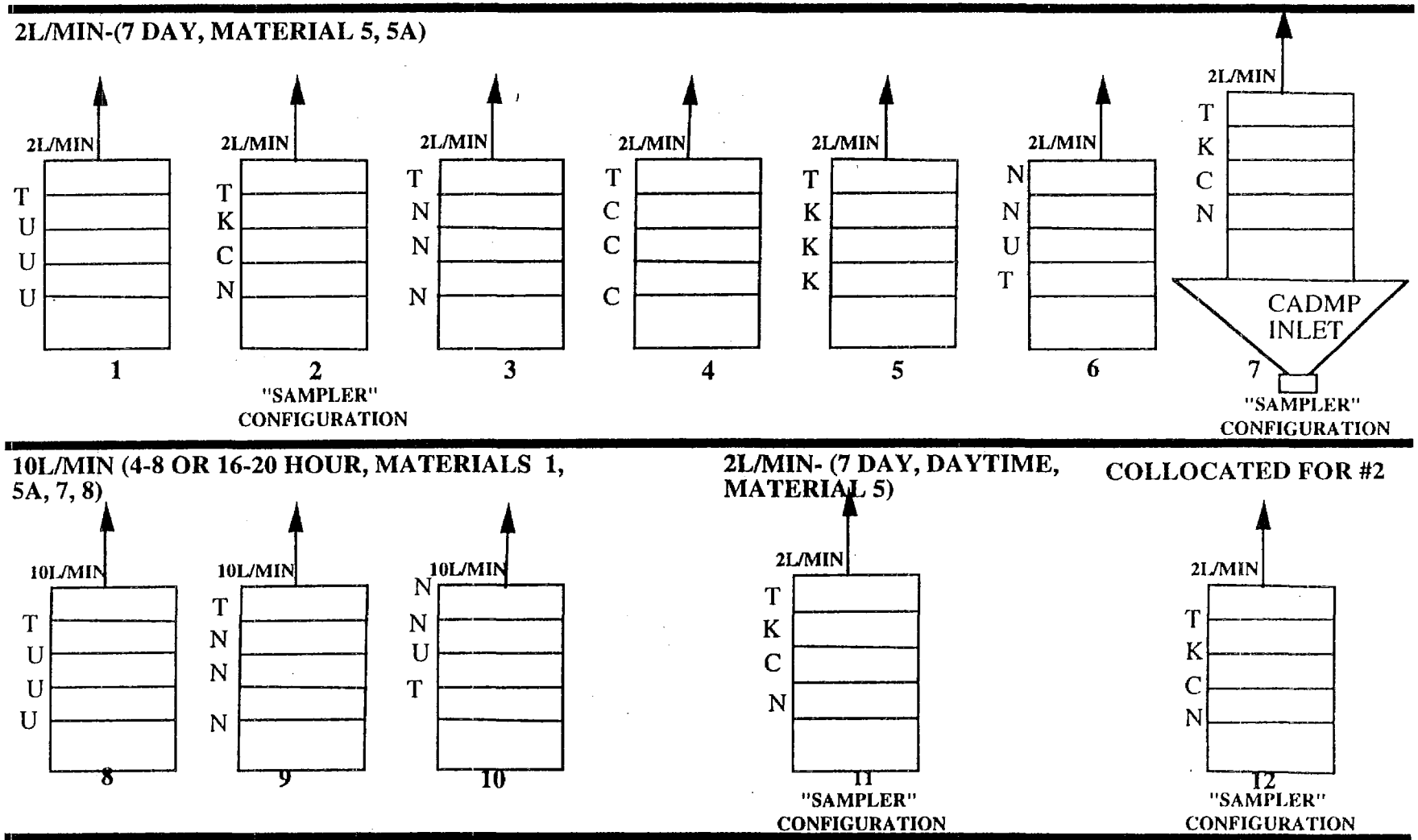
Laboratory experiments (Fitz and Hering, 1996) showed these denuders to be sources of nitric acid when evaluated after the Claremont field study. They also observed particle shedding from the cyclone during the laboratory evaluation using synthetically generated aerosol. This may account for high negative 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.

These data indicate that the denuders of the primary Azusa CADMP sampler were no longer efficiently removing nitric acid.

5.1.5 CE-CERT Denuder Evaluation

During the Claremont evaluation, denuders with three types of material, four types of coatings, and two flow rates were evaluated. The sampling scheme also provided for collocated samples. Figure 5-18 is a schematic diagram of the denuder evaluation. Each denuder pack contains a Teflon filter either before it or after it in order to estimate variability and particulate penetration (as determined by sulfate concentrations). Sampler lines 8, 9, and 10 were operated at 10 L/min during nominal intervals of 1100-1700 hours PDT and 1700-1100 hours PDT. The other samplers were operated for one-week intervals at 2 L/min (they were turned off while the 10 L/min samplers were being changed). Line 7 collected sample from the CADMP plenum, which had a total flow of 115 L/min through a cyclone with a 2.5 μm cut-point. Line 11 was a daytime sampler operated on the same schedule as the 10 L/min samplers. Samplers collected at 2 L/min used the same material (5 or 5A); the 10 L/min sampling substrates were rotated between Materials 1, 5, 7, and 8. Each of these four materials was sampled at 10 L/min six times in this configuration over the first 24 days. For an additional day, each of these four denuder materials was used in the configuration shown in line 2 (the proposed "sampler" configuration at the time of the field study), but operated at 10 L/min. For each of these four days, triplicate samples were obtained using lines 8-10 in order to estimate the precision of the measurement.

The objectives for each sampling line were as follows:



N=NaCl coated denuder
C=Citric acid coated denuder
K=KOH coated denuder
U=Uncoated denuder substrate
T=Gelman Zefluor Teflon filter

Figure 5-18. CE-CERT sampler configuration for Claremont comparison study.

#1: This measures the adsorptive characteristic of the uncoated denuder and particulate penetration at 2 L/min.

#2: This was the prototype sampler, which contained a denuder coated to retain nitric acid (NaCl coating), one for ammonia (citric acid coating) and one for formic and acetic acids (KOH coating).

#3 Three NaCl-coated denuders, used to measure the penetration of nitric acid at 2 L/min.

#4 Three citric acid-coated denuders to measure the penetration of ammonia at 2 L/min.

#5 Three KOH-coated denuders to measure the penetration of formic and acetic acids at 2 L/min.

#6 This contains a Teflon filter prior to the denuders as a reference for particulate penetration. The first denuder is uncoated, allowing for a second determination of gas retention. The second and third denuders provide a second measurement of nitric acid penetration through an NaCl-coated denuder at 2 L/min.

#7 This is the prototype sampler (same as #2) preceded by a CADMP sampler PFA-Teflon -coated plenum and Bendix 240 cyclonet to remove particles greater than 2.5 μm aerodynamic diameter. This system was also used to estimate sampling artifacts due to passing the air through the Teflon-coated aluminum plenum and cyclone.

#8 Same as #1 but samples at 10 L/min. This measures the adsorptive characteristic of the uncoated denuder and particulate penetration at 10 L/min. Four denuder materials, (1, 5, 7, and 8) were alternately evaluated.

#9 Same as #3 but samples at 10 L/min. Three NaCl-coated denuders, used to measure the penetration of nitric acid at 10 L/min. Four denuder materials were again alternately evaluated.

#10 Same as #6, but samples at 10 L/min. The initial Teflon filter provides a reference particle concentration for testing particulate penetration. The second and third denuders provide additional tests of nitric acid collection efficiency at 10 L/min. Four denuder materials were again alternately evaluated.

#11 This is the original prototype sampler again, but it collected samples only during the daytime (nominally from 1000 to 1800 hours PDT) for direct comparison with the FTIR which was operated during this period.

#12 This replicate of sampler #2 was used to estimate the overall precision of the sampling.

Twenty-eight days of collocated samples were collected with this arrangement. All samples collected for one-week intervals were chemically analyzed while eight selected sets of the daily samples were analyzed. The criteria for analysis days included the availability and quality of spectroscopic data in addition to evaluating each denuder material at least twice. The analysis days tended to be those of highest nitric acid concentration, the species of most interest in this study. Two daytime sets for samplers 8, 9, and 10 were analyzed for each of the four denuder materials evaluated. The first set of four were chosen based on days of high nitric acid as determined by the TDLAS. The second set of four were chosen based on the availability of FTIR data. Appendix H is a complete data set of the nitrite, nitrate, sulfate, and ammonium measurements from the analysis of the sampling substrates.

5.1.5.1 Particulate Penetration

2 L/min sampling Flow Rate

Sulfate was used to determine the penetration of fine particles through the denuder sampling system. Denuder Materials 5 or 5A (these materials were believed to be the same except for the color) were used for all of these collection periods. Table 5-1 shows the mean sulfate for each of the samplers averaged over the four seven-day sampling periods of the 2 L/min samplers. The "ratio to remaining" was defined in section 3.2.3 and is the fraction of particulate sulfate apparently collected by each denuder. Figure 5-19 is a schematic diagram of the sampling system with these mean values superimposed. Sampler 6 denuders should be considered the reference since after the Teflon filter removed all particulate sulfate, any sulfate on the following denuders would be a result of the deposition of gas-phase sulfur containing species (such as SO_2).

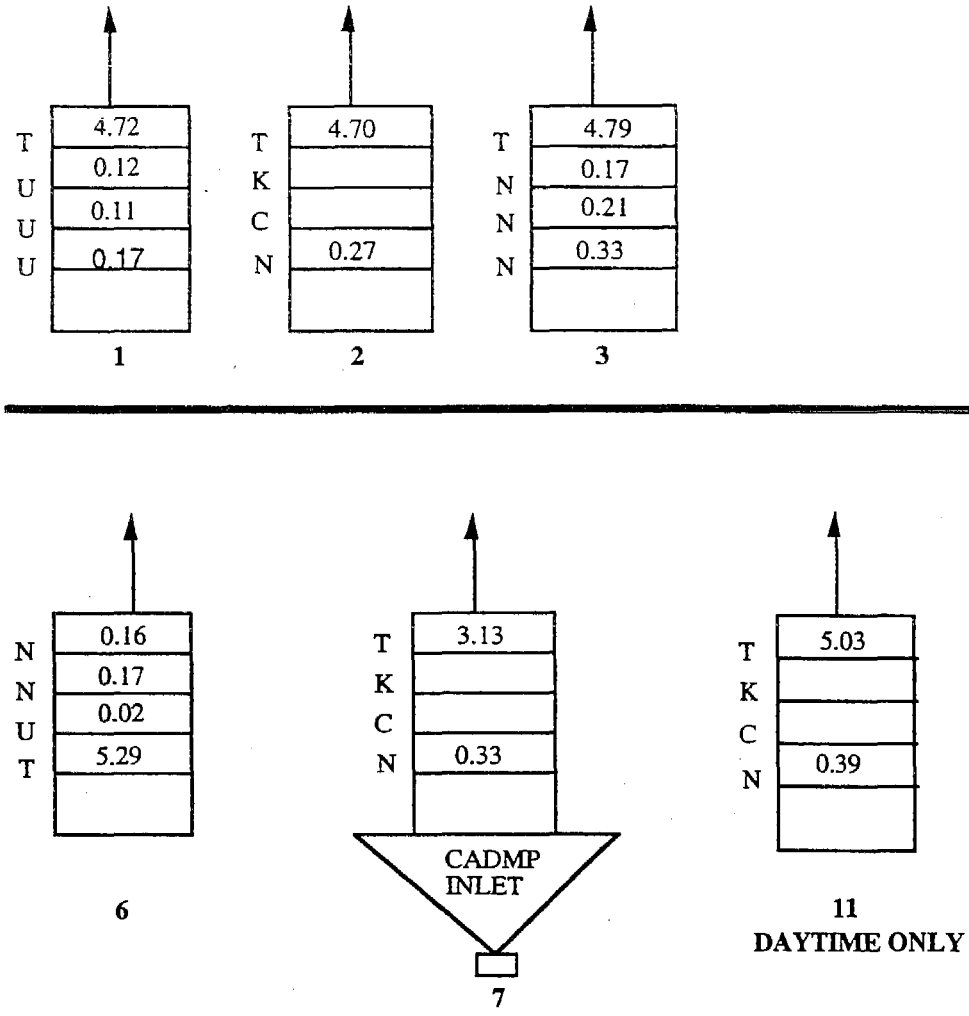
The sulfate on the denuders without prefilter is low, near the expected blank variability and very similar to the Sampler 6 reference. This is a good indication that fine particulate is not being retained by the denuders. Comparing the sulfate on the Teflon filter preceding the denuders to the sulfate on the Teflon filters after the denuders indicate that 11% of the fine particles are lost when passing through three denuders in series. This is probably higher than the sum of particulate sulfate deposited on the denuders since a portion of particulate sulfate may be depositing to the filter holder's Teflon surfaces. This deposition may be enhanced by the electrostatic charge that Teflon

Table 5-1. Summary of sulfate results for one-week CE-CERT denuders (Materials 5 and 5A)

Sampler/ Sample#	Coating*	SO_4 µg/m3	SO_4 Ratio to Remaining
Sampler #1			
D1-Mean	U	0.17	0.03
D2-Mean	U	0.11	0.02
D3-Mean	U	0.12	0.03
T1-Mean		4.72	
Sum of Stages		5.13	
Sampler #2			
D1-Mean	N	0.27	≤0.05
D2-Mean	C	NA	
D3-Mean	K	NA	
T1-Mean		4.70	
Sum of Stages		≥4.97	
Sampler #3			
D1-Mean	N	0.33	0.06
D2-Mean	N	0.21	0.04
D3-Mean	N	0.17	0.03
T1-Mean		4.79	
Sum of Stages		5.50	
Sampler #6			
T1-Mean		5.29	
D1-Mean	U	0.02	0.00
D2-Mean	N	0.17	0.03
D3-Mean	N	0.16	0.03
Sum of Stages		5.64	
Sampler #7 (CADMP inlet)			
D1-Mean	N	0.33	≤0.10
D2-Mean	C		
D3-Mean	K		
T1-Mean		3.13	
Sum of Stages		≥3.46	
Sampler #11			
D1-Mean	N	0.39	≤0.07
D2-Mean	C		
D3-Mean	K		
T1-Mean		5.03	
Sum of Stages		≥5.42	

N = NaCl coated denuder
C = Citric acid coated denuder
K = KOH coated denuder
U = Uncoated denuder
NA: Not Available

Figure 5-19. Summary of sulfate data ($\mu g/m^3$) for the one-week Claremont CE-CERT denuder samples (2 L/min, Materials, 5,5A)



N=NaCl coated denuder
C=Citric acid coated denuder
K=KOH coated denuder
U=Uncoated denuder substrate
T=Teflon Zefluor filter

surfaces tend to acquire (Fitz and Hering, 1996). The raw sulfate data indicate that 2% to 3% of fine particles are collected onto each uncoated denuder and 3% to 6% onto each NaCl coated denuder. After correcting the sulfate data for the adsorption of gas phase sulfur compounds shown by Sampler 6, the corrected data show that each coated or uncoated denuder collects approximately 1% to 3% of the particulate sulfate.

The overall conclusion is that while denuder measurements will be affected only a very little by particulate deposition, approximately 10% of the fine particulate mass may be lost passing through the sampling system. This loss, if not accounted for, would result in the underestimation of particulate concentrations. Note that the sulfate on the Teflon filter sampling below the $PM_{2.5}$ CADMP inlet is 40% lower than the #6 reference although most sulfate would be expected in the $PM_{2.5}$ size fraction.

10 L/min sampling Flow Rate

Particulate sulfate penetration results are summarized in Table 5-2 for five of the eight data sets. The two sampling days are averaged for Material 1; individual days are shown for Materials 5A, 7, and 8. The data for these three materials were not averaged due to missing (for Materials 5A and 7) and inconsistent data (Material 8). For these three materials, data from individual sampling days is presented. Figure 5-20 summarizes the results of the sulfate analyses. Comparison of sulfate on the Teflon filter downstream of three denuders in series with the sulfate on the front Teflon filter shows the following overall losses through three denuders and holders: 31% for Material 1, 18% for Material 5, 20% for Material 7 and 24% for Material 8. Based on the ratio of sulfate on the individual denuders to the total sulfate remaining at that denuder location ("SO_4 ratio to remaining" in Table 5-1), the mean loss of sulfate per denuder is: 9% for Material 1, 3% for Material 5A, 7% for Material 7, and 9% for Material 8. The sum of the loss of sulfate on individual denuders is therefore less than the overall sulfate losses, indicating losses in the Teflon filter holder or the inability of the sulfate to be quantitatively extracted from the denuder. These results are consistent with the third ambient test conducted in Riverside. We conclude that denuder Material 5A allows the highest particulate penetration of the four materials evaluated.

Table 5-2. Summary of sulfate measurements for selected 10 L/min daytime samples

Sample Number	Material	Coating	SO_4 µg/m3 blank corr	SO_4 Ratio to remaining
Sampler #8				
D1-Mean	1	U	0.46	0.11
D1-Mean	1	U	0.23	0.06
D3-Mean	1	U	0.22	0.06
T1-Mean			3.11	
Sum of Stages			4.02	
Sampler #9				
D1-Mean	1	N	0.43	0.10
D1-Mean	1	N	0.19	0.05
D3-Mean	1	N	0.25	0.06
T1-Mean			3.16	
Sum of Stages			4.03	
Sampler #10				
T1-Mean			4.57	
D1-Mean	1	U	-0.06	-0.02
D1-Mean	1	N	-0.07	-0.02
D3-Mean	1	N	-0.07	-0.02
Sum of Stages			4.36	
Sampler #8				
D1	5A	U		
D2	5A	U		
D3	5A	U	-0.06	
T1			1.60	
Sampler #9				
D1	5A	N	0.02	0.01
D2	5A	N	-0.01	-0.01
D3	5A	N	0.04	0.02
T1			1.59	
Sum of Stages			1.64	
Sampler #10				
T1			1.95	
D1	5A	U	-0.06	-0.03
D2	5A	N	-0.04	-0.02
D3	5A	N	-0.02	-0.01
Sum of Stages			1.82	

N=NaCl
U=Uncoated

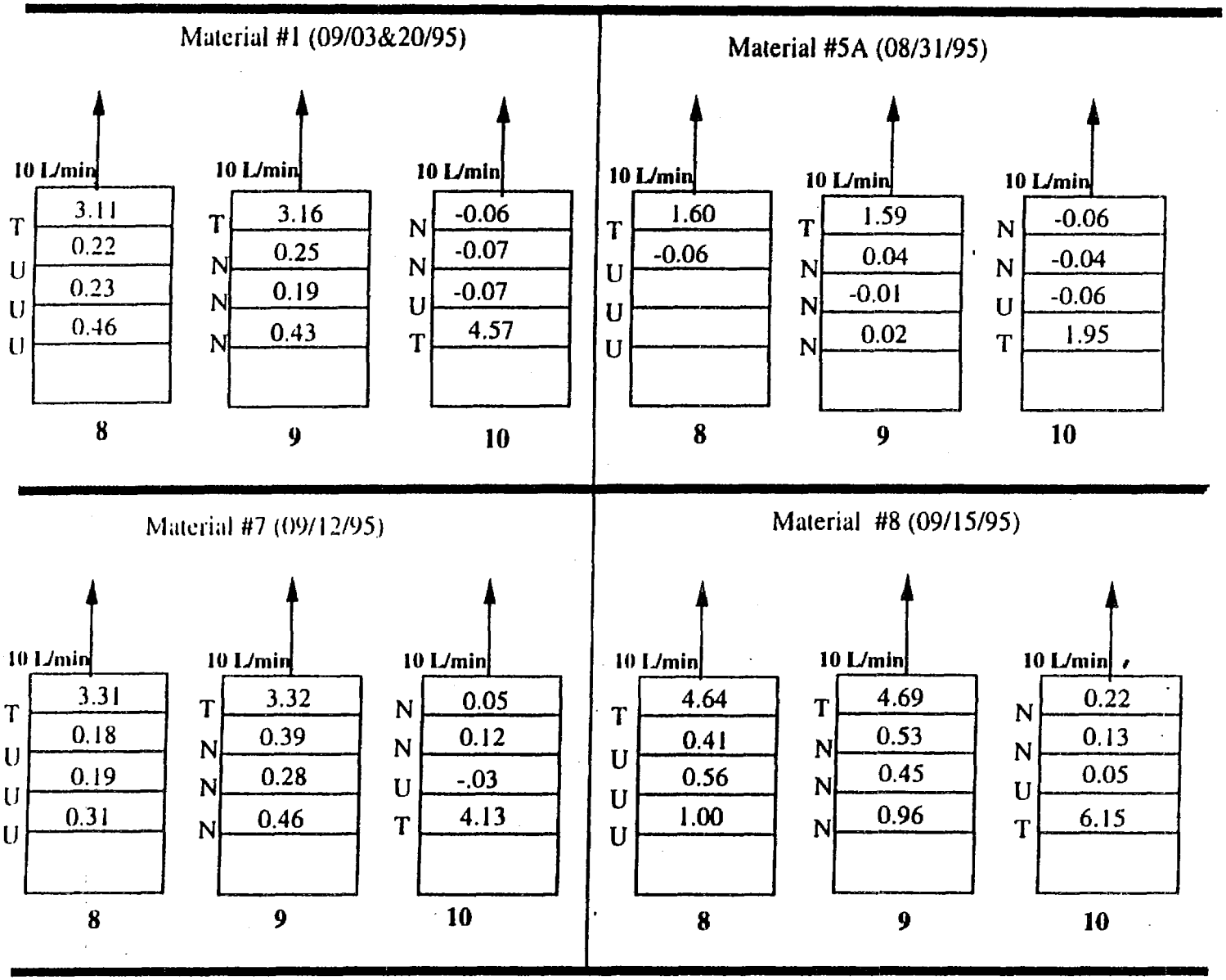
Continued next page

Table 5-2 continued

Sample Number	Material	Coating	SO_4 µg/m3 blank corr	SO_4 Ratio to remaining
Sampler #8				
D1	7	U	0.31	0.08
D2	7	U	0.19	0.05
D3	7	U	0.18	0.05
T1			3.31	
Sum of Stages			3.98	
Sampler #9				
D1	7	N	0.46	0.10
D2	7	N	0.28	0.07
D3	7	N	0.39	0.10
T1			3.32	
Sum of Stages			4.45	
Sampler #10				
T1			4.13	
D1	7	U	-0.03	-0.01
D2	7	N	0.12	0.03
D3	7	N	0.05	0.01
Sum of Stages			4.27	
Sampler #8				
D1	8	U	1.00	0.15
D2	8	U	0.56	0.10
D3	8	U	0.41	0.08
T1			4.64	
Sum of Stages			6.61	
Sampler #9				
D1	8	N	0.96	0.14
D2	8	N	0.45	0.08
D3	8	N	0.53	0.10
T1			4.69	
Sum of Stages			6.63	
Sampler #10				
T1			6.15	
D1	8	U	0.05	0.01
D2	8	N	0.13	0.02
D3	8	N	0.22	0.03
Sum of Stages			6.49	

N = NaCl

U = Uncoated



N=NaCl coated denuder

U=Uncoated denuder substrate
T=Gelman 2 µm pore Zefluor Teflonfilter

Figure 5-20. Summary of Blank-corrected sulfate measurements (µg/m^3) for selected Claremont daytime (10 L/min) samples

5.1.5.2 Nitric Acid Measurements and Penetration

2 L/min sampling Flow Rate

Table 5-3 presents the mean results of the nitrate and sulfate analyses for the four one-week sample sets. Figure 5-21 summarizes the results of nitrate analyses for the 2 L/min testing of denuder penetration for Materials 5 and 5A by showing the means over four collection periods. Also shown is the denuder collection efficiency based on equation (2). Since little particulate retention was observed, these data were not corrected for gains of particulate nitrate. The denuder efficiency calculated for the first denuder is expected to be more accurate than that for the second since most of the nitric acid was removed passing through the first denuder. The collection efficiency for nitric acid was 90% for a single denuder whether the denuder was coated or not. This efficiency of the uncoated denuder was not expected since laboratory testing did not show efficient removal of nitric acid. It is possible that the denuders collected a basic material from the ambient air that aided in retention of nitric acid. Since the uncoated denuder efficiency was high whether the denuder preceded a Teflon filter or not, the basic would therefore need to be gaseous, possibly ammonia. The overall conclusion is that the denuders are 90% efficient in removing nitric acid and therefore two denuders are sufficient to quantify this species.

On Sampler #6, the denuders, which were preceded by a Teflon filter, retained more nitrate than the samplers that did not have a Teflon prefilter. This may be due to the volatilization of particulate nitrate from the front filter. The nitrate on the sample lines with the Teflon filter after the denuders showed less nitrate than the Teflon prefilter. This is expected since the volatilization will be enhanced after nitric acid is removed from the air stream. Basic material deposited on the Teflon prefilter may also contribute to nitric acid retention.

Sampler #7, which sampled from the CADMP plenum, had the highest denuder nitrate and the lowest particulate nitrate on the Teflon back filter. This may be due to increased volatilization of particulate nitrate caused by the solar heating of the large plenum. Temperature increases of several degrees Centigrade have been reported for air passing through a hi-vol size-selective inlet, a device which has a surface area similar to the CADMP plenum but with a flow rate approximately and order of magnitude higher (Sultana and Torrest, 1989).

Table 5-3. Summary of ammonia measurements for selected daytime 10 L/min samples

Sampler/ Sample#	Coating	NO3 µg/m3	SO4 µg/m3	SO4 Ratio to Remaining	Denuder HNO3 Collection Efficiency, %	Corrected Denuder HNO3 Collection Efficiency, %
Sampler #1						
D1-Mean	U	9.59	0.17	0.03	88	88
D2-Mean	U	1.16	0.11	0.02	48	80
D3-Mean	U	0.60	0.12	0.03		
T1-Mean		3.53	4.72			
Sum of Stages		14.88	5.13			
Nitric Acid (sum of denuders)		11.36				
Sampler #2						
D1-Mean	N	9.49	0.27			
D2-Mean	C					
D3-Mean	K					
T1-Mean		3.26	4.70			
Sum of Stages		12.75	4.97			
Sampler #3						
D1-Mean	N	10.21	0.33	0.06	89	90
D2-Mean	N	1.08	0.21	0.04	59	106
D3-Mean	N	0.44	0.17	0.03		
T1-Mean		3.45	4.79			
Sum of Stages		15.19	5.50			
Nitric Acid (sum of denuders)		11.74				
Sampler #6						
D1-Mean	U	12.81	0.02	0.00	89	90
D2-Mean	N	1.46	0.17	0.03	93	139
D3-Mean	N	0.10	0.16	0.03		
T1-Mean		7.50	5.29			
Sum of Stages		21.87	5.64			
Nitric Acid (sum of denuders)		14.37				
Sampler #7						
D1-Mean	N	13.46	0.33			
D2-Mean	C					
D3-Mean	K					
T1-Mean		0.37	3.13			
Sum of Stages		13.83	3.46			
Sampler #11						
D1-Mean	N	24.35	0.39			
D2-Mean	C					
D3-Mean	K					
T1-Mean		2.27	5.03			
Sum of Stages		26.62	5.43			

C=Citric acid coated denuder
K=KOH coated denuder
N=NaCl coated denuder
U=Uncoated denuder substrate

Figure 5-21. Mean nitrate concentrations (μg/m3) of four 7-day samples (2 L/min) for Materials 5 and 5A during the Claremont study (% denuder efficiency in parentheses)

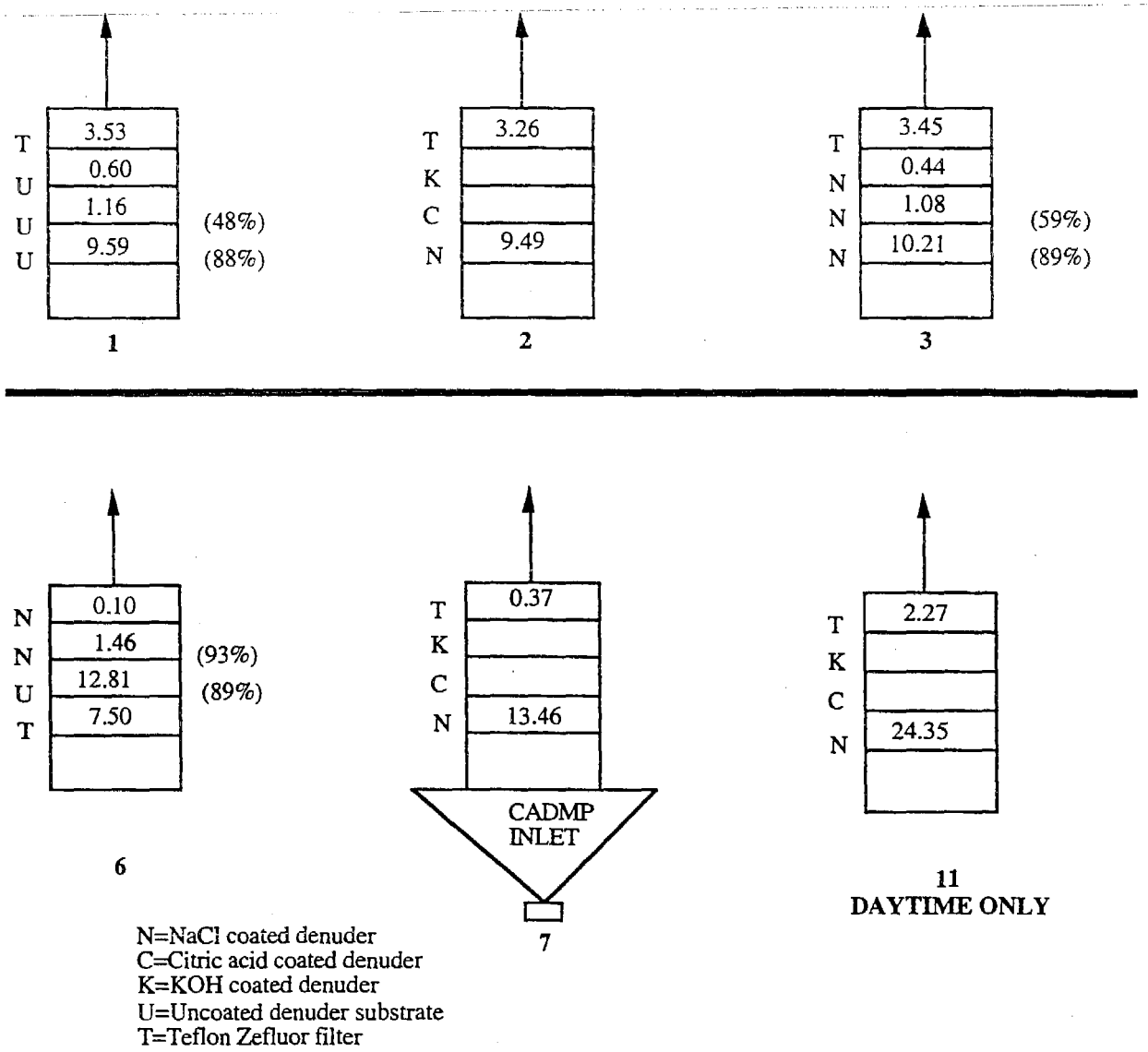
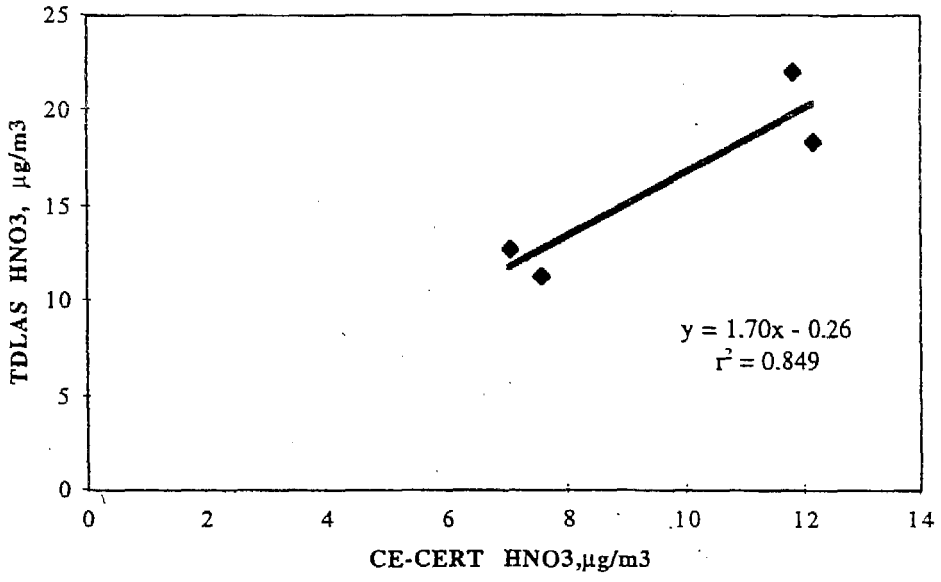


Figure 5-22 is a comparison of nitric acid measured by the one-week denuder sampling approach using the means from Samplers 2, 3, and 12 compared with that of the TDLAS. Some of the TDLAS data were missing for the weeklong sampling intervals. For short downtimes, less than several hours,, the TDLAS nitric acid data were interpolated in computing an average value for the period. This was not done for the two major downtimes (September 7 at 1900 hours to September 9 at 1345 hours and September 13 at 0100 hours to September 15 at 0100 hours). Thus the comparison for the second and third week period of sampling were missing 25% of the TDLAS data. The sum of nitrate from

the first two denuders (Materials 5 and 5A) were used since denuder efficiency is generally 80%-90%. The correlation is quite good, $r^2 = 0.85$, although the TDLAS values are approximately 33% higher on the average. This correlation coefficient should be considered qualitative since it is based on only four comparison points and some of the TDLAS data were missing.

Figure 5-22. Comparison of nitric acid measurements between 7-day, 2 L/min NaCl denuders (the mean from Samplers 2, 3, and 12) and TDLAS



10 L/min sampling Flow Rate

Table 5-4 and Figure 5-23 summarize the results of nitrate measurements for daytime samplers using four materials. Denuder efficiency is presented uncorrected and corrected for particle retention based on the sulfate penetration. The uncoated denuder again removed significant nitric acid but the efficiency varied from 13% to 86% (based on denuders in Sampler #10 with the Teflon prefilter, which eliminates the effects of particulate nitrate collection on the denuder). This may reflect day-to-day variation in the species responsible for enhancing the nitric acid collection efficiency of the uncoated denuder (for the weeklong sampling intervals at 2 L/min, the collection efficiency of the uncoated denuder was consistently 90%). The overall nitric acid removal efficiency for two NaCl-coated denuders sampling unfiltered air (calculated using equation (2) but combining the amounts collected by the first two denuders) were 94 ± 1% regardless of the denuder material. These

efficiencies may reflect the effect of particulate collection, an effect which cannot be quantified. From these results, we conclude that the first two NaCl coated denuders, regardless of material type, remove most of the nitric acid at the 10 L/min flow rate.

Table 5-4. Summary of nitric acid measurements for selected daytime (10 L/min) samples

Sample Number	Material	Coating	NO3 µg/m3 corr	SO4 µg/m3 corr	SO4 Ratio to remaining	Nitric Acid Denuder efficiency (5)	Corrected Nitric Acid Denuder efficiency
Sampler #8 (9/3&20/95)							
D1-Mean	1	U	23.80	0.46	0.11	75	76
D1-Mean	1	U	6.02	0.23	0.06	57	61
D3-Mean	1	U	2.56	0.22	0.06		
T1-Mean			1.72	3.11			
Sum of Stages			34.11	4.02			
Sampler #9 (9/3&20/95)							
D1-Mean	1	N	26.38	0.43	0.10	88	89
D1-Mean	1	N	3.25	0.19	0.05	49	58
D3-Mean	1	N	1.64	0.25	0.06		
T1-Mean			1.75	3.16			
Sum of Stages			33.02	4.03			
Sampler #10 (9/3&20/95)							
D1-Mean	1	U	27.46	-0.06	-0.02	74	73
D1-Mean	1	N	7.01	-0.07	-0.02	93	85
D3-Mean	1	N	0.49	-0.07	-0.02		
T1-Mean			8.85	4.57			
Sum of Stages			43.81	4.36			
Mean Efficiency						**73**	**74**
Sampler #8 (8/31/95)							
D1	5A	U					
D2	5A	U					
D3	5A	U	11.12	-0.06			
T1			2.99	1.60			
Sampler #9 (8/31/95)							
D1	5A	N	15.98	0.02	0.01	47	47
D2	5A	N	8.47	-0.01	-0.01	83	84
D3	5A	N	1.47	0.04	0.02		
T1			2.80	1.59			
Sum of Stages			28.71	1.64			
Sampler #10 (8/31/95)							
D1	5A	U	11.63	-0.06	-0.03	13	13
D2	5A	N	10.11	-0.04	-0.02	83	83
D3	5A	N	1.71	-0.02	-0.01		
T1			4.03	1.95			
Sum of Stages			27.46	1.82			
Mean Efficiency						**56**	**57**

N=NaCl coated denuder
C=Citric acid coated denuder
K=KOH coated denuder
U=Uncoated denuder substrate
T=Gelman 2µm pore Zefluor Teflon filter

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Table 5-4 continued

Sample Number	Material	Coating	NO3 mg/m3 corr	SO4 mg/m3 corr	SO4 Ratio to remaining	Nitric Acid Denuder efficiency (5)	Corrected Nitric Acid Denuder efficiency
Sampler #8 (9/11&12/95)							
D1-Mean	7	U	21.55	0.20	0.06	58	58
D1-Mean	7	U	9.08	0.12	0.04	54	55
D3-Mean	7	U	4.13	0.10	0.03		
T1-Mean			1.78	2.76			
Sum of Stages			36.56	3.18			
Sampler #9 (9/11&12/95)							
D1-Mean	7	N	25.66	0.27	0.07	79	79
D1-Mean	7	N	5.43	0.17	0.05	70	74
D3-Mean	7	N	1.61	0.19	0.05		
T1-Mean			1.25	2.79			
Sum of Stages			33.95	3.42			
Sampler #10 (9/11&12/95)							
D1-Mean	7	U	22.40	0.06	0.62	47	47
D1-Mean	7	N	11.97	0.08	-0.78	82	83
D3-Mean	7	N	2.17	0.05	-0.30		
T1-Mean			3.10	2.00			
Sum of Stages			39.65	2.20			
Mean Efficiency						**65**	**66**
Sampler #8 (9/15&16/95)							
D1-Mean	8	U	35.54	1.14	0.21	73	74
D1-Mean	8	U	9.61	0.65	0.16	61	63
D3-Mean	8	U	3.75	0.50	0.15		
T1-Mean			0.72	3.38			
Sum of Stages			49.62	5.67			
Sampler #9 (9/15&16/95)							
D1-Mean	8	N	34.48	1.26	0.14	86	87
D1-Mean	8	N	4.86	0.64	0.08	52	56
D3-Mean	8	N	2.32	0.53	0.08		
T1-Mean			0.74	6.34			
Sum of Stages			42.39	8.76			
Sampler #10 (9/15&16/95)							
D1-Mean	8	U	35.56	-0.02	0.00	82	86
D1-Mean	8	N	6.28	0.11	0.02	98	126
D3-Mean	8	N	0.14	0.12	0.02		
T1-Mean			11.77	6.16			
Sum of Stages			53.74	6.37			
Mean Efficiency						**75**	**82**

N=NaCl coated denuder
C=Citric acid coated denuder
K=KOH coated denuder
U=Uncoated denuder substrate
T=Gelman 2µm pore Zefluor Teflon filter

Figure 5-23. Summary of 10 L/min nitrate data for Claremont, mg/m^3 (corrected denuder efficiencies shown in parentheses)

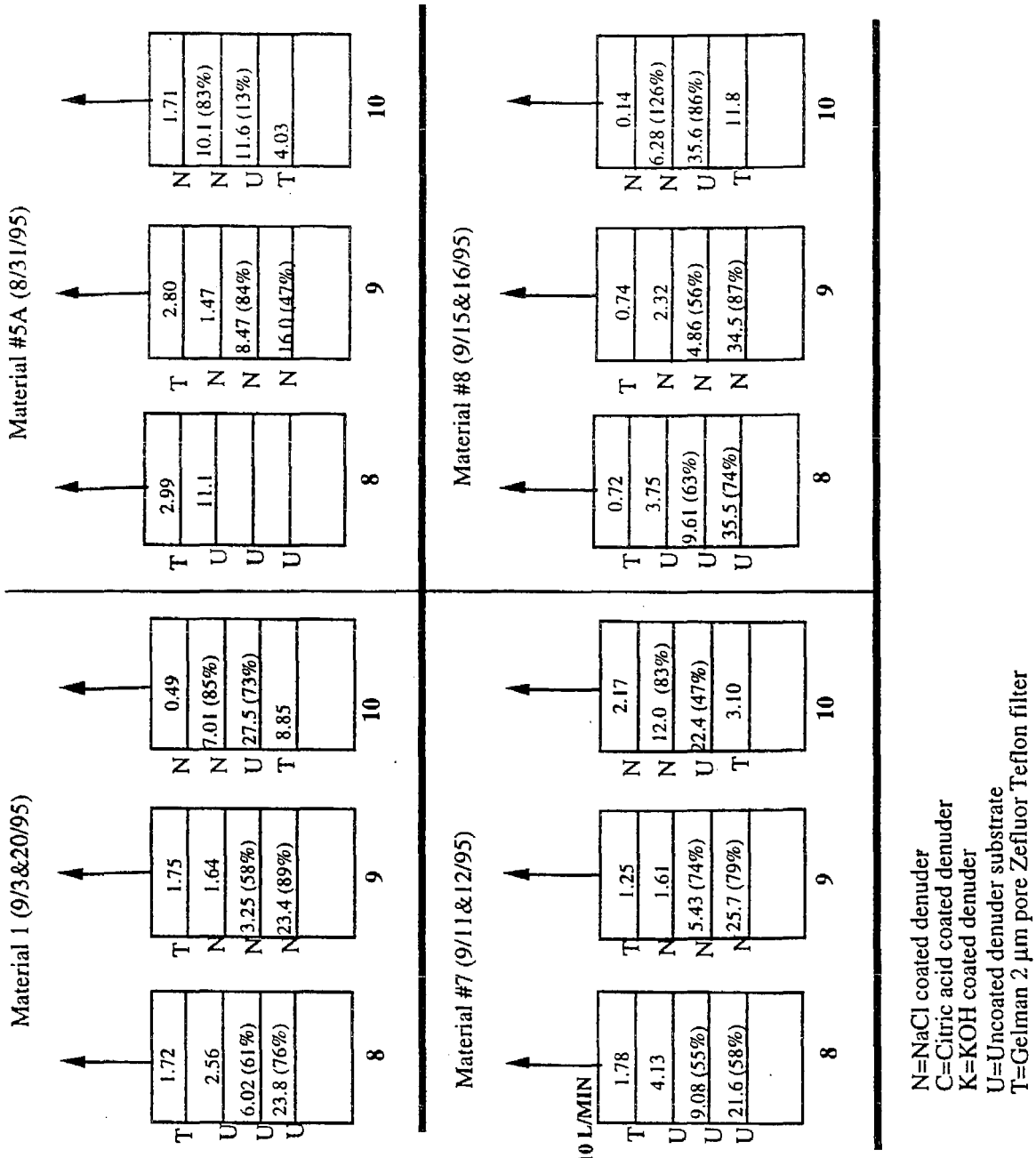


Figure 5-24 compares the nitric acid measured with the CE-CERT 10 L/min denuders with those of the TDLAS. The regression is forced through the origin since nighttime nitric acid concentrations are expected to be near zero, although we did not analyze nighttime denuder samples. As with the SCAQMD sampler, there is a considerable amount of scatter (r^2 of 0.24). The mean of these nitric acid measurements was 30.5 $\mu g/m^3$ for the denuder methods compared with 43.6 $\mu g/m^3$ for the TDLAS. The denuder measurements were therefore an average of 30% lower than the TDLAS. This is consistent with the larger data set of denuder difference measurements using the SCAQMD sampler.

Figure 5-24. Nitric acid by TDLAS compared with the CE-CERT daily denuder sampler (#9)

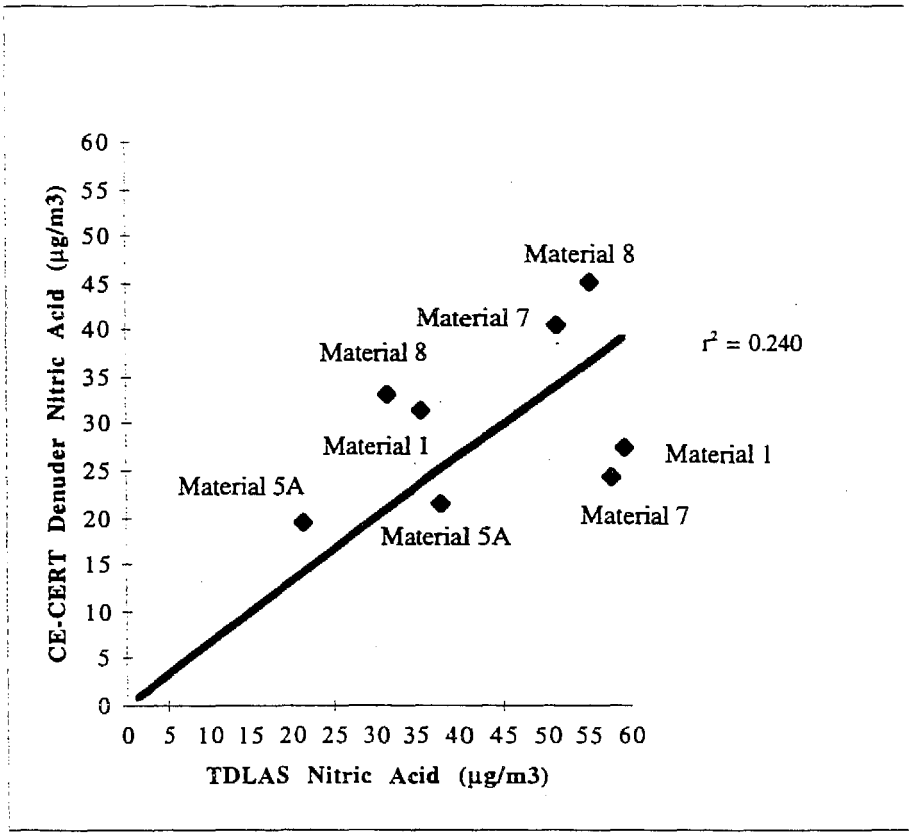


Figure 5-25 compares the nitric acid measured with the CE-CERT 10 L/min denuders with those of the FTIR. The linear regression line again is forced through zero. The plot appears linear with one of the better correlation coefficients we have observed (r^2= 0.73). While the slope of 1.15 indicated the FTIR values were lower, the means indicated that they were higher (35.5 compared to 32.0 $\mu g/m^3$). This is the result of a substantial intercept (-8.6 $\mu g/m^3$). The application of the Wilcoxan two tailed ranked sum test (Mendenhall, 1971) showed that the data sets were equivalent at the 95% confidence level ($R_- = 3$, $R_+ = 18$ and $R_C = 2$). We conclude that the nitric acid measurements obtained with any of the denuder materials is in good agreement with the FTIR reference method.

Figure 5-25. Nitric acid measured by FTIR compared with that measured by the CE-CERT daily denuder sampler

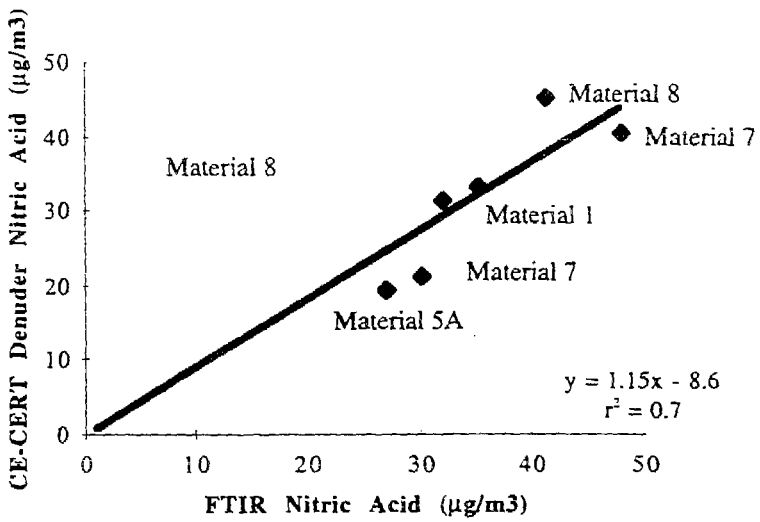


Figure 5-26 is a comparison of the TDLAS and FTIR nitric acid measurements for the same periods for which CE-CERT denuder data were available. The linear regression line is again forced through zero. The correlation coefficient, $r^2 = 0.69$, shows significant correlation, although the intercept was again substantial (-10.0 $\mu g/m^3$). For these periods, the FTIR values were lower than the TDLAS based on both the mean (35.5, compared with 38.7 $\mu g/m^3$) and slope of the regression line (1.37). Application of the Wilcoxan test showed that the two data sets were equivalent at the 95% confidence level ($R_- = 14.5$, $R_+ = 6.5$ and $R_C = 2$).

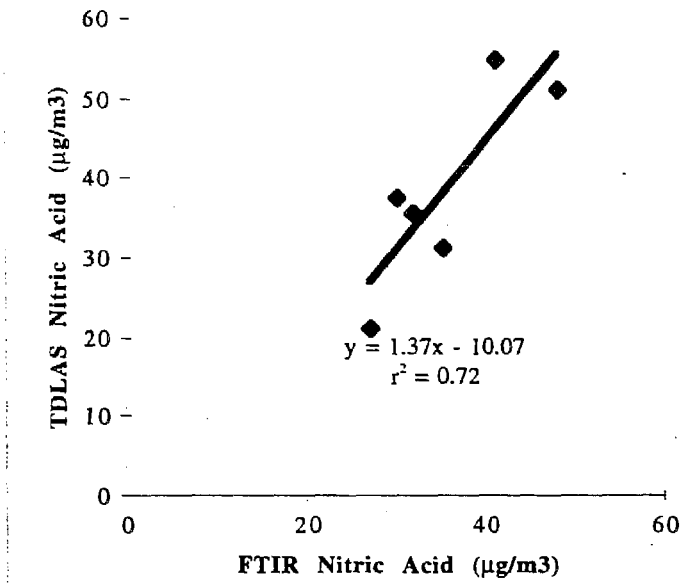
5.1.5.3 Ammonia Measurements and Penetration

2 L/min Flow Rate

Table 5-5 presents the means of the ammonium measurements for the four one-week periods for which ammonia was sampled. Figure 5-27 summarizes these results on a filter sampling schematic drawing. Denuder Material 5 or 5A was used for all of these collection periods. As with the nitric acid, ammonia was retained with high efficiency on the uncoated denuder. Again, this is not in agreement with the laboratory testing. While the first denuder in sample line 1 appeared to collect over 80% of the ammonia, comparison with the citric acid coated denuders in sampling line 4 shows that this denuder was only 50% effective. A possible explanation of this result is that the first uncoated denuder effectively retaining nitric or some other gas phase acid and thus not "activating"

the following two uncoated denuders. The citric acid denuder in sample line 2 (the prototype sample) collected only 60% of the ammonia retained by the first denuder in sample line 4. This indicated that the sodium chloride-coated denuder in sample line 2 also retained a significant amount of ammonia (this denuder was not analyzed for ammonia since we did not expect to find it). These results are also not in agreement with the laboratory testing, in which NaCl coated denuders did not retain ammonia.

Figure 5-26. Nitric acid by FTIR compared with TDLAS



Sample line 2 and 7 used the identical "prototype sampler" denuder configuration except that 7 was placed inside the $PM_{2.5}$ sampling plenum of the CADMP sampler. The ammonia (determined by the citric acid coated denuder) in line 7 was significantly higher than that of line 2 while the ammonium was lower. This suggests volatilization of ammonium nitrate within the CADMP, a result consistent with the nitrate measurements.

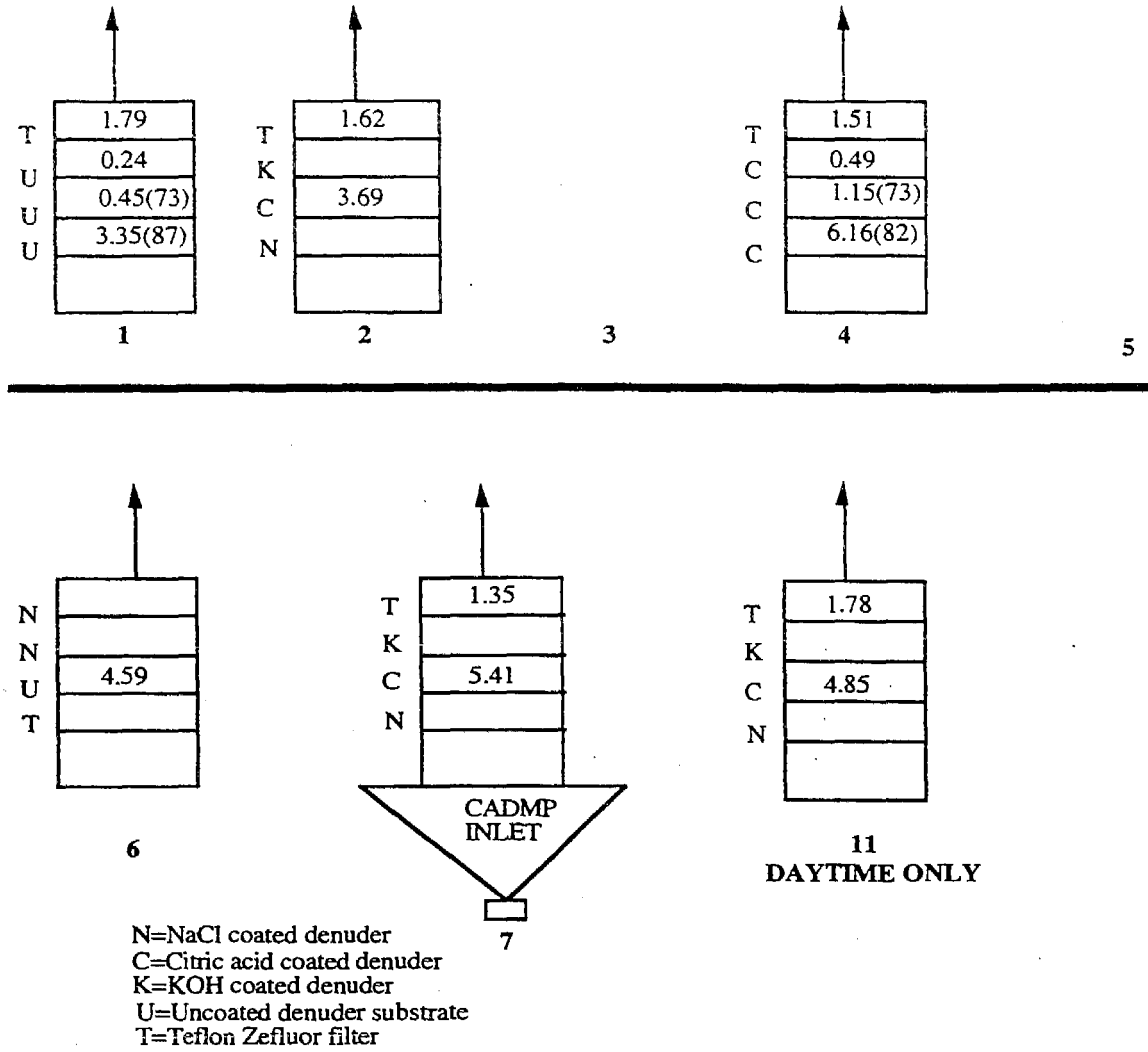
The citric acid coated denuders were each approximately 80% effective in retaining ammonia. Thus, two denuders are sufficient for measurement (overall mean calculated efficiency of 93%). Since the sodium chloride-coated denuder also retained ammonia, either this denuder should be analyzed for ammonia, or separate sampling lines should be used for ammonia and nitric acid.

Table 5-5. Summary of ammonia measurements for one-week (2 L/min) CE-CERT denuders

Sampler/ Sample# Sampler #1	Coating	SO4 µg/m3	NH4 µg/m3	SO4 Ratio to Remaining	Denuder NH3 Collection Efficiency, %	Corrected Denuder NH3 Collection Efficiency, %
D1-Mean	U	0.17	3.35	0.03	87	87
D2-Mean	U	0.11	0.45	0.02	47	73
D3-Mean	U	0.12	0.24	0.03		
T1-Mean		4.72	1.79			
Sum of Stages		5.13	5.83			
Sampler #2						
D1-Mean	N	0.27				
D2-Mean	C		3.69			
D3-Mean	K					
T1-Mean		4.70	1.62			
Sum of Stages		4.97	5.31			
Sampler #4						
D1-Mean	C		6.16		81	82
D2-Mean	C		1.15		57	73
D3-Mean	C		0.49			
T-1 Mean			1.51			
Sum of Stages		0.00	9.30			
Sampler #6						
T1-Mean		5.64				
D1-Mean	U	0.02	4.59			
D2-Mean	N	0.17				
D3-Mean	N	0.16				
Sum of Stages		5.64	4.59			
Sampler #7						
D1-Mean	N	0.33				
D2-Mean	C		5.41			
D3-Mean	K					
T1-Mean		3.13	1.35			
Sum of Stages		3.46	6.75			
Sampler #11						
D1-Mean	N	0.39				
D2-Mean	C		4.85			
D3-Mean	K					
T1-Mean		5.03	1.78			
Sum of Stages		5.43	6.62			

N=NaCl coated
U=Uncoated
C=Citric acid coated
K=KOH coated

Figure 5-27. Summary of 2 L/min ammonium data for Claremont, μg/m^3 (corrected denuder efficiencies shown in parentheses)



10 L/min Flow Rate

Table 5-6 presents the limited data available for ammonium from the 10 L/min flow rate denuder evaluation samplers. The data are limited because these samplers, with the exception of the last four days of sampling, did not contain citric acid-coated denuders as they were used to evaluate nitric acid collection on sodium chloride-coated denuders. Since the 2 L/min samples unexpectedly retained ammonia on the uncoated denuders, extracts from selected days (September 12, 16, and 20) the similarly uncoated denuders operated daily at 10 L/min were subsequently analyzed as shown in the table. During the last four days of sampling, the cassettes in samplers 8, 9, and 10 were loaded with

identical substrates for triplicate sampling. A different denuder material (1, 5A, 7, or 8) was used for each day. These cassettes consisted of a denuder coated with sodium chloride, followed by one coated with citric acid, and then one coated with potassium hydroxide. The first two denuders were analyzed for ammonium on samples collected on September 22 using Material 5A.

Table 5-6. Summary of ammonia measurements for selected daytime samples

Sample Number		Material	Coating	NH4 mg/m3 corr	Ammonia Denuder Efficiency	Comments
D18RT45-	920	1	U	5.62	90	
D28RT45-	920	1	U	0.57	77	
D38RT45-	920	1	U	0.13		
D110RT45-	920	1	U	9.00		Teflon prefilter
D18RT45-	922	5A	N	3.81		
D28RT45-	922	5A	C	3.01		
D19RT45-	922	5A	N	3.55		
D29RT45-	922	5A	C	2.99		
D110RT45-	922	5A	N	2.93		No prefilter
D210RT45-	922	5A	C	-0.60		No prefilter
D18RT45-	912	7	U	1.86	92	
D28RT45-	912	7	U	0.15	224	
D38RT45-	912	7	U	-0.19		
D110RT45-	912	7	U	2.12		Teflon prefilter
D18RT45-	916	8	U	4.37	82	
D28RT45-	916	8	U	0.77	67	
D38RT45-	916	8	U	0.26		
D110RT45-	916	8	U	5.90		Teflon prefilter

U = Uncoated
N - NaCl coated
C = Citric acid coated

As shown in the Table, the uncoated denuders (Materials 1, 7, and 8) effectively retained ammonia at 10 L/min, since the majority was found on the first of the three denuders in series. Since collocated citric acid coated denuders were not used for sampling, we cannot calculate the overall sampling efficiency for ammonia. The collection efficiencies of the first denuder in series ranged from 82-90% calculated using Method 1.

The triplicate sample from the coated denuders showed that the sodium chloride denuder passed about half the ammonia, in agreement with the 2 L/min ambient tests, but not with the laboratory results. Efficiencies could not be calculated since the denuders were coated differently. The lack of ammonium on one of the triplicate citric acid-coated denuders could not be explained and is possibly

the result of laboratory mislabeling. Excluding this data point, and using the mean ammonium collection from the NaCl and citric acid coated denuders results in a concentration of 6.66 μg/m3. This compares with 4.87 μg/m3 measured with the FTIR..

5.1.5.4 Formic Acid Measurements

Due to the limitations of the FTIR operation, only denuder samples collected daily could be used to compare formic acid concentrations with the FTIR. Appropriately coated denuder substrates for formic acid collection were used for only the last four days of the study when the "sampler" configuration (NaCl, citric acid, KOH coated denuders in series) was operated. Of these four days, FTIR data were available for only September 22 and 24. Each of the triplicate KOH denuders collected on September 24 was analyzed for formate by ion chromatography, yielding an average concentration of 13.4 ± 1.5 μg/m3. This compares with the integrated FTIR measurement of 7.8 μg/m3 for the same period. Formate acid was below the detection limit of 1 $\mu g/m^3$ for the preceding NaCl and citric acid coated denuders, indicating that formic acid was not removed by them.

5.2 1995 Integrated Monitoring Study

Three episodes were selected by IMS95 management for detailed chemical analysis of substrates collected. These were as follows:

- December 9 at 0000 hours to December 10 at 2400 hours
- December 25 at 1200 hours to December 28 at 1200 hours
- January 4 at 0000 hours to January 6 at 2400 hours.

Since the CE-CERT sampling was conducted on a 24-hour basis starting at midnight, seven days were suitable for comparison with other measurement methods (December 8, 9, 26, 27 and January 4-6). Sample substrates were lost in shipping, preventing sample collection on January 4. Based on the results of the Claremont study, the samples collected with the CE-CERT Fine Particulate Sampler denuder substrates were not analyzed, since the study conducted in Claremont suggested significant volatilization artifacts from the CADMP cyclone and plenum though which samples were collected. Appendix I is a complete data set of all analyses conducted for the six days.

5.2.1 Acids Sampler

Table 5-7 shows the results of anion analysis for the study days. All of the samples have been corrected for the blank values shown at the bottom of the table; these are typical values for filters.

Table 5-7. Blank-corrected anion measurements from samples collected during IMS95 with CE-CERT acids sampler.

Date(95)	Sample ID	Coating	Nitrite µg/m3 corr	Nitrate µg/m3 corr	Sulfate ug/m3 corr	SO4 Ratio to Remaining	Denuder Efficiency HONO	Denuder Efficiency HNO_3	Estimated Particulate Nitrate, µg/m3*
9-Dec	AA1D1	U	0.10	0.70	0.25	0.06		40	1.03
9-Dec	AA1D2	N	0.02	0.42	0.08	0.02		6	0.34
9-Dec	AA1D3	Co	4.62	0.40	0.23	0.06	80	15	0.94
9-Dec	AA1D4	Co	0.94	0.34	0.16	0.05			0.70
9-Dec	AA1Q5	N	0.01	14.31	3.26				
9-Dec	DA1D1**	U	0.31	0.62	0.23	0.06		7	0.97
9-Dec	DA1D2**	N	0.02	0.58	0.16	0.04		-3	0.66
9-Dec	DA1D3**	Co	5.20	0.60	0.25	0.07	79	35	1.08
9-Dec	DA1D4**	Co	1.09	0.39	0.19	0.05			0.84
9-Dec	DA1Q5**	N	0.00	15.25	3.37				
10-Dec	AA2D1	U	0.11	0.98	0.53	0.10		10	2.65
10-Dec	AA2D2	N	0.02	0.88	0.30	0.06		9	1.62
10-Dec	AA2D3	Co	7.57	0.80	0.29	0.06	83	23	1.61
10-Dec	AA2D4	Co	1.30	0.61	0.26	0.06			1.48
10-Dec	AA2Q5	N	0.00	23.96	4.07				
26-Dec	AA16D1	U	0.11	0.68	0.36	0.12		51	1.54
26-Dec	AA16D2	N	0.00	0.33	0.25	0.09		1	1.15
26-Dec	AA16D3	Co	4.30	0.33	0.44	0.18	84	3	2.18
26-Dec	AA16D4	Co	0.68	0.32	0.16	0.08			0.96
26-Dec	AA16Q5	N	0.00	11.74	1.91				
27-Dec	AA17D1	U	0.11	0.60	0.71	0.15		20	3.31
27-Dec	AA17D2	N	0.01	0.48	0.47	0.11		22	2.49
27-Dec	AA17D3	Co	6.48	0.38	0.60	0.17	86	-12	3.53
27-Dec	AA17D4	Co	0.89	0.42	0.17	0.06			1.20
27-Dec	AA17Q5	N	0.01	20.46	2.83				

U=Uncoated denuder
N=NaCl coating
Co=Na_2CO_3 coating

* Collected by denuder
** Collocated

Continued next page

Table 5-7, continued

Date(96)	Sample ID	Coating	Nitrite ug/m3 corr	Nitrate ug/m3 corr	Sulfate ug/m3 corr	SO4 Ratio to Remaining	HONO Denuder Efficiency	HNO3 Denuder Efficiency	Estimated Particulate Nitrate, µg/m3*
5-Jan	AA26D1	U	0.07	0.77	0.47	0.11		62	2.00
5-Jan	AA26D2	N	0.01	0.29	0.25	0.06		-7	1.13
5-Jan	AA26D3	Co	5.95	0.31	0.17	0.05	82	-10	0.79
5-Jan	AA26D4	Co	1.06	0.34	0.13	0.04			0.65
5-Jan	AA26Q5	N	0.00	16.66	3.33				
6-Jan	AA27D1	U	0.08	0.78	0.38	0.09		45	2.46
6-Jan	AA27D2	N	0.03	0.42	0.27	0.07		-5	1.85
6-Jan	AA27D3	Co	6.86	0.45	0.29	0.08	81	0	2.07
6-Jan	AA27D4	Co	1.31	0.44	0.13	0.04			0.97
6-Jan	AA27Q5	N	0.00	25.53	3.24				
Average Denuder Values				0.52	0.29	0.08	82		1.51
BLANK CORRECTION			µg	µg	µg				
	AA11D1	U	-0.22	-0.38	0.51				
	AA11D2	N	-0.20	-0.34	0.52				
	AA11D3	Co	1.35	0.33	-0.09				
	AA11D4	Co	1.33	-0.37	-0.26				
	AA11Q5	N	-0.18	0.70	1.26				

U=Uncoated denuder
N=NaCl coating
Co=Na_2CO_3 coating
* Collected by denuder

*Collected by denuder
** Collocated

Since six cubic meters was the nominal sample volume, these values can be divided by six to obtain the nominal blank correction in terms of $\mu g/m^3$. At low concentrations the uncertainty was estimated as half the value of the blank; at higher concentrations, the uncertainty is estimated to be half the blank value plus 7% based on flow and analytical precision. Collocated samples were obtained on December 9; all pairs were within the estimated uncertainty of the measurements.

The particle penetration through the denuders was similar to that observed during the Claremont Study, averaging 92% based on the amount of sulfate collected. This is expected to be an upper limit as some of the sulfate on the denuders was likely to be due to adsorption of gaseous sulfurous species as previously observed. Nitric acid concentrations were low, as expected for this time of year, with none of the denuders collecting more than 1.0 $\mu g/m^3$. Analysis uncertainty is estimated to be 0.1 $\mu g/m^3$. It is likely that a portion of this nitrate was due to collection of particulate nitrate by the denuder. Multiplying the fraction of sulfate collected by the denuders times the sum of available particulate nitrate, the column on the far right estimates the amount of particulate nitrate that the denuders could be expected to collect. These values are three time higher, on the average, than the actual nitrate collected on the denuders. This is further evidence that the sulfate ratio represents an upper limit of particle collection by the denuder. The only clear-cut trend in nitric acid denuder collection efficiency is that the first (uncoated) denuder collects more nitrate than the following ones. We conclude that under these conditions, the nitric acid concentrations are low, but cannot be quantified due to nitrate being close to the experimental uncertainty and being a combination of both nitric acid and particulate nitrate.

Nitrous acid concentrations were significant on the carbonate coated denuders, ranging from 4.30 to 7.57 $\mu g/m^3$. This is in reasonable agreement of measurements made spectroscopically over a decade ago in the Los Angeles area (Harris et al., 1982). Adsorption by the preceding uncoated and NaCl coated denuders was within the estimated analytical detection limit of 0.1 $\mu g/m^3$. The denuder efficiency was constant at 82 $\pm$ 2%. This indicates that two denuders are sufficient to collect more than 90% of the nitrous acid.

Figures 5-28 and 5-29 compare the particulate sulfate and nitrate, respectively, measured by the Acids Sampler (on the NaCl coated quartz filter) and that reported by DRI using a sampler similar to the CADMP. The DRI sampler collected for eight 3-hour periods, which required averaging the data over the 24 hours sampled by the acids sampler. The sulfate data are too tightly grouped together to provide a meaningful comparison; the concentrations are sufficiently low that the uncertainty, especially for the averaged DRI measurements, may be significant compared with the measurement. The CE-CERT mean was somewhat higher than that reported by DRI (3.12 compared with 2.66 $\mu g/m^3$). The nitrate measurements were somewhat higher and are well correlated (r^2 = 0.934), although the CE-CERT measurements are biased higher. These data indicate that little particulate

nitrate or sulfate was collected by the CE-CERT denuders above the quartz filter. The positive biases may be due to particulate removed by the $PM_{2.5}$ cyclone of the DRI sampler (the Acids Sampler did not have a size-selective inlet). Only a single day of data was available from the CADMP sampler operated by the ARB. These values, on December 27, were 19.5 $\mu g/m^3$ for nitrate and 2.30 $\mu g/m^3$ for sulfate These compared reasonably well with both the Acids Sampler (20.5 $\mu g/m^3$ nitrate, 2.83 $\mu g/m^3$ sulfate) and the DRI sampler (17.5 $\mu g/m^3$ nitrate and 2.79 $\mu g/m^3$ sulfate).

Figure 5-28. Comparision of CE-CERT and DRI sulfate measurements

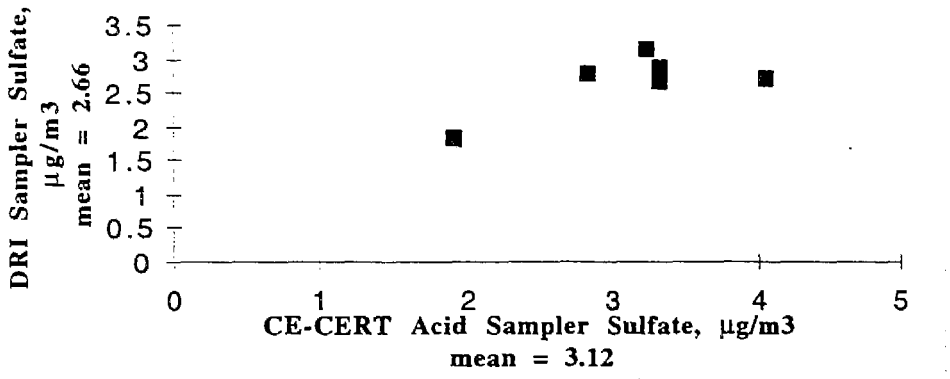
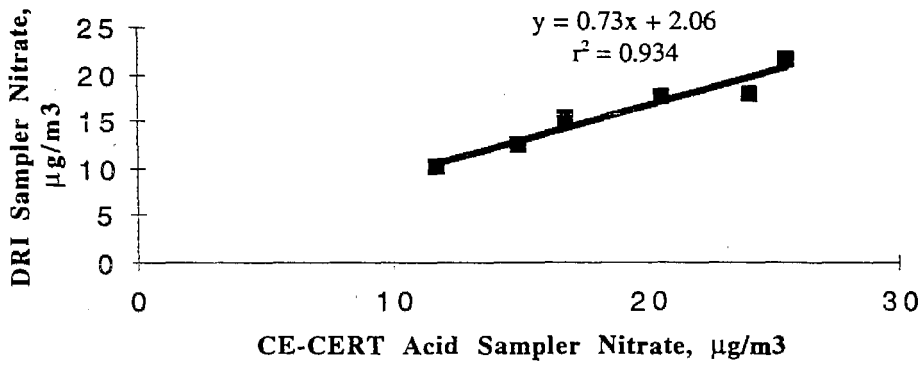


Figure 5-29. Comparison of CE-CERT and DRI nitrate measurements



5.2.2 Bases (ammonium, ammonia) Sampler

Table 5-8 shows the results of ammonium analysis for the study days for the CE-CERT sampling in addition to those from CADMP operated by the ARB, the DRI sampler, and a Thermoenvironmental

continuous NH_3 analyzer. All of the CE-CERT samples have been corrected for the blank values shown at the bottom of the table. While the blank value of the uncoated denuder is typical of previous work, the values for the citric acid coated denuders is a factor of three higher than those observed during the Claremont study. Since six cubic meters was the nominal sample volume, these values can be divided by six to obtain the nominal blank correction in terms of $\mu g/m^3$. Half the blank values are a good measure of the uncertainty at low concentrations; while at higher concentrations, the uncertainty is estimated to be this blank value plus 7% based on flow and analytical precision. Collocated samples were obtained on December 10; both pairs were within the estimated uncertainty of the measurements.

In contrast to results obtained from the Claremont study, little ammonia was collected by the uncoated denuder, the values ranging from 0.27-0.64 $\mu g/m^3$. Some portion of this may be due to ammonium collected by the denuder. This result is further evidence that nitric acid deposition on the denuders in the previous field studies activated the uncoated denuder. For all sample days the concentration of ammonia was higher than ammonium assuming that most of the ammonia is removed by the single citric acid coated denuder.

As shown in Table 5-8, only a limited amount of data are available from other collocated samplers for comparison. For ammonia the concentrations measured by DRI for the two days where data are available show the DRI values approximately 30% lower than the CE-CERT denuder. For ammonium, the two data set agree within the expected uncertainty of ±15%. The single ammonium measurement obtained by the CADMP sampler for this comparison was nearly 60% lower than the CE-CERT measurement. The CADMP ammonium is expected to be a lower limit since it is collected on a Teflon filter and is therefore subject to a volatilization artifact. This artifact will be enhanced if ammonia is removed by the sampler's inlet system. The ammonia measured by the continuous analyzer was apparently not validated since a large number of negative values were reported.

Table 5-8. Ammonium measurement from samples collected during IMS95 with CE-CERT bases sampler ($\mu g/m^3$)

Date	Substrate	Coating	CE-CERT* NH_4^+ blank-corrected	CADMP** NH_4^+	Thermo Environmental NH_3	DRI‡ NH_4^+	DRI‡ NH_3	Comments
9-Dec 95	Denuder 1	U	0.27					
9-Dec 95	Denuder 2	C	12.50		ND		8.28	NH_3
9-Dec 95	Quartz	C	7.68	I			6.62	NH_4^+
9-Dec 95	Denuder 1C	U	0.31					Collocated
10-Dec 95	Denuder 1	U	0.64					
10-Dec 95	Denuder 2	C	18.14		ND		11.60	NH_3
10-Dec 95	Quartz	C	10.02	ND		9.58		NH_4^+
10-Dec 95	Denuder 2C	C	16.15					Collocated NH_3
10-Dec 95	Quartz C	C	12.11					Collocated NH_4^+
26-Dec 95	Denuder 1	U	0.54					
26-Dec 95	Denuder 2	C	17.94		IC		IC	NH_3
26-Dec 95	Quartz	C	6.81	ND		IC		NH_4^+
27-Dec 95	Denuder 1	U	0.51					
27-Dec 95	Denuder 1	U	0.58					Collocated
27-Dec 95	Denuder 2	C	16.17		IC		IC	NH_3
27-Dec 95	Quartz	C	13.09	5.55		IC		NH_4^+
5-Jan 96	Denuder 1	U	0.35					
5-Jan 96	Denuder 2	C	15.35		6		IC	NH_3
5-Jan 96	BB26Q3	C	7.93	ND		IC		NH_4^+
6-Jan 96	Denuder 1	U	0.52					
6-Jan 96	Denuder 2	C	12.68		7		IC	NH_3
6-Jan 96	Quartz	C	10.13					NH_4^+
	Blank Correction							
	Sample		µg					
	Denuder 1	U	2.02					
	Denuder 2	C	6.37					
	Quartz	C	9.28					

U=Uncoated
C=Citric Acid Coated
I=Invalid Data
IC=Incomplete Data
ND = No Data

* No size cut
** 2.5 µm size cut
‡ 2.5 µm size cut, composite of 8 3-hr. collections

5.2.3 Fine Particulate Sampler

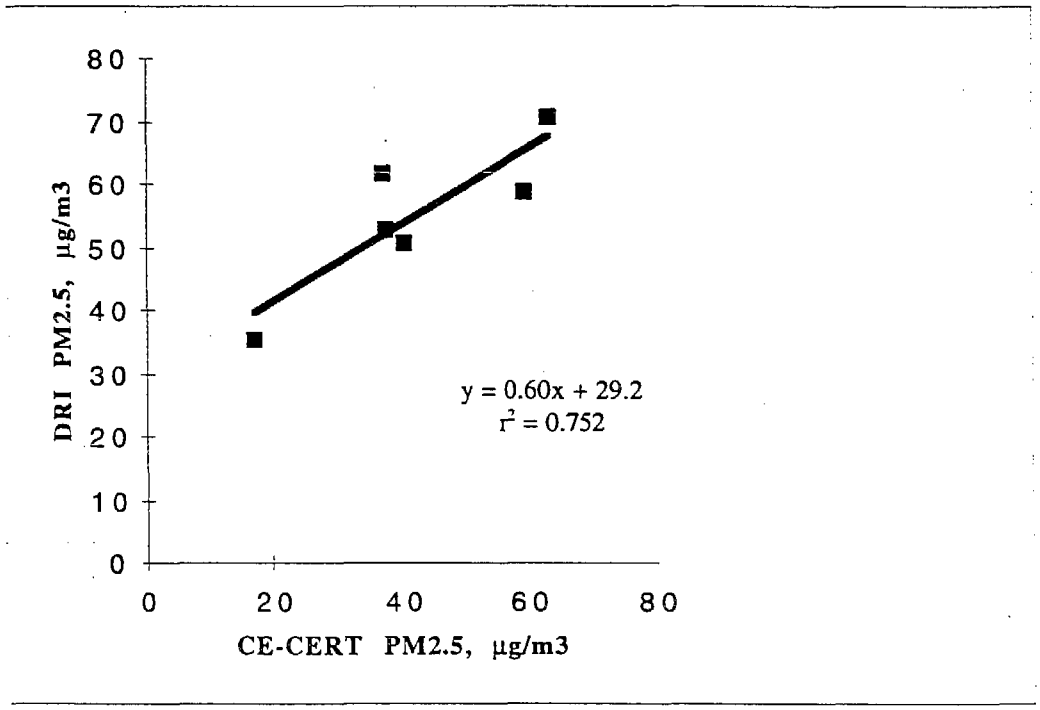
Table 5-9 shows the $PM_{2.5}$ mass concentrations sampling from a CADMP sampler in addition to that report by DRI and the ARB-operated samplers. Figure 5-30 is a plot comparing the results from the DRI and CE-CERT $PM_{2.5}$ concentrations. The data sets appear to be linearly related despite the data points being clumped about 50 $\mu g/m^3$ and the need to composite 8 DRI sampling intervals to compare with single 24-hour CE-CERT sampling periods, (which will lead to a higher uncertainty in the measurement, especially at lower concentrations). The significance of the rather large intercept (nearly half the mean concentration) is not known. The mean concentrations (42.5 vs 55.0 $\mu g/m^3$) indicate that the CE-CERT data is biased high relative to DRI's.

Table 5-9. $PM_{2.5}$ mass concentrations sampling from the CADMP plenum

Sample ID	Date	Mass Concentration ($\mu g/m^3$)	DRI Mass Concentration ($\mu g/m^3$)	ARB-operated CADMP ($\mu g/m^3$)
CC1T3	9-Dec-95	40.5	50.8	ND
CC2T3	10-Dec-95	37.2	61.6	ND
CC16T3	26-Dec-95	16.8	35.5	ND
CC17T3	27-Dec-95	59.8	58.8	79.5
CC26T3	5-Jan-96	37.9	52.7	ND
CC27T3	6-Jan-96	63.3	70.5	ND

* Composite of eight 3-hour collections
ND=No Data

Figure 5-30. Comparison of CE-CERT and DRI $PM_{2.5}$ measurements



6.0 SAMPLER DESIGN RECOMMENDATION

For sampling ammonium, nitrate and gaseous acids and bases, we propose two denuder cassettes. The cassette recommended is the open-face Savillex 47mm Multiple Stage Filter Holder with spacers used between each substrate. We have found that wrapping the threads of the Savillex "nut" with Teflon tape can result in a leak-tight seal when up to four spacers are used. O-rings, which have been successfully used by some research groups to seal each substrate, resulted in greater leakage than the Teflon tape approach. We recommend Material 5 for all denuders.

The first cassette consists of two NaCl coated denuders (9% coated as described in Appendix A) to remove nitric acid followed by two carbonate coated denuders (2% coated as described in Appendix A) to remove nitrous and the bulk of carboxylic acids. These denuders will be followed by a sodium chloride-coated quartz filter (2% coated as described in Appendix A) to quantitatively collect particulate nitrate. The second cassette consists of two phosphoric acid coated denuders (9% coated as described in Appendix A) to remove ammonia, followed by either a citric or phosphoric acid coated quartz filter (2% coated as described in Appendix A) to quantitatively collect particulate ammonium.

A separate sampling line is recommended for the collection of non-volatile particulate species. These should sample using a sampler that is equivalent to the EPA reference method for either $PM_{2.5}$ or PM_{10}. These are commercially available. They are microprocessor-controlled and use either mass flow or active volumetric flow control.

The simplicity of the CE-CERT fabric denuder allows the easy adaptation of commercially available low-volume filter sampling instruments rather than customized samplers. These instruments have a variety of timer and flow control mechanisms to choose from depending on the budget and the accuracy and precision requirements in addition to the need for remote control and monitoring of performance. The two models mentioned above would meet most air sampling needs.

The denuder Material 5 or 5A is described as follows:

White Rose Fabric

44-45" Imported Permanent Finish Organdy, RN17948

Heberlein Finish, 100% cotton

It may be purchased from:

A.E. Nathan Co. Inc.

11 E. 36th Street

New York, NY 10016