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Further Evaluation of A Two-Week Sampler for Acidic Gases and Fine Particles

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY
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FURTHER EVALUATION OF A TWO-WEEK SAMPLER FOR ACIDIC GASES AND FINE PARTICLES

Final Report

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ABSTRACT

Reported here is a further evaluation of a Two-Week Sampler used to measure concentrations of acidic gases and fine particulate inorganic ions for the ARB-sponsored Epidemiologic Investigation to Identify Chronic Health Effects of Ambient Air Pollutants in Southern California. The Main Leg of the Two Week Sampler consists of a sodium carbonate-coated honeycomb denuder to remove nitric acid followed by a Teflon particulate filter and then a sodium carbonate-coated quartz filter to trap volatilized particulate nitrate. The Organic Acids Leg of the sampler has a Teflon prefilter to remove particulate material followed by two potassium hydroxide (KOH) -coated quartz filters to trap organic acids.

Two-week collections using components of the Main Leg of the sampler in conjunction with filtered ambient air were made in Riverside in the fall of 1994, and Claremont in the summer of 1995, to evaluate the penetration of nitric acid. For both studies, the nitrate on the carbonate-coated denuders agreed quite well with the front nylon reference filter, although during the Riverside collection a positive artifact was indicated on the nylon reference filter. For the Riverside sampling, the carbonate-coated denuders were the only substrates that contained significant nitrite. While sodium chloride-coated substrates showed little artifact collection, the sodium chloride-coated denuder did not appear to remove nitric acid effectively. In all cases, carbonate-coated back filters collected much more nitrate than could be due to nitric acid, indicating an interference; this will cause particulate nitrate to be over-estimated. The denuder was also shown to remove nitric acid effectively at six times its design flow rate.

The Main Leg of the sampler was also evaluated for interferences from peroxyacetyl nitrate (PAN) and nitrous acid generated in the laboratory. An average of sixteen percent of the PAN was trapped by the denuder of the Main Leg and three percent by the back filters. With nitrous acid, the carbonate-coated denuder removed from 50-100 percent of this species as nitrite, and the rest was removed by the back filters. With ozone present, essentially all of the nitrite was converted to nitrate. Sodium chloride-coated denuders and back filters showed no affinity for removing either PAN or nitrous acid.

The Organic Acids Leg was tested for PAN interferences under laboratory conditions and for sampling artifacts using ambient air. When exposed to PAN, the KOH-coated filters of the Organic Acids Leg of the Two-Week Sampler removed PAN as acetate with approximately 60 percent efficiency for each filter. When sampling filtered ambient air, approximately 20 percent of the acetate

was collected by the second filter, most likely due to the partial adsorption of PAN. Long sampling intervals did not appear to lead to a significant deterioration of the acetate or formate collected.

A One-Day Sampler was constructed using tandem denuders of the same type used in the Two-Week Sampler, but operated at six times the flow rate. In tests with filtered ambient air, the One-Day Sampler (using sodium carbonate-coated denuders) produced nitric acid values in agreement with those from parallel nylon filters. Values from sodium chloride-coated denuders were lower, similar to that observed for long-term sampling. Ambient nitric acid measured by the One-Day Sampler using sodium carbonate-coated denuders was about 30% lower than parallel measurements with a collocated tunable diode laser absorption spectrometer (TDLAS); however, nitric acid measured by a collocated long path Fourier transform infrared spectrometer (FTIR) was also about 30% lower during this period.

This study confirms that the Main Leg of the Two Week Sampler, although potentially subject to both positive and negative sampling artifacts, provides a useful measure of nitric acid concentrations. The carbonate-coated back filter leads to an over-correction for particulate nitrate. As expected, the KOH-coated filters used to measure the upper limit of acetic acid were found to collect PAN, and thus would give a positive bias if the data were interpreted as acetic acid. For both legs of the Two-Week Sampler, no sample collection artifact was observed for this sampling duration, compared to 24 hours. The Main Leg of the Sampler was shown to be capable of operating at a flow rate suitable for collecting daily samples.

TABLE OF CONTENTS

PAGE

Disclaimer ii
Acknowledgments iii
Abstract iii
List of Figures viii
List of Tables x

1.0 Introduction and Background 1
- 1.1 Sampler Description 2
- 1.2 Summary of Development and Testing of the Two-Week Sampler 4
- 1.3 Suspected Interferences 7
  - 1.3.1 Main Leg 7
  - 1.3.2 Organic Acids Leg 9
- 1.4 One-Day Sampler 10
- 1.5 Objectives 10

2.0 Approach 13
- 2.1 Evaluation of the Main Leg of the Two-Week Sampler 13
  - 2.1.1 Main Leg Laboratory Evaluation 13
  - 2.1.2 Main Leg Field Evaluation 17
- 2.2 Evaluation of the Organic Acids Leg of the Two-Week Sampler 21
  - 2.2.1 Organic Acids Leg Laboratory Evaluation 21
  - 2.2.2 Organic Acids Leg Field Evaluation 21
- 2.3 Design and Evaluation of a One-Day Sampler Based on a High Flow Rate Adaptation of the Two-Week Sampler 22
  - 2.3.1 Laboratory Evaluation of Nitric Acid Penetration 23
  - 2.3.2 Redesign and Evaluation of the Impactor 23
  - 2.3.3 Evaluation of Particle Losses 24
  - 2.3.4 Field Evaluation 24

3.0 Results and Discussion 27
- 3.1 Evaluation of the Main Leg of the Two-Week Sampler 27
  - 3.1.1 Laboratory Evaluation 27
  - 3.1.2 Field Evaluation: Riverside Sampling of Filtered Air 33

    - 3.1.3 Field Evaluation: Claremont Substrate Testing with Filtered Air.....40
  - 3.2 Evaluation of the Organic Acids Leg of the Two-Week Sampler.....48
    - 3.2.1 Laboratory Evaluation.....48
    - 3.2.2 Field Evaluation.....51
  - 3.3 Design and Evaluation of a One-Day Sampler Based on a High Flow Rate Adaptation of the Two-Week Sampler.....59
    - 3.3.1 Configuration of the One-Day Sampler.....59
    - 3.3.2 Theoretical Considerations for the One-Day Sampler Denuder.....61
    - 3.3.3 Laboratory Evaluation of Denuder Nitric Acid Penetration.....61
    - 3.3.4 Redesign and Evaluation of the Impactor.....63
    - 3.3.5 Evaluation of Particle Losses.....63
    - 3.3.6 Field Evaluation.....63
      - 3.3.6.1 Initial Riverside One-Day Denuder Testing.....63
      - 3.3.6.2 Claremont Field Evaluation of the One-Day Sampler.....67
- **4.0 Summary and Conclusions.....81**
  - 4.1 Summary of Experimental Results.....81
    - 4.1.1 Evaluation of the Main Leg of the Two-Week Sampler.....81
    - 4.1.2 Evaluation of the Organic Acids Leg of the Two-Week Sampler.....82
    - 4.1.3 Design and Evaluation of the One-Day Sampler.....83
  - 4.2 Conclusions.....84
- **5.0 Recommendations.....87**
- **6.0 References.....89**

APPENDIX A: Two-Week Sampler SOP.....91
APPENDIX B: ADI Claremont Study Workplan.....103

LIST OF FIGURES

FIGURE		PAGE
1-1	Schematic of the Main Leg of the Two-Week Sampler	3
2-1	Schematic diagram of laboratory evaluation of nitric acid, nitrous acid and PAN penetration through the Main Leg of the Two-Week Sampler.	14
2-2	Schematic diagram of substrate testing system for field evaluation of the Two-Week Sampler components.	18
3-1	Sum of nitrate on series substrates during Riverside sampling.	37
3-2	Scatter plot of nitrate on front vs back nylon filters during Riverside sampling of particle free air.	38
3-3	Nitrate measured in substrate testing system in Riverside for sodium carbonate-coated quartz filters and sodium chloride-coated quartz filters, with and without a Teflon or Kevlar Impactor.	39
3-4	Nitrate measured in substrate testing system in Riverside for glass honeycomb denuders coated with sodium carbonate and sodium chloride, both with and without glycerol.	41
3-5	Comparison of sum of nitrate from tandem substrates on the primary leg of the substrate testing system in Claremont to that on the replicate leg.	46
3-6	Nitrate measured in substrate testing system in the Claremont area for sodium carbonate-coated quartz filters, sodium chloride-coated quartz filters and Gelman nylon filters, each operated in series of three.	47
3-7	Nitrate measured in substrate testing system in Claremont for glass honeycomb denuders coated with sodium carbonate and sodium chloride, with and without glycerol.	49
3-8	Line 1(sampler 1) vs Line 6 (sampler 2) acetate, front filters (blank corrected).	53

3-9 Line 1(sampler1) vs Line 6 (sampler 2) formate, front filter (blank corrected). 54

3-10 Scatterplot of front filter vs back filter acetate (blank corrected). 55

3-11 Schematic of the One-Day Sampler showing impactor precutter, tandem denuders and backup filter housed in Teflon filter cassette. 60

3-12 Penetration of nitric acid through honeycomb denuders. 62

3-13 Collection efficiency for the impactor precutter of the One-Day Sampler, shown as a function of Stokes number, and particle diameter at a flow rate of 2.5 ℓ/min. 64

3-14 Particle penetration through the One-Day Sampler cassette. 65

3-15 Results of inlet and inline flow checks done as part of the field quality assurance procedures at Claremont, showing one outlier. 69

3-16 Nitric acid measured by the daily nylon filters and by the One-Day denuder pairs operated at 2.5 ± 0.5 ℓ/min in the substrate testing system at Claremont. (For the 8/30 sample the sum of denuders and after filter was substituted for the nylon filter value). 73

3-17 Nitric acid measured by One-Day Sampler compared to that measured by One-Day denuder pairs of the same type and on the same day from the substrate testing system at Claremont. 76

3-18 Nitric acid measured at Claremont by One-Day Sampler compared to that measured by the TDLAS. 78

3-19 Nitric acid measured at Claremont by daily nylon filters in the substrate testing system compared to that measured by the TDLAS. 79

3-20 Comparison of nitric acid by TDLAS and FTIR at Claremont for eight composited days in September, 1995. 80

LIST OF TABLES

TABLE **PAGE**

1-1 Mean concentrations and precision from the Two-Week Sampler 6

1-2 Ratio of Two-Week Sampler to the 24-hour Sampler and to the TDLAS 6

2-1 Configuration of substrate testing system for Riverside Study. 19

2-2 Configuration of substrate testing system for Claremont Study. 20

2-3 Substrates evaluated for One-Day Sampler in Claremont. 25

3-1 PAN Captured as nitrite and nitrate by substrates of the Main Leg of the Two-Week Sampler (blank corrected). 28

3-2 PAN percent captured through the substrates of the Main Leg of the Two -Week Sampler. 29

3-3 HONO captured as nitrite and nitrate by substrates of the Main Leg of the Two-Week Sampler (blank corrected). 31

3-4 HONO percent captured by substrates of the Main Leg of the Two-Week Sampler. 32

3-5 Species concentration data from substrate testing system: Riverside Two-Week Values. 34

3-6 Summary of nitrate results from substrate testing system: Riverside Two-Week Values. 36

3-7 Species concentration data from substrate testing system: Claremont Two-Week Values. 42

3-8 Summary of nitrate results from substrate testing system: Claremont Two-Week Values. 44

3-9 PAN acetate and formate deposition to substrates of the Organic Acids Leg of the Two-Week Sampler. 50

3-10 Acetate and formate collected on the Organic Acids Leg of the Two-Week Sampler at Riverside (blank corrected). 52

3-11 Summary of formate and acetate analysis for the Biodegradation Study. 57

3-12 Theoretical HNO_3 collection efficiencies for honeycomb denuder. 61

3-13 Summary of measurements made with the One-Day Sampler denuders operated at Riverside for two days at 2ℓ/min. 66

3-14 Summary of nitrate measurements made with the One-Day Sampler denuders operated at Riverside for two days at 2ℓ/min. 67

3-15 Species concentration data from daily samples on substrate testing system at Claremont (Legs 17 & 18). 70

3-16 Summary of nitrate results from One-Day Substrate Testing at Claremont. 71

3-17 Concentrations from One-Day Sampler at Claremont. 74

3-18 Summary of One-Day denuder results for nitric acid at Claremont. 75

1.0 INTRODUCTION AND BACKGROUND

Acidic species in the atmosphere are of concern because of effects on human health and materials. Methods to monitor these species on a routine basis involve the collection of acidic gases and fine particle ions on filter media, followed by chemical analysis. Due to the expense of these methods, annual averages are typically established by averaging data from two 12-hour, every sixth day sampling, resulting in 122 samples per year. For accurate particle nitrate and nitric acid measurements, samples should be retrieved immediately at the end of sampling, which requires two trips to the site for each sample. Proper operation of such a network is therefore costly because of the number of samples and personnel requirements.

As part of CARB Contract #A033-186, Epidemiologic Investigation to Identify Chronic Health Effects of Ambient Air Pollutants in Southern California (Children's Health Study), it was necessary to obtain annual mean concentrations of acidic gases and fine particle ions from twelve sites at low cost. The objective of the study is to determine the effects of prolonged exposure to community air. The existing ARB-operated California Acid Deposition Monitoring Program (CADMP) network was deemed too costly to meet the needs of this study and, in addition, did not provide measurements of organic acids. To meet this monitoring need, a Two-Week Sampler was developed. It is designed to collect integrated two-week samples, with continuous operation throughout the year. Sample collection is halted by the operator, completed samples are retrieved immediately, and the next sample is started. Coordination of sampling times among sites is not critical because the sampler is operated continuously throughout the year. This approach simplifies the logistics of network operations and reduces the number of samples to be analyzed, yet still characterizes the composition of community air.

The development of the Two-Week Sampler involved both laboratory and field testing of the Main Leg of the Sampler, which is used to measure nitric acid and particulate ions. Candidate collection substrates were examined in the laboratory for loss of nitric acid from collection substrates during repeated exposure to hot, dry conditions, and were compared in the field against sampling substrates which were changed daily. Also, the completed Sampler was compared against other nitric acid measurement methods over two, two-week periods. These tests guided in the selection of collection substrates for the Sampler, but also pointed out the possibility of positive interferences expected from nitrous acid (HONO) or peroxyacetyl nitrate (PAN). Testing had not been conducted on the Organic Acids Leg of the Sampler for suspected interferences from PAN when trapping acetic acid or the effect of long sampling times on the stability of formate and acetate after collection by the filters. Thus, further evaluation of the Sampler performance, beyond that already conducted, was needed.

1.1 Sampler Description

The Two-Week Sampler was designed to provide 14-day, integrated measurements of ambient vapor phase nitric, hydrochloric and formic acids, upper limit concentrations of acetic acid, and fine particle mass and inorganic ions ($NH4^+$, $SO4^=$, $NO3^-$, and Cl^- below 2.5 µm). The Sampler has three legs as described below.

The *Main Leg* measures nitric and hydrochloric acid and inorganic particulate ions. Nitric and hydrochloric acid are adsorbed on a sodium carbonate-coated glass honeycomb denuder, particulate ions are then collected on a Teflon filter, and a carbonate-coated quartz fiber filter is used to trap volatilized particulate nitrate. Figure 1-1 shows how these substrates are loaded into a single all-Teflon 47mm filter holder with spacing elements. The honeycomb denuder is based on a design by the Harvard School of Public Health. This is followed by a Teflon front filter and a carbonate-coated quartz back filter. The Teflon filter removes particulate matter and the carbonate-coated back filter is used to remove nitric acid originating from the volatilization of particulate ammonium nitrate on the Teflon filter. The concentration of nitrate on this back filter is then used to correct for the amount of ammonium nitrate volatilized from the front filter. A single-jet Teflon impactor ahead of the denuder removes particles greater than 2.5 µm aerodynamic diameter. This leg of the Sampler operates at 0.4 ℓ/min to give a sample volume of 8 m^3 over the 14-day period. Due to the short length of the denuder (8 mm), it can be housed, along with two filters, in a commercial Teflon filter holder.

The *Organic Acids Leg* is a filter pack, with a Teflon front filter followed by two potassium hydroxide-coated quartz fiber filters. These are installed in a filter holder similar to that of the Main Leg. Aqueous extracts of the coated filters are analyzed by ion chromatography for formate and acetate to give formic acid and an upper limit value for acetic acid. There is a known positive interference from PAN for the acetic acid measurement. This leg also operates at 0.4 ℓ/min.

The Auxiliary Leg is a single prefired quartz filter which can be analyzed by ion chromatography for inorganic ions, or by a variety of techniques for organic and non-volatile carbonaceous species. The flow rate, 1.4 ℓ/min, is sufficient to allow the sample to be split for both analyses.

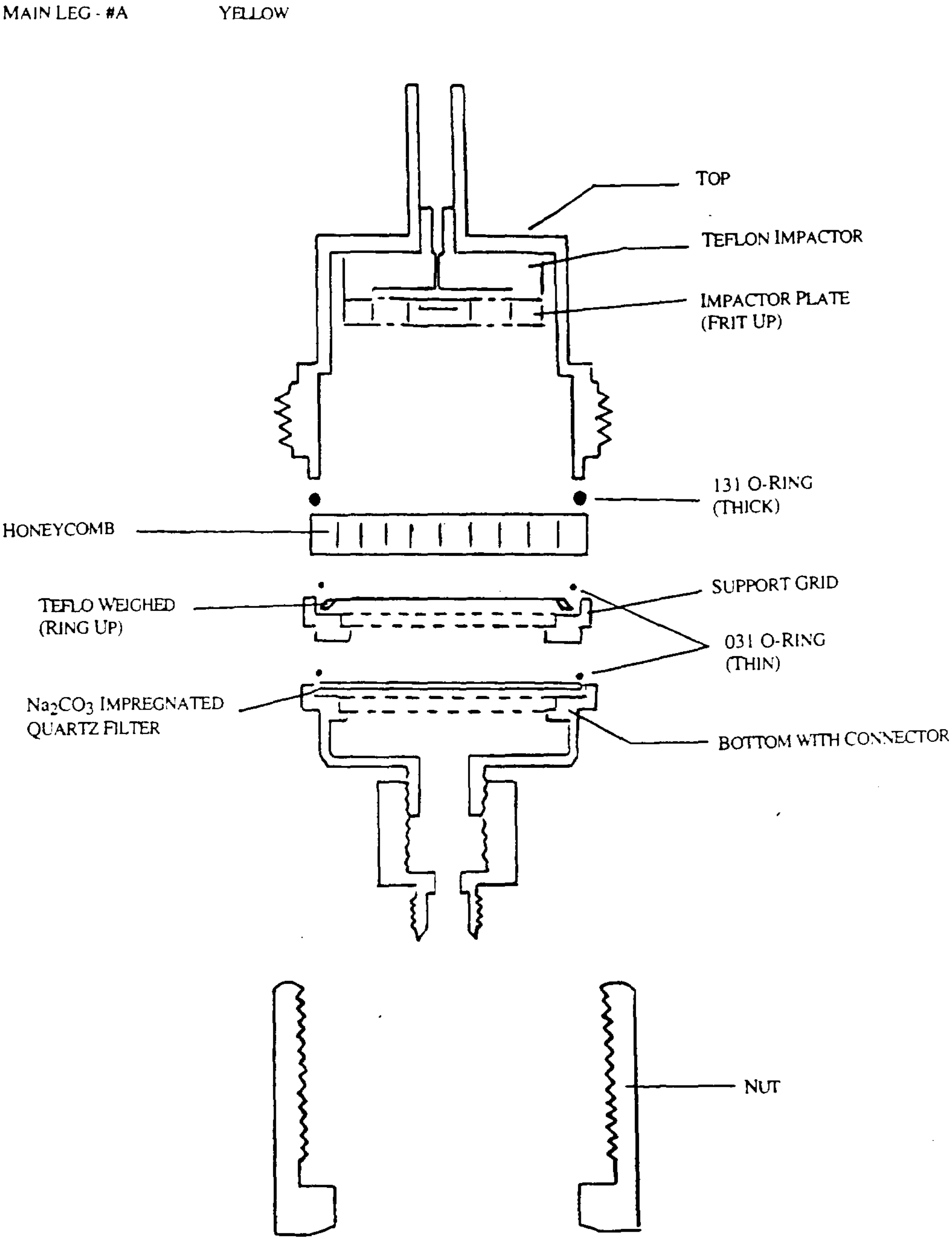

Figure 1-1 Schematic of the Main Leg of the Two-Week Sampler

The sampling cassettes are mounted upside down in a Teflon hood (or box), which provides shielding from both sun and rain. A small box fan at the top of the box prevents stagnation of air around the entrance of the sampling cassettes. The total flow rate is indicated by a pressure transducer mounted in the pumping manifold which is recorded on the data system and can be interrogated remotely via modem to verify proper operation of the system during the two-week sampling period

1.2 Summary of Development and Testing of the Two-Week Sampler

The Two-Week Sampler was designed by Aerosol Dynamics Inc. on a basis of laboratory and field tests conducted over an eight-month period in 1993, as described by Lurmann et al. (1994). These tests were done for the Main Leg of the Sampler to determine the collection, retention and artifactual collection of nitric acid and nitrate in the Main Leg of the Sampler, and to evaluate fine particle cutpoint and collection characteristics. Testing was also done to evaluate the overall performance and precision of the completed samplers prior to deployment in the epidemiology study network. This section summarizes the pertinent results from that testing.

Several types of nitric acid collection substrates were tested in the laboratory and the field. In the laboratory, collection and retention efficiencies for nitric acid were measured on substrates which had been exposed to hot, dry air. One of the major results from the laboratory testing showed that while nitric acid has a retention efficiency of greater than 99% on nylon filters, it is also slowly lost from the nylon filters after exposure to hot, dry air at a rate of ~0.5%/hr at 40°C. There is little detectable loss at 25°C. In contrast, carbonate-coated filters have high collection (>99%) and retention efficiencies (>99%). MgO denuders also tested well in all experiments, with loading and retention efficiencies greater than 99%.

Three types of glass honeycomb denuders were tested in the laboratory. An all-glass, 10 mm honeycomb denuder from the Harvard School of Public Health, coated with 2% carbonate and 1% glycerol, has a collection efficiency of >99% at room temperature and in hot air. As with the MgO denuder, no losses were seen in multiday exposure to 40 ± 5°C and 25 ± 5°C air. These denuders were analyzed directly, and showed complete, efficient extraction. These were not commercially available at the time. Newer, epoxied glass honeycomb denuders from Harvard have a more regular hole pattern, and were found to be >99% efficient. However, in our first experiment only 40% of the deposited nitric acid was recovered by the extraction of the denuder. Experiments were repeated after acid washing the denuder, and these showed good, but not perfect, extraction efficiencies. These are now available from Ogawa, but are expensive. All-glass honeycomb denuders from Adams Scientific Glass in Berkeley were developed just prior to the first field study, and were included as part of that study. Subsequent laboratory tests with these denuders showed that collection and extraction efficiencies were essentially 100%. These denuders were subsequently utilized in the final version of the Two-Week Sampler.

Four inlets were also tested for nitric acid vapor penetration in the laboratory: (1) 10 µm pore, untreated Nuclepore filters; (2) 12 µm pore Nuclepore filters washed in 1 N acetic acid and dipped in 1 N sulfuric acid; (3) a single jet Teflon impactor mounted on the inside of the filter holder cap and (4) the same type of impactor made of aluminum and coated with Halocarbon wax. For Nuclepore filters, penetrations were 99% for hot, dry conditions, but only 90% for moist or cool conditions. For the Teflon impactor, penetrations were 99% for hot, dry conditions and 100% for cool (10°C) conditions. For the Halocarbon-coated aluminum impactor, penetrations were 92% for cool conditions.

In the field, a comparison was made of nitric acid (measured as nitrate) collected by candidate substrates operated downstream of a Teflon filter to remove particles and allow pollutant gases to pass through. The candidate substrates were operated for two weeks in parallel with a nylon filter which was changed daily. Impactor inlets were also tested for nitric acid penetration in this manifold. Nitric acid values from the carbonate-coated glass denuder were 16% higher than from the nylon filter changed daily. Similarly, a 3-stack nylon filter pack operated for two weeks also had values 16% higher than those from the daily nylon filter. The highest values were from KOH-coated quartz filters which are believed to show interference from the collection of PAN (Grosjean and Parmar, 1990). No losses of nitric acid were found through the Teflon impactor.

In addition to the component testing, two field tests were conducted with the completed Two-Week Sampler. In both field tests the Two-Week Sampler was operated, collocated with a 24-hour sampler. The 24-hour sampler measured fine particulate nitrate by means of a nylon filter operated downstream of a 2.5 µm cut-point cyclone and a tubular denuder coated with magnesium oxide. Total nitrate was measured with a nylon filter using the same cyclone but without a denuder. Nitric acid was determined by the difference in nitrate between the total nitrate and the fine particulate nitrate. Its sampling substrates were changed daily during the two-week sampling period. Field tests were conducted in the Los Angeles Basin in August and October, 1993. For the October tests, nitric acid was also measured by Unisearch (Toronto, Canada) using a tunable diode laser absorption spectrometer.

Mean concentrations and precision for the Two-Week Sampler are shown in Table 1-1. Precisions were generally good for nitric acid, sulfate and ammonium ion. Particle nitrate values were more variable. It was noted that most of the nitrate was on the carbonate backup filter to the Teflon filter. The ratio of the mean concentrations measured by the Two-Week Sampler to those measured by the 24-hour sampler and the TDLAS are shown in Table 1-2. Two-Week Sampler nitrate (the sum of nitrate collected on the Teflon front and carbonate-coated back filters) was compared to the fine particulate nitrate of the 24-hour sampler. It was found that the particulate nitrate, ammonium, and sulfate concentrations were within 10% of those reported from the 24-hour sampler. However, the nitric acid values from the Two-Week Sampler were about 30% higher than the TDLAS.

Table 1-1. Mean Concentrations and Precision from the Two-Week Sampler (µg/m^3)

	August Test		October Test	
No. of Samplers	4		8	
HNO_3	11.6	±3.4%	11.1	±1.7%
NO_3^-	6.1	±13.0%	8.8	±7.6%
$SO_4^=$	4.7	±3.7%	2.7	±6.1%
NH_4^+	2.8	±6.1%	NA	

Table 1-2. Ratio of Two-Week Sampler to the 24-hr Sampler and to TDLAS

Species	**Ratio to 24-hr Sampler**	**Ratio to 24-hr Sampler**	**Ratio to TDLAS**
	August Test	**October Test**	**October Test**
HNO_3	1.26	2.02	1.29
NO_3^-	1.03	1.03	
$SO_4^=$	0.90	0.90	
NH_4^+	0.93		

1.3 Suspected Interferences

1.3.1 Main Leg

The higher values of nitric acid from the Two-Week Sampler are possibly due to a positive interference from nitrous acid. It is known that carbonate-coated denuders collect nitrous acid in the form of nitrite. This can become oxidized to nitrate during further sampling, especially in the presence of ozone (Sickles and Hodson, 1989; Perrino et al., 1990). Over-estimation of nitric acid by oxidation of collected nitrite to nitrate has also been reported when using annular denuders during week-long sampling intervals (Sickles, 1987). This is apparently not a problem for samples collected for less than 24 hours, based on comparisons with nitric acid measured by a tunable diode laser (Paur and McClenny, 1987).

Estimates of interferences from other nitrogenous species have been derived by analysis of two or three denuders in series. The acids are efficiently removed while other nitrogenous species are generally only partially removed. The removal efficiency for these other compounds can be estimated by measuring the amounts of nitrate and nitrite on the second and third denuders in series (assuming that the first denuder removes all of the nitric and nitrous acid) and applying corrections to the first denuder. Corrections of 3-4% for nitric acid and 5-10% for nitrous acid were reported for Boston in the summer (Koutrakis et al., 1988). Samples collected with similar denuders in the winter in Research Triangle Park, NC were corrected for approximately twice these percentages (Vossler et al., 1988). Perrino et al., (1990) found that nitrite is oxidized to nitrate on carbonate-coated glass denuders even during 24-hour sampling, and that this oxidation is faster if glycerol is not used in the coating. This is in contrast to the findings of Paur and McClenny (1987).

It is possible that there could be an interference from PAN since peroxyacetyl nitrates are known to decompose in the presence of strong bases to produce nitrites and the corresponding carboxylate (Stephens, 1969). PAN concentrations in ambient air in the South Coast Air Basin were found to be comparable to those of nitric acid during the Southern California Air Quality Study (SCAQS). For example, peak concentrations of PAN in Claremont were 20-30 ppb (Williams and Grosjean, 1990), while nitric acid peaks at the same location were in the same range in the summer (Lawson, 1990, Anlauf et al., 1991). Decomposition within the carbonate-coated denuder in the Two-Week Sampler and the subsequent oxidation of nitrite to nitrate would result in a positive nitric acid artifact, while decomposition in the coated filter would result in a positive particulate nitrate measurement artifact. Both of these processes may occur simultaneously if PAN partially penetrates the denuder. Grosjean and Parmar (1990) reported an

11% conversion of PAN on potassium carbonate impregnated cellulose filters. While they concluded that this would be a 'negligible' interference, they used only pure PAN and 'particle free ambient air' presumably at room temperature. They did not appear to test conversion under all of the ambient conditions of concentration, temperature, and humidity expected from a year-long sampling program.

Similar artifacts are possible from other nitrogenous species that are removed by the sampling media. Nitrous acid is probably the only other such compound that would be found in ambient air at concentrations significant to nitric acid. Nitrous acid concentrations are very low in the daytime due to rapid photolysis, but concentrations at night of 10 ppb have been reported (Harris et al., 1982; Appel et al., 1990). Sodium carbonate-coated denuders are used to collect samples to determine nitrous acid concentrations (Ferm and Sjodin, 1985) by measuring the nitrite in the denuder. Indeed, they concluded that PAN was partially adsorbed by the denuder to produce nitrite, and that perhaps nitrite was formed at the denuder surface by a reaction involving NO, NO_2 and water vapor. In order to correct for these interferences, multiple denuders were used in series. The efficiency of these processes can be estimated by comparing the nitrite on the second and third denuder (the nitrous acid is effectively removed by the first denuder). Oxidation of nitrite to nitrate on carbonate-coated filters has been shown to be significant and facilitated by the presence of ozone (Sickles and Hodson, 1989).

Another sampling artifact of the carbonate-coated denuders and filters is that when significant concentrations of both SO_2 and NO_2 are present, a conversion of NO_2 to nitrite has been observed, apparently due to the sulfite formed when SO_2 is scrubbed by the carbonate (Febo et al., 1993). Below 100 ppb of SO_2 this artifact formation is likely to be one ppb of nitrite or less.

It is likely that the Two-Week Sampler carbonate-coated denuder efficiently collects nitrous acid and that a portion of the nitrite is converted to nitrate during the long residence time in the sampler. It is less likely, based on the work of Grosjean, that PAN is efficiently collected. The denuder extracts from the field testing of the Two-Week Sampler were not analyzed for nitrite, a measurement that could partially resolve the magnitude of these sampling artifacts. It is unlikely that SO_2 concentrations in California are sufficiently high to promote significant artifact nitrite formation from NO_2.

Perrino et al. (1990) found that a sodium chloride-coated glass denuder was quite specific for nitric acid (did not adsorb any nitrous acid), while Febo et al. (1993) observed a nitrite interference from a combination of high NO_2 and SO_2. Given the relatively low SO_2

concentrations in California, this denuder could still be a viable alternative to the carbonate denuder for the two-week sampling for nitric acid. A possible problem is that the use of sodium chloride-coated denuders necessarily precludes the possibility of measuring hydrochloric acid (HCl) on the denuder; however, HCl could also be measured by the organic acids filter pack if necessary.

1.3.2 Organic Acids Leg

PAN is a potential interferent when collecting acetic acid on base-impregnated filters since collected PAN is subject to base-catalyzed hydrolysis to nitrite and acetate ions. Grosjean and Parmar (1990) reported that hydroxide-coated filters removed nearly twice the PAN of carbonate-coated filters. For this reason, acetate data from the Organic Acids Leg of the Two-Week Sampler should be treated as a measure of the upper limit acetic acid concentration. Grosjean and Parmar (1990) also reported the potential for interferences from formaldehyde and acetaldehyde. Using ambient or purified matrix air and aldehydes derived from permeation tubes, liquid injection, or synthetic photochemical smog, only a few percent of the aldehyde showed up on the carbonate-coated filters as a carboxylate. While this study was limited in the range of concentration, temperature, and humidity, it did appear that aldehydes would not be significant interferents. A comparison of formic acid measured with a Fourier Transform Infrared Spectrometer (FTIR) compared to a filter pack with an annular aldehyde denuder (coated with 2,4-dinitrophenylhydrazine) showed good agreement, although the data were quite scattered ($R^2 = 0.645$ with n=38).

Another potential problem for the Two-Week Sampler is that adsorbed acetate and formate could be degraded by microbes during the relatively long sampling period. This needs to be evaluated for the Two-Week Sampler. The Teflon front filter should protect the KOH-coated substrates from microbes.

The occurrence of positive and negative sampling artifacts (from adsorption/desorption, etc.) is often accentuated when samples are collected on a shorter interval and then compared with results from samples collected during a concurrent longer sampling schedule. Therefore, it was decided to collect samples for organic acids analysis over two weeks and compare results with samples collected daily. If the composite daily samples are significantly less than the single sample, a desorption artifact is indicated, and conversely if the daily samples are greater than the single sample an adsorption artifact would be suspected.

1.4 One-Day Sampler

The two-week period used for this sampler was selected based on the needs of the epidemiology study for which it was developed. Specifically, it was designed to obtain long-term average concentrations of airborne pollutants at many sites at low cost. However, shorter sampling times are often desirable to study episodic pollution events, as well as special events such as measurements within homes. An immediate application within the Children's Health Study would be for evaluating indoor/outdoor ratios of these pollutants. The shorter sampling times will also better characterize peak concentrations.

Because of the simplicity and ease of operation of the Two-Week Sampler, we examined the possibility of its reconfiguration for 24-hour operation. In many ways, 24-hour sampling presents fewer problems than the two-week sampling. The potential is lower for degradation of the sample during collection and there is less opportunity for the conversion of nitrite to nitrate on the collection surfaces. The higher flow rate required will also result in smaller electrostatic particle losses to the Teflon surfaces of the sampler.

1.5 Objectives

The primary objective of this work was to evaluate the ability of the Two-Week Sampler to accurately collect the nitric acid, formic acid, acetic acid, and particle-phase nitrate as part of the routine measurements being performed in support of the Children's Health Study. A secondary objective was to evaluate the potential of the Sampler at flow rates high enough to allow for single day sampling. The specific objectives of this project were:

Main Leg

(1) Determine the penetration of nitric acid through the various components (inlets, denuders, and filter packs) of the Two-Week Sampler.

(2) Compare the performance of the carbonate-coated glass denuder to the sodium chloride-coated denuder under field conditions.

(3) Evaluate the potential for sampling artifacts that may be exacerbated by long sampling intervals.

(4) Quantify the extent of nitrous acid and PAN interferences on the carbonate-coated glass denuder as currently employed in the Two-Week Sampler.

(5) Evaluate possible positive interferences on the carbonate back-up filter.

Organic Acids Leg

(6) Evaluate the uptake of PAN by the KOH-coated filters.

(7) Evaluate the biogenic degradation of acetate and formate on the KOH-coated filters.

(8) Determine the potential for sampling interval artifacts by varying the collection interval.

One-Day Sampler

(9) Evaluate adapting the main leg of the Two-Week Sampler for 24-hour sampling intervals.

2.0 APPROACH

2.1 Evaluation of the Main Leg of the Two-Week Sampler

2.1.1 Main Leg Laboratory Evaluation

The laboratory evaluation involved the synthetic generation of potentially interfering gases—PAN and nitrous acid—followed by introduction into the Two-Week Sampler at the usual sampling flow rate. The evaluation also included a test of the penetration of nitric acid. Figure 2-1 shows a schematic of the exposure system. This was done at two concentrations (typical and worst case), two temperatures (20°C and 40°C), and two humidities (20 and 80 percent). Each species was, therefore, evaluated over a matrix of eight combinations of environmental conditions. In addition, several experiments were performed using a combination of interferents to determine synergistic effects and with added ozone to evaluate the increase of the oxidation of nitrite to nitrate. Two experiments were performed with added concentrations of hydrochloric acid (at a concentration equal to the highest total ambient acid concentration) to evaluate whether the capacity of the substrates for acid adsorption was being reached. For several denuder exposures a NO-NO_X analyzer was used to directly measure PAN and nitrous acid concentrations before and after the denuder. This was not done on a regular basis since the NO-NO_X analyzer required a flow rate of 600 ml/min; thus sampling at the outlet would result in flow rates higher than that specified for the Two-Week Sampler. In addition, it was felt that the nitrate and nitrite on the substrates themselves would be a more accurate measure of the penetration through the system.

Denuders and quartz filters were coated by methods described in the laboratory SOP for the Two-Week Sampler. This SOP, included as Appendix A, addresses the detailed laboratory procedures. Substrate holders and honeycomb denuders were washed by sonicating twice in deionized water and were then air-dried prior to use. Honeycomb denuders were coated with a solution of either 2% sodium carbonate or sodium chloride dissolved in a 50/50 water/methanol solution by dipping them into the solution. For the glycerol treatment, 1% (by weight) of glycerol was added to the coating solution. Denuders were then removed from the solution, blotted with Kimwipes, and allowed to air dry. Quartz filters were coated using either a 0.47% sodium carbonate or a 2% sodium chloride solution of 50/50 water/methanol. The filters were laid on aluminum foil and 1 ml of solution was pipeted onto each one. The filters were then dried at room temperature (unlike the SOP which described drying in an oven at 80-120°C). All

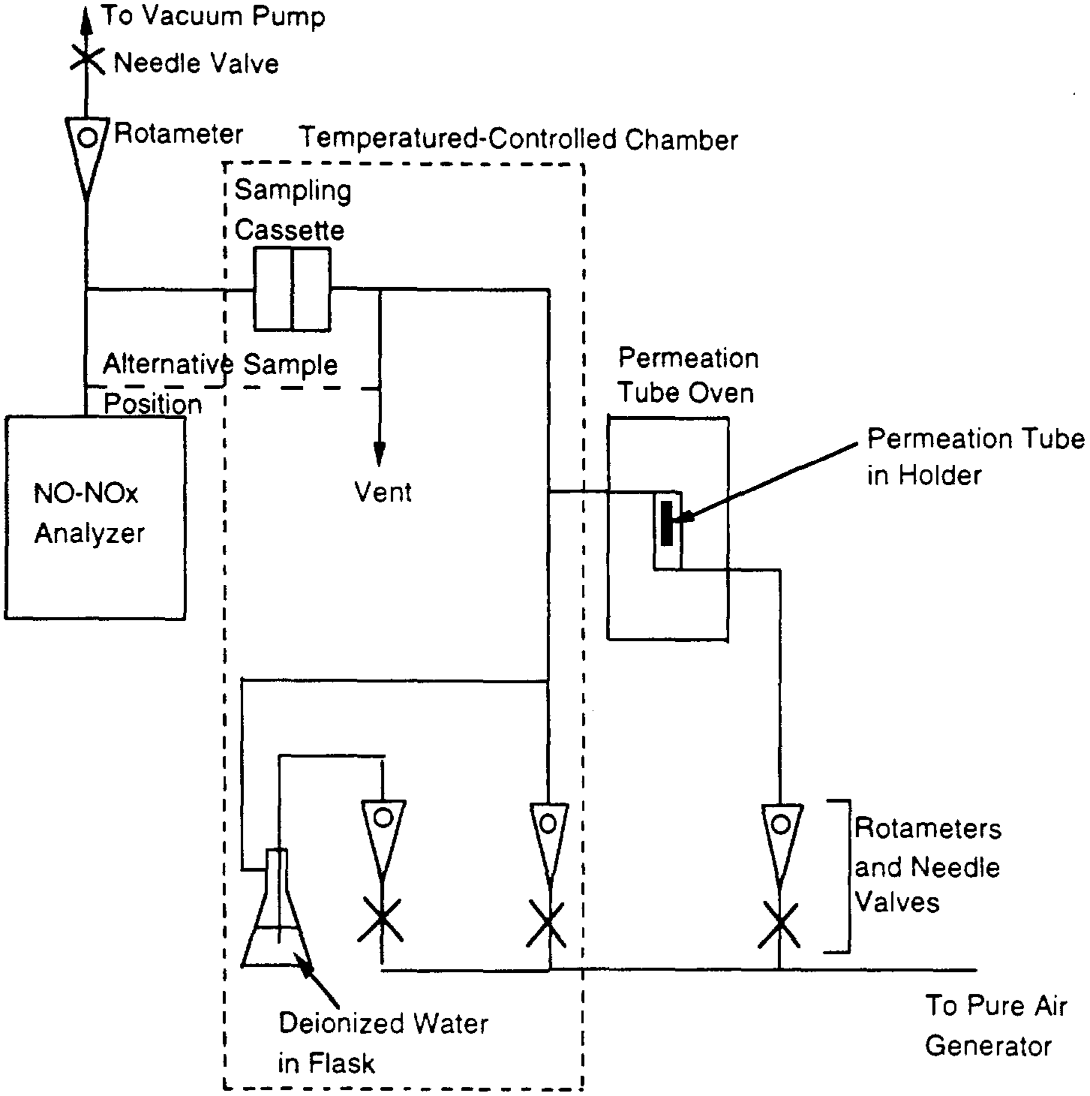

Figure 2-1 Schematic Diagram of laboratory evaluation of nitric acid, nitrous acid and PAN penetration through the Main Leg of the Two-Week Sampler

sampling substrates were stored under refrigeration in Petri dishes sealed with Teflon tape before and after sampling. Savillex multiple filter holders with a special o-ring modification were used for collecting samples.

Samples were collected over one week intervals in order to evaluate break-through and oxidation of collected nitrite to nitrate. Filters were extracted by sonication in 10 ml of deionized water, while denuders were shaken with 25 ml of deionized water. The extracts were generally analyzed for nitrite and nitrate by ion chromatography (IC). When using sodium chloride as an adsorbent, selected sample substrates were analyzed by a colorimetric method since the chloride interfered in the IC analysis. In addition, selected sampling cassettes were evaluated in real-time using a gas chromatograph and/or chemiluminescent NO-NO_X analyzer.

Gases for the exposure to the Two-Week Sampler were generated as follows:

- NITRIC ACID

  A permeation tube (Vicy/Metronics) containing a 68% solution of nitric acid in water was used to generate nitric acid for laboratory tests. This concentration is known as 'constant boiling' and provides a steady release rate at constant temperature. The nitric acid permeation tube was maintained at 90°C in a GC oven (Varian model 1400) and was flushed with 125 ml/min of purified air (Aadco model 737). It was then blended with additional purified air which had been humidified by splitting part of the flow through a temperature controlled bubbler (filled with deionized water) and then recombining.

- PAN

  PAN was prepared in solution by reacting peracetic acid with nitric acid (Holdren and Spicer, 1984) in a tridecane solvent. The amount and purity in the solution was quantified by IR in a 0.25mm liquid cell. The PAN mixture was placed in a diffusion tube and maintained at -4°C. Pure air was used to flush out the PAN, which was then blended with dilution air, as described above, to produce concentration of 10-50 ppb.

  The PAN was introduced into the inlet of the Main Leg of the Two-Week Sampler and concentrations measured at the inlet with a commercial NO-NO_X analyzer. These measurements were confirmed by collecting 50ml aliquots with an all glass syringe and quantifying the concentration with a gas chromatograph equipped with an electron capture detector.

A matrix of twelve samples was collected (seven with varying temperature, humidity and concentration, one with added ozone, one with added nitrous acid, one with both added nitrous acid and ozone, one with added hydrochloric acid vapor, and one using a sodium chloride-coated denuder). Two experiments were replicated and three dynamic blank values were determined by sampling pure air alone. Filters and denuder substrates which had been collected were extracted and assayed for nitrate and nitrite.

- NITROUS ACID

  The standard method of mixing sodium nitrite and sulfuric acid (Chan et al., 1978) has, in our experience, invariably led to the production of nitrogen dioxide and nitric acid. While the nitric acid could be somewhat selectively removed using sodium chloride-coated filters or aluminum-based denuders, for example, Vecera and Dasgupta (1991) demonstrated that ammonium nitrite can be sublimed as a clean and constant nitrous acid source. Their method was therefore used to introduce samples into the Two-Week Sampler. Ammonium nitrite was packed into a 1/4 inch diameter Teflon tube and placed into a refrigerator maintained at -4°C. Purified nitrogen was used to purge the tube and the effluent was blended with a known flow of diluent zero air. The inlet concentration to the denuder was determined by sampling with a commercial NO-NO_x analyzer and the nitrous acid concentration was adjusted by varying both the flow rate of the diluent air and the purging nitrogen. The concentration of nitrous acid cycled with the refrigerator and varied sinusoidally, with an amplitude of approximately 20% of the mean concentration.

  A matrix of ten samples was collected (seven with varying temperature, humidity and concentration, one with added ozone, one with added hydrochloric acid vapor, and one with a sodium chloride-coated denuder). Two experiments were replicated. The dynamic blank values with zero air alone collected for the PAN exposure were used for blank corrections. Denuders and filters collected were also assayed for nitrite and nitrate.

- OZONE

  Ozone was added using a commercial gas calibrator equipped with a low pressure mercury lamp ozonizer. Nitrous acid or PAN vapor was then added from the sources described above.

- HYDROCHLORIC ACID

  Hydrochloric acid was generated from a commercial permeation tube (Vicy/Metronics) filled with concentrated hydrochloric acid in the same manner as nitric acid.

2.1.2 Main Leg Field Evaluation

Field testing was done to compare the collection characteristics of various types of substrates for nitric acid under ambient conditions. Of interest are the extent of positive interferences and overall collection efficiencies under ambient sampling conditions. These field experiments were conducted twice, once in Riverside, CA in October 1994, and again in Claremont, CA in August-September 1995. The ambient conditions at these two sites were expected to differ in that nitric acid concentrations at Riverside are usually lower compared to ozone and PAN than at Claremont. Thus, the Riverside site was selected as one which has high interferent concentrations, while that at Claremont was to be high in nitric acid.

The experimental arrangement for the field testing consisted of 18 sampling legs to allow simultaneous sampling from a common Teflon manifold, as shown in Figure 2-2. Ambient air was drawn into the manifold at 12 ℓ/min through a pair of 47 mm Teflon filters. The Teflon filters removed airborne particles while passing nitric acid and other ambient constituents such as nitrous acid, ozone, and peroxyacetyl nitrate (PAN). The nitric acid downstream of the Teflon filters consisted of ambient nitric acid plus nitric acid from volatilized particulate nitrate. Individual flows were controlled by orifices and monitored by rotameters. The entire system was housed in an insulated box to prevent overheating. This system was similar to that used in the initial development and testing of the Two-Week Sampler.

Legs labeled 1 through 16 were used to test substrates for the Two-Week Sampler, and each of these legs was operated at 0.4 ℓ/min over the two-week period without changing substrates. Legs 17 and 18 sample from the same manifold at 2.5 ℓ/min to 3 ℓ/min and the substrates on these legs were changed daily. One of these legs was a reference leg, consisting of a double nylon filter changed daily. The other leg was used to test various substrates and denuders for 24-hour sampling, as described below in the feasibility studies for development of a One-Day Sampler.

Tables 2-1 and 2-2 give a complete breakdown of the substrate configuration for the Riverside and Claremont experiments, respectively. Substrates tested included: carbonate-coated filters and denuders, sodium chloride-coated filters and denuders and nylon filter packs. Additionally, impactors were evaluated for nitric acid penetration. For the most part, the same configurations of substrates tested on Legs 9-16 duplicated those on Legs 1-8. Coated substrates were prepared as described in Section 2.1.1, with the exception of the NaCl-coated filters used in the Claremont study in which a 0.47% solution was used. Analyses were done for both nitrite and nitrate, as well as for chloride and sulfate. Comparisons were made against nylon filters changed daily.

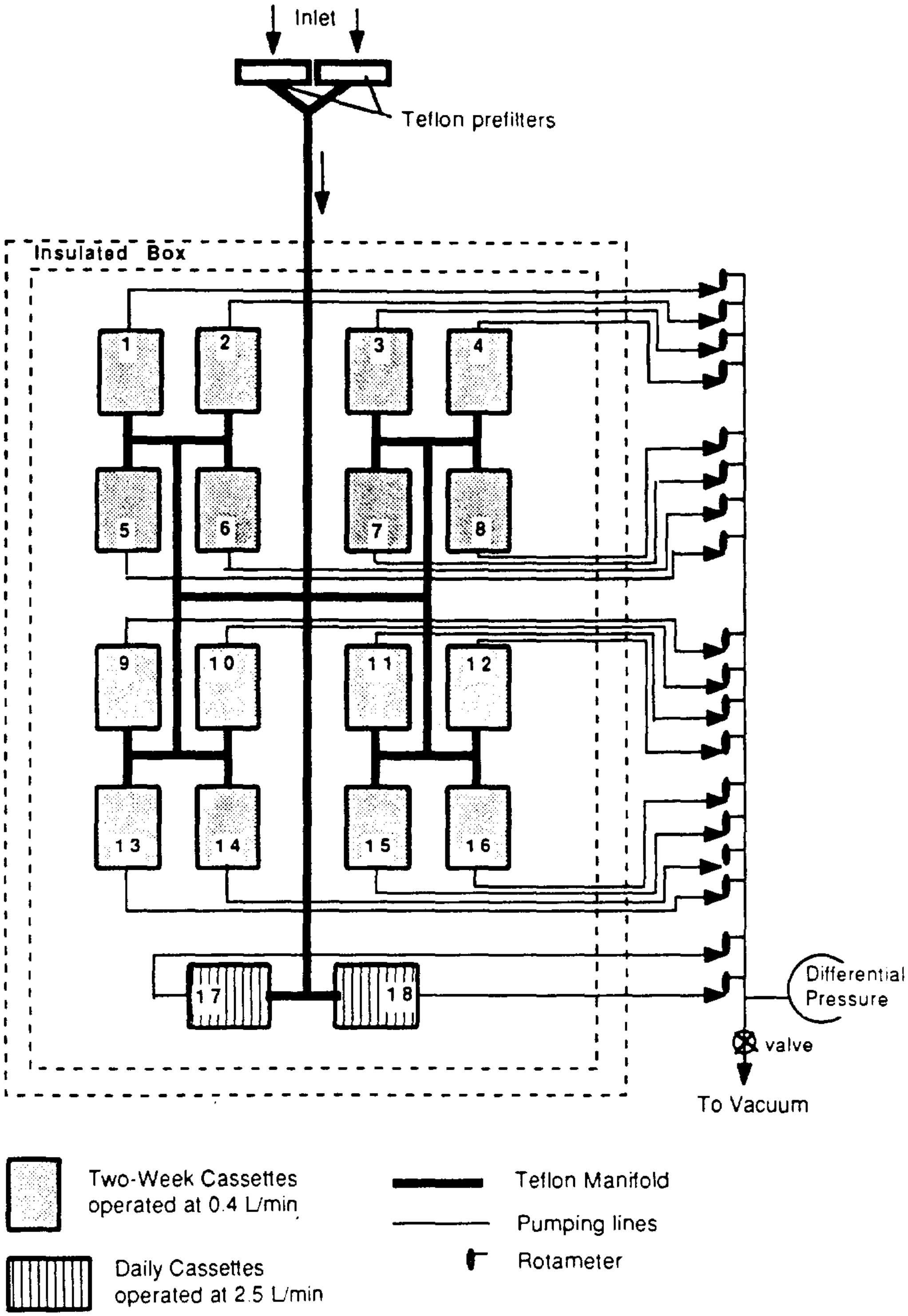

Figure 2-2 Schematic diagram of Substrate Testing System for field evaluation of the Two-Week Sampler components

	Substrates Operated in Series on Each Leg of System†			Nominal	Nominal
Leg	Position 1	Position 2	Position 3	Flow (L/min)	Duration
1	Cb-Q filter	Cb-Q filter	Cb-Q filter	0.4	14 days
2	NaCl-Q filter	NaCl-Q filter	NaCl-Q filter	0.4	14 days
3	CbDo denuder	Cb-Q filter	Cb-Q filter	0.4	14 days
4	NaDo denuder	NaCl-Q filter	NaCl-Q filter	0.4	14 days
5	CbDg denuder	Cb-Q filter	Cb-Q filter	0.4	14 days
6	NaDg denuder	NaCl-Q filter	NaCl-Q filter	0.4	14 days
7	Teflon Impactor	Cb-Q filter	Cb-Q filter	0.4	14 days
8	Kevlar Impactor	Cb-Q filter	Cb-Q filter	0.4	14 days
9	Cb-Q filter	Cb-Q filter	Cb-Q filter	0.4	14 days
10	NaCl-Q filter	NaCl-Q filter	NaCl-Q filter	0.4	14 days
11	CbDo denuder	Cb-Q filter	Cb-Q filter	0.4	14 days
12	NaDo denuder	NaCl-Q filter	NaCl-Q filter	0.4	14 days
13	CbDg denuder	Cb-Q filter	Cb-Q filter	0.4	14 days
14	NaDg denuder	NaCl-Q filter	NaCl-Q filter	0.4	14 days
15	Teflon Impactor	NaCl-Q filter	NaCl-Q filter	0.4	14 days
16	Kevlar Impactor	NaCl-Q filter	NaCl-Q filter	0.4	14 days
17	2-day Denuder/Nylon filter replicates			2.0	48 h, Changed every other day
18	Nylon Filter	Nylon Filter	none	2.5	24 h, Changed Daily

† Substrate Codes:

Cb-Q filter: Pallflex quartz filter impregnated with 1 mL of 0.5% sodium carbonate.

NaCl-Q filter: Pallflex quartz filter impregnated with 1 mL of 2% sodium chloride.

Nylon filter: Gelman nylasorb filter.

CbDo denuder, coated with sodium carbonate, without glycerol.

CbDg denuder, coated with sodium carbonate, with glycerol.

NaDo denuder, coated with sodium chloride, without glycerol.

NaDg denuder, coated with sodium chloride, with glycerol.

Note: All of the glass honeycomb denuders are 8 mm in length with approximately 200 parallel sintered glass tubes.

Table 2-1 Configuration of Substrate Testing System for Riverside Study

	Substrates Operated in Series on Each Leg of System†			Nominal	Nominal
Leg	Position 1	Position 2	Position 3	Flow (L/min)	Duration
1	Cb-Q filter	Cb-Q filter	Cb-Q filter	0.4	14 days
2	NaCl-Q filter	NaCl-Q filter	NaCl-Q filter	0.4	14 days
3	CbDo denuder (#114)	Cb-Q filter	Cb-Q filter	0.4	14 days
4	NaDo denuder (#<100)	NaCl-Q filter	NaCl-Q filter	0.4	14 days
5	NaDg denuder (#109)	NaCl-Q filter	NaCl-Q filter	0.4	14 days
6	CbDg denuder (#91)	Cb-Q filter	Cb-Q filter	0.4	14 days
7	Nylon filter	Nylon filter	Nylon filter	0.4	14 days
8*	CbDo denuder (#<100)	Teflo filter	Cb-Q filter	0.4	14 days
9	Cb-Q filter	Cb-Q filter	Cb-Q filter	0.4	14 days
10	NaCl-Q filter	NaCl-Q filter	NaCl-Q filter	0.4	14 days
11	CbDo denuder (#92)	Cb-Q filter	Cb-Q filter	0.4	14 days
12	NaDo denuder (#31)	NaCl-Q filter	NaCl-Q filter	0.4	14 days
13	NaDg denuder (#108)	NaCl-Q filter	NaCl-Q filter	0.4	14 days
14	CbDg denuder (#93)	Cb-Q filter	Cb-Q filter	0.4	14 days
15	Nylon filter	Nylon filter	Nylon filter	0.4	14 days
16*	CbDo denuder (#119)	Teflo filter	Cb-Q filter	0.4	14 days
17	Nylon Filter	Nylon Filter	none	2.5	24 h, Changed Daily
18	Substrates for One-Day Sampler, listed in Table 2-3.			2.5	24 h, Changed Daily

† Substrate Codes:

Cb-Q filter: Pallflex quartz filter impregnated with 1 mL of 0.5% sodium carbonate.

NaCl-Q filter: Pallflex quartz filter impregnated with 1 mL of 0.5% sodium chloride.

Nylon filter: Gelman nylasorb filter.

CbDo denuder (#nn): glass honeycomb, serial no "nn", coated with sodium carbonate, without glycerol.

CbDg denuder (#nn): glass honeycomb, serial no "nn", coated with sodium carbonate, with glycerol.

NaDo denuder (#nn): glass honeycomb, serial no "nn", coated with sodium chloride, without glycerol.

NaDg denuder (#nn): glass honeycomb, serial no "nn", coated with sodium chloride, with glycerol.

* Substrates were preceded by a Teflon impactor from network

Note: All of the glass honeycomb denuders are 8 mm in length with approximately 200 parallel sintered glass tubes. Those with serial numbers below 150 are used in Two-Week Sampler network.

Table 2-2 Configuration of Substrate Testing System for Claremont Study

2.2 Evaluation of the Organic Acids Leg of the Two-Week Sampler

Quartz filters were prepared in accordance with the Two-Week Sampler SOP provided in Appendix A. A 0.1M solution of potassium hydroxide in a 50/50 water/methanol mixture was used. The samples were otherwise prepared and stored as described in Section 2.1.1.

2.2.1 Organic Acids Leg Laboratory Evaluation

The laboratory evaluation involved the synthetic generation of PAN, as described previously, followed by introduction into the Two-Week Sampler Organic Acids Leg at the usual sampling flow rate. This was done at two concentration levels (typical and worst case), two temperatures (20°C and 40°C), and two humidities (20 and 80 percent). In addition, one experiment was performed using hydrochloric acid to evaluate the capacity of the hydroxide-coated filter. Samples were collected over one week intervals in order to evaluate break-through. The hydroxide-coated filters were analyzed for acetate by ion chromatography. In addition, samples were be withdrawn for immediate analysis (by a gas chromatograph and/or chemiluminescent NO-NO_x analyzer).

2.2.2 Organic Acids Leg Field Evaluation

Collection Interval Artifacts

The formate and acetate on the KOH-coated filters of the Organic Acids Leg (collected in quadruplicate) were compared with samples collected daily and composited over the two-week period. This provided an indication of potential sampling artifacts. Sampling was conducted in Riverside from late October to early November 1994, collocated with the field evaluation of the Main Leg of the Two-Week Sampler. A limited number of collocated carbonate-coated filters were sampled to determine whether they behaved in a similar manner to the hydroxide-coated ones (hydroxide may react with ambient levels of CO_2 to produce carbonate during prolonged sampling).

Two samplers were used to collect daily samples. All filters were analyzed (two were in each sampling cassette) from the Two-Week Samplers and from one of the One-Day Samplers. A total of ten back filters from the second daily sampler were analyzed to provide replicate comparisons and precision estimates.

Biogenic Degradation

The effect of biogenic degradation of acetate and formate from the filters collected from collocated samples over a two-week period was determined. Each filter pack consisted of the usual Teflon front filter followed by two KOH-coated quartz filters. Each collocated sampling interval of two weeks consisted of three filter packs. One of the second quartz filters was spiked with the equivalent of several ppb of formic and acetic acids (typical ambient concentrations) prior to sampling, one was spiked after sampling, and a third was not spiked at all. The spiking solution was 1000 ml of 50/50 water/methanol with the addition of 100 mg sodium acetate (72 mg as acetate) and 50 mg sodium formate (33 mg as formate). Two successive additions of 0.5 ml were pipeted on a quartz filter and dried by gentle warming from a heat gun. By comparing the formate and acetate concentrations between the two spiked filters after correction for the unspiked or blank filter, it was determined if losses occurred during the sampling.

Claremont Sampling

A long-path infrared spectrometer was used to measure formic acid during a month-long period from August 27-September 26, 1995 as part of a separately funded ARB study. During the second two week period, triplicate samples were collected using the Organic Acids Leg of the Two-Week Sampler. The KOH-coated front and back filters were analyzed separately for formate to compare formic acid measured with this technique with that of the spectroscopic method.

2.3 Design and Evaluation of a One-Day Sampler Based on a High Flow Rate Adaptation of the Two-Week Sampler

The Two-Week Sampler was designed for a specific purpose — to determine, at low cost, the annual averaged concentrations of nitric acid and fine particle inorganic ion species concentrations at a 12-site network. However, 24-hour time periods are used for most applications. Calculations for vapor collection by the denuder, based on Gormley-Kennedy relations, indicate that the denuder as currently configured could be operated at a flow rate as high as 3 ℓ/min. This is sufficient for 24-hour sampling in most urban locations. In fact, 3 ℓ/min is the sampling rate used in a previous study in the Los Angeles area (Solomon et al., 1988). These calculations indicate that the Two-Week Sampler could be readily adapted to 24-hour sampling. Further, the small size of the sampler could simplify the logistics when intensive sampling is desired.

Experiments with sampler components, and with several configurations of a prototype One-Day Sampler, were conducted to test the feasibility of adapting the Two-Week Sampler technology to 24-hour sampling. The specific issues evaluated in these tests were:

(1) The collection efficiency of the denuder at the higher flow rate to obtain the required sample volume within 24 hours;

(2) The performance of a new particle impactor, designed to maintain a 2.5 µm particle cut point at the increased flow rate;

(3) The penetration of particles through the cassette and denuder at the increased flow rate;

(4) The magnitude of interferences under field conditions.

Experimental methods are described below.

2.3.1 Laboratory Evaluation of Nitric Acid Penetration

Denuder collection efficiencies were evaluated in the laboratory under hot, dry conditions. The evaluation was conducted in the laboratory using nitric acid generated from a diffusion tube and injected into the denuder. A commercial NO-NO_X analyzer, sampling before and after the denuder, was used to determine the removal efficiency of the denuder at increasing flow rates until a noticeable drop in efficiency was observed.

2.3.2 Redesign and Evaluation of the Impactor

Because of the change in flow rate it was necessary to redesign the impactor precutter used to exclude coarse particles. Flow rate was selected on the basis of laboratory evaluation of denuder efficiencies, and then a new impactor was constructed to give the same fine particle cutpoint at the higher flow rate. The new impactor was calibrated using laboratory-generated polystyrene latex (PSL) particles, following the same experimental configuration as used for the testing of the Two-Week Sampler (Hering, 1993). In this configuration the penetration through the impactor of 2.35 µm PSL spheres was measured using an optical counter (Climet model 208, Redlands, CA) coupled to a pulse height analyzer board mounted within a personal computer (Nucleus Corp, model PCA, Oak Ridge, TN). The system is described in more detail by Lurmann et al. (1994). Small variations in the flow rate through the impactor were used to vary the particle Stokes number and thereby sweep through the entire collection efficiency curve. The data yielded both the cut point and the steepness of the efficiency curve.

2.3.3 Evaluation of Particle Losses

In the Two-Week Sampler, particles were lost to Teflon surfaces of the sampling cassette as a result of electrostatic effects. One expects these losses to be lower at higher flow rates. For the One-Day Sampler configuration, particle losses were determined by measuring the penetration of room air through the sampler. Losses were measured as a function of flow rate through the cassette. The experimental configuration used the Climet 208 particle counting system described above. An electrostatic precipitator allowed charged particles to be removed, to determine the mechanism responsible for the detection of particle losses (Luhrman, 1994).

2.3.4 Field Evaluation

Field tests of the One-Day Sampler, and of the One-Day Sampler denuders were conducted in Claremont from August 29 through September 12, 1995. Prior to this, feasibility tests were conducted by collecting two-day samples as part of the Riverside Study. Denuders were tested in the field by the operation downstream of a Teflon filter, in parallel with a nylon filter reference. This was done as part of the field experiment to test components of the Two-Week Sampler, as described in Section 2.1. One-Day Sampler denuders were incorporated into the same multi-legged Teflon test system described in that section. These consisted of tandem glass honeycomb denuders operated for 24 hours at 2.5 ℓ/min. Each day this study provided a double nylon filter pack, operated for 24 hours, as reference. Carbonate-coated backup filters allowed the determination of penetration through the denuder, and comparison with reference nylon filters allowed testing for positive artifacts. Both sodium chloride and sodium carbonate-coated denuders were tested.

A prototype One-Day Sampler was operated for 12 days during this two-week period. The purpose was to compare nitric acid values from the One-Day Sampler to results from other measurement methods, including a tunable diode laser absorption spectrometer (TDLAS), long path-length FTIR, and California Acid Deposition Monitoring Program (CADMP) sampler. Also, once fine particle sulfate data becomes available, the data can be used to evaluate particle penetration through the denuder under field conditions. Additionally, the nitric acid collected by the denuder was compared to that on the daily denuders collected by the multi-legged Teflon test system.

For the Claremont field study, four configurations of the One-Day Sampler were tested. There are two types of denuders. Those with ID numbers below 130 are etched with HF, as are Two-Week Sampler denuders. Those with ID numbers above 400 have been etched first with the HF, and then etched again with the same commercial etching solution used on the Harvard denuder systems. In addition, two types of coatings were tested, 2% Na_2CO_3 in 50/50 water/methanol with 1% glycerol, and 2% NaCl in 50/50 water/methanol with 1% glycerol. The NaCl denuders were always operated with a quartz filter impregnated with 1 ml of 0.5% NaCl in 50/50 water/methanol. The Na_2CO_3 coated denuders were operated with either a Nylasorb back filter or a NaCl impregnated quartz back filter. These same configurations, without the Teflon impactor, were operated on Leg 18. The One-Day Sampler and Leg 18 configurations are summarized in Table 2-3. A complete description of the field procedures are given in the field protocol, attached as Appendix B.

(a) Substrates used in Leg 18 of Substrate Testing System:Operated at 2.5±.5 L/min for 24 h

Day	First Two Substrates†	Third substrate
8/29	Tandem carbonate coated Denuders,SN#450, #449	Nylon Filter
8/30	Tandem carbonate coated Denuders, SN#121, #106	Nylon Filter
8/31	Tandem NaCl coated quartz filters	none
9/01	Tandem NaCl coated quartz filters	none
9/02	Tandem NaCl coated quartz filters	none
9/03	Tandem NaCl coated denuders, SN#115, #116	NaCl coated quartz filter
9/04	Tandem NaCl coated quartz filters	none
9/05	Tandem NaCl coated denuders, SN#453, #454	NaCl coated quartz filter
9/06	Tandem NaCl coated quartz filters	none
9/07	Tandem Nylon Filters	none
9/08	Tandem Nylon Filters	none
9/09	Tandem carbonate coated Denuders, SN#457, #458	none
9/10	Tandem carbonate coated Denuders, SN#11, #73	NaCl coated quartz filter
9/11	Tandem NaCl coated quartz filters	none

(b) Substrates used on One-Day Sampler

Day	First Two Substrates†	Third Substrate
8/29	Tandem carbonate coated Denuders, SN#451, #452	Nylon Filter
8/30	Tandem carbonate coated Denuders, SN#113, #105	Nylon Filter
8/31	Tandem NaCl coated Denuders, SN#448, #447	NaCl coated quartz filter
9/01	Tandem NaCl coated Denuders, SN#104, #96	NaCl coated quartz filter
9/02	none operated	-
9/03	Tandem NaCl coated Denuders, SN#117, #95	NaCl coated quartz filter
9/04	Tandem NaCl coated Denuders, SN#443, #444	NaCl coated quartz filter
9/05	Tandem NaCl coated Denuders, SN#459, #460	NaCl coated quartz filter
9/06	Tandem NaCl coated Denuders, SN#445, #446	NaCl coated quartz filter
9/07	none operated	-
9/08	Tandem carbonate coated Denuders, SN#101, #118	none
9/09	Tandem carbonate coated Denuders, SN#455, #456	none
9/10	Tandem carbonate coated Denuders, SN#82, #83	NaCl coated quartz filter
9/11	none	

† All denuders are glass honeycombs, 8 mm in length, and had ~1% glycerol in coating solution.

Table 2-3 Substrates Evaluated for One-Day Sampler in Claremont

3.0 RESULTS AND DISCUSSION

3.1 Evaluation of the Main Leg of the Two-Week Sampler

3.1.1 Laboratory Evaluation

PAN Penetration

These experiments were performed in order to determine whether PAN was a potential sampling artifact using the main leg of the Two-Week Sampler. Synthetically generated PAN was used to expose a sampling cassette consisting of a sodium carbonate-coated denuder followed by two sodium carbonate-coated quartz filters. The substrates were coated using the protocol in the EPI program and did not include glycerol in the coating mixture. Note that the Teflon filter normally used in the Two-Week Sampler's main leg was omitted since PAN retention was not expected. A second carbonate-coated quartz filter was used to better characterize the precision of the measurements made.

Table 3-1 presents the results obtained from measuring the PAN concentration at the inlet with a NO-NO_x analyzer and extracting and measuring the nitrate and nitrite on the denuder and filter extracts. These results are presented in $\mu g/m^3$, and all of the filter and denuder measurements were blank corrected. Dynamic blanks were obtained by exposing the sampling cassette to pure air alone for the same time and at the same flow rates as used for the PAN exposure tests.

Experiment 1bNaCl used a denuder coated with a 2 percent solution of sodium chloride; the filters were carbonate-coated as usual.

The percentage of PAN converted to both nitrite and nitrate is summarized in Table 3-2, and this percentage was estimated using the measured input concentration as the reference and blank-corrected filter data. The percentage of conversion when PAN alone was exposed to denuders was low, averaging 16 percent. Experiments 1b and 2aR did appear to be outliers, significantly raising this mean (mean w/o 1b & 2aR = 8%).

The addition of ozone to the exposure gas appeared to have a positive effect on the conversion of PAN on the denuder to nitrate. The filters were not affected in the same way, perhaps due to decomposition of ozone within the denuder. Adding nitrous acid resulted in some conversion to nitrite on the denuder and much more on the filters. Unlike the other tests, when nitrous acid was

Table 3-1 PAN Captured as Nitrite and Nitrate by Substrates of the Main Leg of the Two Week Sampler (blank corrected)

Exp	Start Date	Temp °C	RH	PAN µg/m^3	O_3 ppm	HONO µg/m^3	HCl ppm	Samp Vol m^3	Denuder NO_2^- µg/m^3	Denuder NO_3^- µg/m^3	Front Filter NO_2^- µg/m^3	Front Filter NO_3^- µg/m^3	Back Filter NO_2^- µg/m^3	Back Filter NO_3^- µg/m^3	Comments
1a	28-Apr	20	low	31	none	none	none	3.98	1.35	1.82	0.19	0.03	0.09	-0.06	NO_2^- den by color.
1b	21-Apr	40	low	37	none	none	none	4.01	0.44	7.30	0.32	-0.01	0.19	-0.03	
1bNaCl	21-Apr	40	low	37	none	none	none	3.98	-0.27	6.46	0.47	1.65	0.41	0.03	NaCl den,$NO_2^-$by col
2a	8-Mar	20	high	54	none	none	none	3.45	0.21	1.76	1.19	0.58	2.28	4.45	
2aR	19-May	20	high	29	none	none	none	4.01	3.71	1.86	0.38	-0.03	0.47	0.04	NO_2^- den by color.
3a	24-Mar	20	low	120	none	none	none	3.45	0.31	0.45	0.92	0.18	1.79	0.08	
3b	30-Mar	40	low	78	none	none	none	3.45	1.28	0.86	1.71	0.39	1.01	0.57	
3bR	14-Jul	40	low	146	none	none	none	4.08	2.16	1.60	1.15	0.05	2.10	0.12	
4a	17-Mar	20	high	128	none	none	none	4.03	0.44	1.88	1.10	0.21	0.67	0.03	
4b	6-Apr	40	high	44	none	none	none	4.03	0.96	0.29	0.86	0.19	1.12	0.07	
5	12-May	40	low	100	0.2	none	none	3.96	2.92	13.3	0.10	1.09	-0.08	0.76	NO_2^- den by color.
6	13-Apr	40	low	42	none	44	none	3.45	2.93	1.88	3.54	0.15	2.91	0.08	
7	14-Jun	40	low	67	0.2	23	none	4.54	-0.54	19	-0.05	2.66	-0.17	1.68	
8	7-Jul	40	low	89	none	none	0.05	3.87	0.68	3.39	0.39	0.01	0.49	0	

Table 3-2 PAN Percent Captured through the Substrates of the Main Leg of the Two Week Sampler

Exp	Temp °C	RH	PAN $\mu g/m^3$	O_3 ppm	HONO $\mu g/m^3$	HCl ppm	Denuder NO_2^- % converted	Denuder NO_3^- % converted	Front Filter NO_2^- % converted	Front Filter NO_3^- % converted	Back Filter NO_2^- % converted	Back Filter NO_3^- % converted	Sum NO_2^- % converted	Sum NO_3^- % converted
1a	20	low	31	none	none	none	11%	11%	2%	0%	1%	0%	14%	11%
1b	40	low	37	none	none	none	3%	39%	2%	0%	1%	0%	7%	38%
1bNaC	40	low	37	none	none	none	-2%	34%	3%	9%	3%	0%	4%	43%
2a	20	high	54	none	none	none	1%	6%	6%	2%	11%	16%	18%	25%
2aR	20	high	29	none	none	none	34%	13%	3%	0%	4%	0%	41%	13%
3a	20	low	120	none	none	none	1%	1%	2%	0%	4%	0%	7%	1%
3b	40	low	78	none	none	none	4%	2%	6%	1%	3%	1%	13%	5%
3bR	40	low	146	none	none	none	4%	2%	2%	0%	4%	0%	10%	2%
4a	20	high	128	none	none	none	1%	3%	2%	0%	1%	0%	5%	3%
4b	40	high	44	none	none	none	6%	1%	5%	1%	7%	0%	18%	2%
5	40	low	100	0.2	none	none	8%	26%	0%	2%	0%	1%	8%	30%
6	40	low	42	none	44	none	18%	9%	22%	1%	18%	0%	59%	10%
7	40	low	67	0.2	23	none	-2%	55%	0%	8%	-1%	5%	-3%	68%
8	40	low	89	none	none	0.05	-2%	7%	1%	0%	1%	0%	5%	7%
Means (w/o 1bNaCl,5-8)														
Mean High Temperature							4%	11%	4%	0%	4%	0%	12%	12%
Mean Low Temperature							10%	7%	3%	1%	4%	3%	17%	11%
Mean High RH							7%	4%	4%	1%	5%	3%	16%	7%
Mean Low RH							5%	11%	3%	0%	3%	0%	10%	12%
Overall Mean							7%	9%	3%	1%	4%	2%	15%	11%
Overall Mean (w/o 1b, 1bNaCl, 2aR, 5-8)							4%	4%	4%	1%	4%	3%	12%	7%

added, the back filters collected primarily nitrite. This was mostly likely due to the conversion of the nitrous acid, not enhanced PAN conversion. This phenomenon is discussed in the next section. Since the conversion percentage was low and did not vary from the initial denuder to the final filter, it was assumed that the collection efficiency for PAN is not large for these substrates. The combination of nitrous acid and ozone resulted in only nitrate being detected on the sampling substrates. This is most likely due to the oxidation of collected nitrite to nitrate by the ozone. The addition of hydrochloric acid had little or no effect on the PAN being collected on these substrates. The use of a NaCl-coated denuder appeared to have caused a significant conversion of PAN based on the single test conducted. More data would be needed to confirm this conclusion as several other outliers were observed.

HONO Penetration

These experiments were performed in order to determine whether HONO was a potential sampling artifact using the main leg of the Two-Week Sampler. Synthetically generated HONO was used to expose sampling cassettes configured as described in the previous section. It should be noted that the HONO used for exposure contained an equal molar amount of ammonia due to the method of generation. The effect of ammonia and other nitrogenous species, potentially generated using this approach, on the test results presented here is not known. Table 3-3 presents the results obtained from measuring the HONO concentration with a NO-NO_X analyzer and extracting and measuring the nitrate and nitrite on the denuder and filter extracts. These results are presented in $\mu g/m^3$ and all of the filter and denuder measurements were blank corrected. The blank data were those described in the previous section.

The percentage of HONO converted to both nitrite and nitrate is summarized in Table 3-4, and this percentage was estimated using the measured input concentration as the reference. Run 3a appears to be an outlier and was not used to calculate means. The carbonate-coated denuder collected a substantial amount of nitrous acid as nitrite, especially at low temperatures. The combination of the denuder and two back filters removed all of the nitrous acid, yielding a mean collection efficiency of 102 percent. As expected, the conversion by the sodium chloride-coated denuder did not occur. The addition of ozone apparently enhanced the denuder's collection efficiency and converted all collected nitrite to nitrate. Although there is insufficient data to treat statistically, it appears that high temperatures inhibit the trapping of nitrous acid by the denuder. High RH may have a similar but lower effect.

The data are inconsistent in several cases. The nitrate on the back filter in experiment 6 was much higher than that on the front filter or on the denuder or in the measure of input nitrous

Table 3-3 HONO captured as nitrite and nitrate by substrates of the Main Leg of the Two-Week Sampler (blank corrected)

Exp	Start Date	Temp °C	RH %	HONO µg/m^3	O_3 ppm	HCl ppm	Samp Vol m^3	Denuder NO_2^- µg/m^3	Denuder NO_3^- µg/m^3	Front Filter NO_2^- µg/m^3	Front Filter NO_3^- µg/m^3	Back Filter NO_2^- µg/m^3	Back Filter NO_3^- µg/m^3	Sum NO_2^- µg/m^3	Sum NO_3^- µg/m^3	Comments
1a	21-Jul	20	low	33	none	none	4.01	28.94	-0.3	0.27	-0.07	0.02	-0.32	29.23	-0.69	
1aNaCl	28-Apr	20	low	90	none	none	3.98	-0.41	-0.73	35	0.17	10.31	-0.07	44.94	-0.63	NaCl den,NO_2^- by color.
2a	19-May	20	high	14	none	none	4.01	15.34	0.54	0.6	0.05	0.27	0.27	16.21	0.86	NO_2^- by color.
3a	24-Mar	20	low	53	none	none	3.45	59.44	-0.46	128	0.26	21.41	0.18	208.69	-0.02	
3aR	12-May	20	low	38	none	none	3.96	45.54	0.31	2.71	0.03	2.44	-0.05	50.69	0.29	NO_2^- by color.
3b	30-Mar	40	low	116	none	none	3.45	69.34	-0.66	12.1	0.37	44.91	0.2	126.39	-0.09	
4a	5-May	20	high	86	none	none	3.98	75.64	-0.02	1.36	-0.06	0.6	0.01	77.6	-0.07	NO_2^- by color.
4b	6-Apr	40	high	93	none	none	4.03	37.14	-0.61	11.6	0.19	7.87	0.21	56.65	-0.21	
5	22-Jun	40	low	56	0.2	none	4.61	0.18	68.4	-0.01	1.21	-0.18	1.1	-0.01	70.71	
6	14-Jul	40	low	53	none	0.05	4.08	12.84	-0.29	9.51	0.04	84.31	0.97	106.66	0.72	

Table 3-4 HONO Percent Captured by Substrates of the Main Leg of the Two Week Sampler

Exp	Temp °C	RH %	HONO µg/m³	O_3 ppm	HCl ppm	Denuder NO_2^- % Converted	Denuder NO_3^- % Converted	Front Filter NO_2^- % Converted	Front Filter NO_3^- % Converted	Back Filter NO_2^- % Converted	Back Filter NO_3^- % Converted	Sum NO_2^- Converted	Sum NO_3^- Converted
1a	20	low	35	none	none	90%	-1%	1%	0%	0%	-1%	91%	-2%
1aNaCl	20	low	97	none	none	0%	-1%	40%	0%	12%	0%	51%	-1%
2a	20	high	15	none	none	112%	3%	4%	0%	2%	1%	118%	5%
3a	20	low	58	none	none	115%	-1%	246%	0%	41%	0%	402%	0%
3aR	20	low	41	none	none	122%	1%	7%	0%	7%	0%	136%	1%
3b	40	low	125	none	none	61%	0%	11%	0%	40%	0%	111%	0%
4a	20	high	91	none	none	90%	0%	2%	0%	1%	0%	92%	0%
4b	40	high	101	none	none	41%	0%	13%	0%	9%	0%	62%	0%
5	40	low	60	0.2	none	0%	91%	0%	2%	0%	1%	0%	94%
6	40	low	58	none	0.05	25%	0%	18%	0%	163%	1%	206%	1%
Means (w/o 1aNaCl,3a, 5,6)													
Mean High Temp						51%	0%	12%	0%	24%	0%	87%	0%
Mean Low Temp						103%	1%	4%	0%	2%	0%	109%	1%
Mean High RH						81%	1%	6%	0%	4%	1%	91%	1%
Mean Low RH						91%	0%	6%	0%	15%	0%	113%	0%
Overall Mean (w/o 1aNaCl,3a,5,6)						86%	0%	6%	0%	10%	0%	102%	1%

acid. The nitrite on the back filter in experiment 3b was also higher than the front filter, although not higher than the denuder. For experiment 3a, there was twice as much nitrite on the front filter than on the denuder. While the data from the three substrates indicated a nitrous acid concentration sufficiently high as to cause saturation, it was observed that the NO-NO_X analyzer provided a stable and consistent measure of the nitrous acid concentration, which was also quite stable with respect to time.

The overall mean (withholding data from experiments 1aNaCl, 5, and 6 which were set up differently and 3a, which was an obvious outlier) provides the most accurate picture of the magnitude of nitrous acid uptake. The total amount of nitrous acid measured on the substrates was 102% of that measured with the NO-NO_X analyzer. Most (86%) of the nitrous acid is removed by the denuder, 6% by the front filter, and 10% by the back filter.

3.1.2 Field Evaluation: Riverside Sampling of Filtered Air

The first phase of field testing was conducted in Riverside, California for the two week period beginning October 13, 1994. Table 2-1 lists the Two-Week Sampler substrates which were evaluated in this experiment. The substrates include two types of filter: carbonate-coated quartz and sodium chloride-coated quartz. Four types of denuder coatings were tested: carbonate and sodium chloride, with and without added glycerol. Each of these substrate combinations was collected in duplicate. A total of four impactor combinations were also tested individually: a pair of Teflon impactors, one with carbonate and the other with sodium chloride-coated quartz back filters; and a pair of Kevlar impactors, one with carbonate and the other with sodium chloride-coated quartz back filters. Each of these substrates was sampled for two weeks at a flow rate of 0.4 lpm. The results were compared to a double nylon filter which was changed daily. Additionally, leg 17 was used to collect replicate double nylon filters and a combination of One-Day Sampler denuders operated at 2 ℓ/min for two days each.

Table 3-5 presents the nitrate, nitrite, and sulfate blank-corrected concentration data from the sampling conducted in Riverside, and Table 3-6 summarizes the results for nitrate.

Precision

Figure 3-1 is a scatter plot of the sum of nitrate collected on one leg compared to that of the replicate leg for legs 1-16. With the exception of the nitrate collected on the legs with carbonate-coated denuders with glycerol, the precision of the replicate determinations was within ten percent. A great deal of variation was observed between the carbonate and sodium chloride-coated substrates.

Table 3-5 Species Concentration Data from Substrate Testing System: Riverside Two Week Values

				Volume	Ambient Concentrations ($\mu g/m^3$)		
ID	Substrate (Denuder#)†	Leg	Pos.	(m^3)	NO_2^-	NO_3^-	$SO_4^=$
043	Cb-Q filter	1	- 1	8.46	0.06	7.04	3.72
044	Cb-Q filter	1	- 2	8.46	-0.03	1.32	-0.15
045	Cb-Q filter	1	- 3	8.46	0.00	0.79	-0.03
046	NaCl-Q filter	2	- 1	8.54	0.00	1.48	0.89
047	NaCl-Q filter	2	- 2	#N/A	0.00	0.15	0.48
048	NaCl-Q filter	2	- 3	#N/A	0.00	0.10	0.53
051	CbDo denuder	3	- 1	#N/A	1.92	3.42	4.78
050	Cb-Q filter	3	- 2	#N/A	0.13	3.09	0.22
049	Cb-Q filter	3	- 3	#N/A	0.01	1.50	0.11
054	NaDo denuder	4	- 1	#N/A	ND	1.81	1.72
052	NaCl-Q filter	4	- 2	#N/A	ND	0.41	0.56
053	NaCl-Q filter	4	- 3	#N/A	ND	0.12	0.25
057	CbDg denuder	5	- 1	#N/A	2.26	2.74	4.21
055	Cb-Q filter	5	- 2	#N/A	0.01	2.31	-0.09
056	Cb-Q filter	5	- 3	#N/A	-0.03	1.06	-0.07
060	NaDg denuder	6	- 1	#N/A	ND	1.11	1.42
058	Cb-Q filter	6	- 2	#N/A	ND	0.44	0.59
059	Cb-Q filter	6	- 3	#N/A	ND	0.18	0.20
	T-Impactor						
061	Cb-Q filter	7	- 1	#N/A	0.12	6.31	3.49
062	Cb-Q filter	7	- 2	#N/A	-0.04	1.28	-0.05
	K-Impactor						
063	Cb-Q filter	8	- 1	#N/A	0.10	5.53	3.40
064	Cb-Q filter	8	- 2	#N/A	0.01	1.84	0.47
065	Cb-Q filter	9	- 1	#N/A	0.04	7.08	3.79
066	Cb-Q filter	9	- 2	#N/A	0.04	1.33	0.21
067	Cb-Q filter	9	- 3	#N/A	0.04	0.88	0.10
068	NaCl-Q filter	10	- 1	#N/A	ND	1.40	0.76
069	NaCl-Q filter	10	- 2	#N/A	ND	0.20	0.62
070	NaCl-Q filter	10	- 3	#N/A	ND	0.10	0.48
073	CbDo denuder	11	- 1	#N/A	0.25	2.12	3.33
071	Cb-Q filter	11	- 2	#N/A	0.06	4.45	0.65
072	Cb-Q filter	11	- 3	#N/A	-0.02	1.13	-0.10
076	NaDo denuder	12	- 1	#N/A	ND	1.10	2.41
074	NaCl-Q filter	12	- 2	#N/A	ND	0.46	0.45
075	NaCl-Q filter	12	- 3	#N/A	ND	0.17	0.30
079	CbDg denuder	13	- 1	8.15	0.65	2.44	3.13
077	Cb-Q filter	13	- 2	8.15	0.57	3.68	0.53
078	Cb-Q filter	13	- 3	8.15	0.01	1.40	0.14
082	NaDg denuder	14	- 1	8.46	ND	1.03	0.77
081	Cb-Q filter	14	- 2	8.46	ND	0.70	1.52

Table 3-5 Species Concentration Data from Substrate Testing System: Riverside Two Week Values

ID	Substrate (Denuder#)†	Leg	Pos.	Volume (m^3)	Ambient Concentrations ($\mu g/m^3$)		
					NO_2^-	NO_3^-	$SO_4^=$
080	Cb-Q filter	14	- 3	8.46	ND	0.11	0.22
	T-Impactor						
083	NaCl-Q filter	15	- 1	8.85	ND	1.03	0.90
084	NaCl-Q filter	15	- 2	8.85	ND	0.16	0.61
	K-Impactor						
085	NaCl-Q filter	16	- 1	8.46	ND	0.85	0.98
086	NaCl-Q filter	16	- 2	8.46	ND	0.17	0.63
Average of daily nylon front filter		18	- 1		0.12	2.67	1.12
Average of daily nylon back filter		18	- 2		0.14	0.67	0.71

† Substrate Codes:

Cb-Q filter: Pallflex quartz filter impregnated with 1 mL of 0.5% sodium carbonate.
NaCl-Q filter: Pallflex quartz filter impregnated with 1 mL of 0.5% sodium chloride.
Nylon filter: Gelman nylasorb filter.
CbDo denuder : honeycomb, coated with sodium carbonate, without glyecerol.
CbDg denuder : honeycomb, coated with sodium carbonate, with glyecerol.
NaDo denuder: honeycomb, coated with sodium chloride, without glyecerol.
NaDg denuder: honeycomb, coated with sodium chloride, with glyecerol.

Note: All of the glass honeycomb denuders are 8 mm long with approximately 200 parallel sintered glass tubes.

N.D. = No data due to interference of chloride using ion chromatography

		Repli-		NO_3^- Values ($\mu g/m^3$)			Ratio‡ of	Ratio‡ of
	First	cate					Pos. 1 to	Leg Sum to
Substrate†	Leg	Leg	Pos.	from First Leg	from Replicate	Average	Daily Nylon	Daily Nylon
Cb-Q filter	1	9	- 1	7.04	7.08	7.06	2.64	3.45
Cb-Q filter	1	9	- 2	1.32	1.33	1.33		
Cb-Q filter	1	9	- 3	0.79	0.88	0.84		
NaCl-Q filter	2	10	- 1	1.48	1.40	1.44	0.54	0.64
NaCl-Q filter	2	10	- 2	0.15	0.20	0.18		
NaCl-Q filter	2	10	- 3	0.10	0.10	0.10		
CbDo denuder	3	11	- 1	3.42	2.12	2.77	1.04	2.94
Cb-Q filter	3	11	- 2	3.09	4.45	3.77		
Cb-Q filter	3	11	- 3	1.50	1.13	1.32		
NaDo denuder	4	12	- 1	1.81	1.10	1.46	0.54	0.76
NaCl-Q filter	4	12	- 2	0.41	0.46	0.44		
NaCl-Q filter	4	12	- 3	0.12	0.17	0.15		
CbDg denuder	5	13	- 1	2.74	2.44	2.59	0.97	2.55
Cb-Q filter	5	13	- 2	2.31	3.68	3.00		
Cb-Q filter	5	13	- 3	1.06	1.40	1.23		
NaDg denuder	6	14	- 1	1.11	1.03	1.07	0.40	0.67
NaCl-Q filter	6	14	- 2	0.44	0.70	0.57		
NaCl-Q filter	6	14	- 3	0.18	0.11	0.15		
T-Impactor	7						2.36	2.84
Cb-Q filter	7		- 1	6.31		6.31		
Cb-Q filter	7		- 2	1.28		1.28		
K-Impactor	8						2.07	2.76
Cb-Q filter	8		- 1	5.53		5.53		
Cb-Q filter	8		- 2	1.84		1.84		
T-Impactor	15						0.39	0.45
NaCl-Q filter	15		- 1	1.03		1.03		
NaCl-Q filter	15		- 2	0.16		0.16		
K-Impactor	16						0.32	0.38
NaCl-Q filter	16		- 1	0.85		0.85		
NaCl-Q filter	16		- 2	0.17		0.17		
Average of front daily nylon filter:						2.67		
Average of back daily nylon filter:						0.67		

† See Table 3-7 for explanation of substrate codes.

¥ Leg 3 position 2 had Na-Q filter, Leg 11 position 2 had Cb-Q filter.

‡ Ratios calculated from Leg average

Table 3-6 **Summary of Nitrate Results from Substrate Testing System, Riverside Two Week Values**

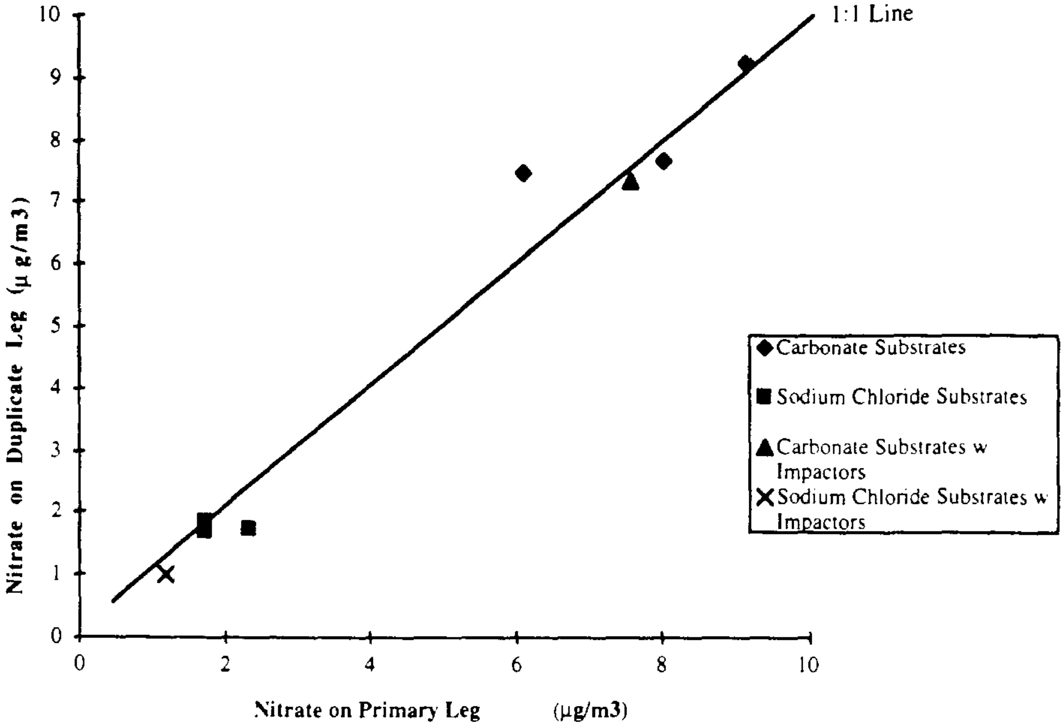

Figure 3-1 Sum of Nitrate on Series Substrates during Riverside Sampling

Reference Value

Nitric acid is a difficult species to measure due to potential sampling artifacts such as the volatilization of ammonium nitrate, condensation onto previously collected particulate matter and adsorption/desorption from the surfaces of sampling equipment. The most artifact free method is direct spectroscopy such as long path infrared. This is a labor intensive measurement that was conducted only during the daytime sampling intervals at Claremont. The sensitivity of the instrument is such that the detection limit is several ppb. Since peak concentrations are in the order of 20-30 ppb, measurements can therefore be made only during episodes of high concentration. For the studies of filtered ambient air described here, we are not concerned about artifact gains and losses of nitric acid, only the amount that is actually in the sample line. To determine the nitric acid, the nylon filter approach was chosen, which has been shown to collect nitric acid quantitatively with little artifact collection due to other nitrogenous species (Appel et al., 1980).

The reference value to which the two-week samples were compared is the mean from the first of the two tandem nylon filters which were changed daily, 2.67 μg/m^3. The back nylon filters consistently collected about 25 percent of the nitrate on the front filter, averaging 0.67 μg/m^3. Figure 3-2 is a scatter plot of the nitrate on the front filter compared to nitrate on the back nylon filter. No relationship between the two is evident. The source of this nitrate on the back filter is not clear. Nylon filters are generally quantitative with respect to nitric acid collection. If the back filter represents collection of another nitrogenous species, then the upper limit of nitrate on the front filter would average 2.00 μg/m^3. One cannot rule out, however, that this batch of nylon filters did not quantitatively remove nitric acid

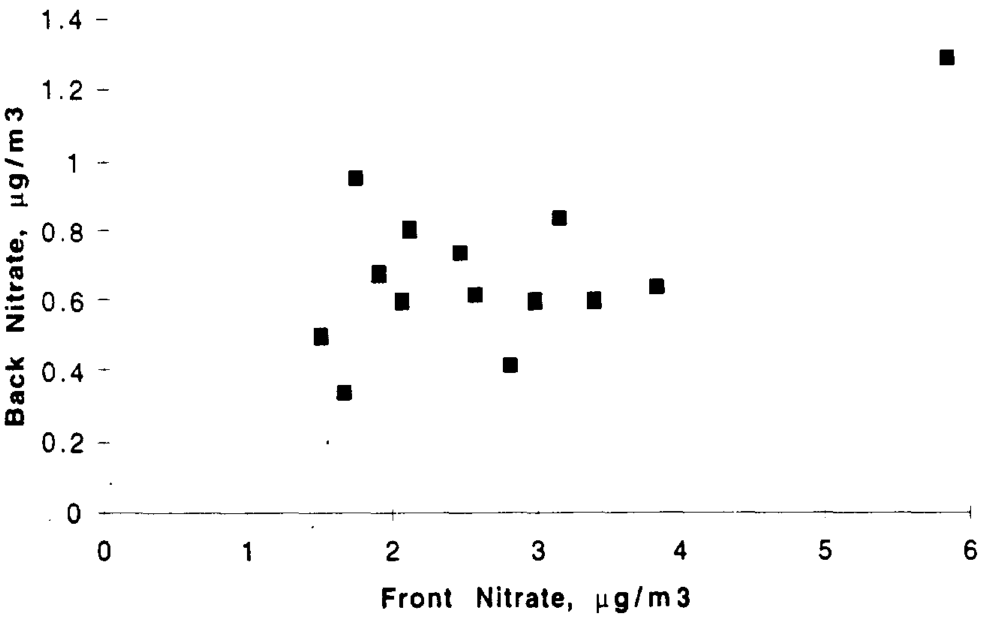

Figure 3-2 Scatter plot of nitrate on front vs. back nylon filters during Riverside sampling of particle free air

Results for Filter Substrates

Figure 3-3 summarizes the nitrate results comparing filters sampled for two weeks compared to the mean of the daily nylon front filter. The two-week filters without impactors were operated with three of the same type in series, while those with impactors had two in series. The horizontal line shows the average nitrate concentration of 2.67 $\mu g/m^3$ from the front nylon filter, which was changed daily. The nitrate on the back filter is most likely not a result of poor collection efficiency of the front filter. This conclusion is based on the nitrate collected on the triple sodium chloride-coated filters. The nitrate on the front sodium chloride-coated filter was 1.44 $\mu g/m^3$ or nearly 50 percent lower than the nitrate average of the front nylon filters. Relatively little nitrate was found on the second and third sodium chloride-coated filters, indicating high collection efficiency. The only other source of nitrate on the nylon filters would be the collection of a nitrogenous species other than nitric acid.

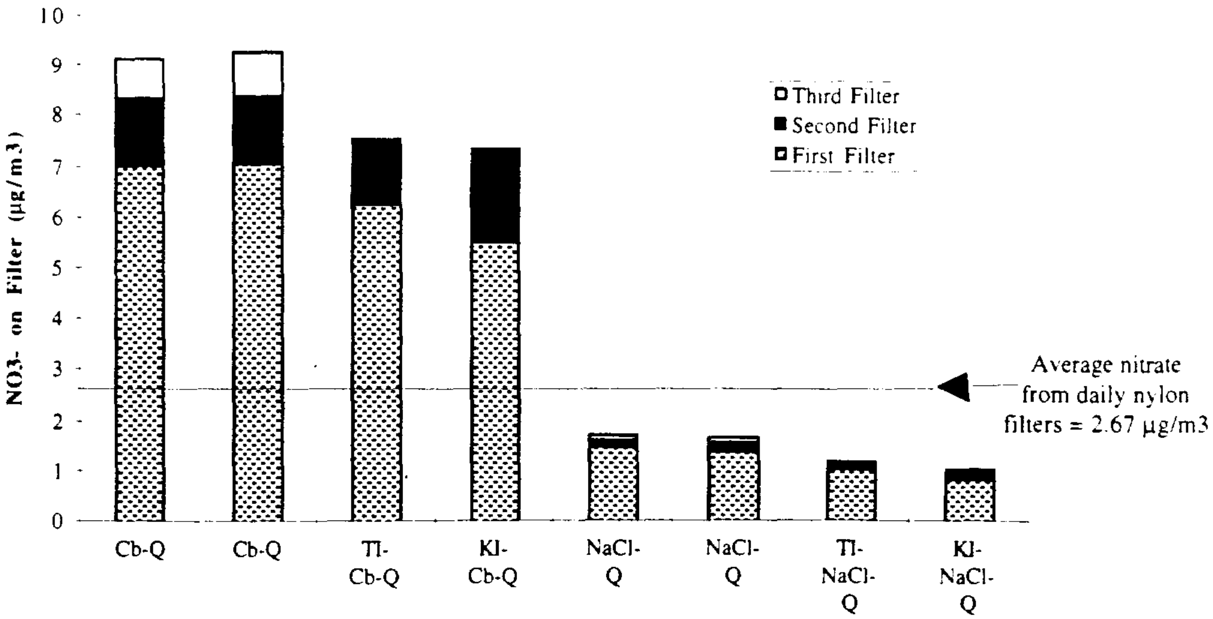

Figure 3-3 Nitrate measured in substrate testing system in Riverside for sodium carbonate-coated quartz filters (Cb-Q) and sodium chloride-coated filters (NaCl-Q); with and without a Teflon (Tl) or Kevlar (Kl) Impactor

The nitrate on the front carbonate-coated filter, 7µg/m^3 was over twice that of the front nylon filter average. The nitrate was much lower on the second and lower yet on the third carbonate-coated filters in this series, indicative of poor adsorption efficiency of a nitrogenous species other than nitric acid. The filters operated below both the Teflon and Kevlar impactors showed less nitrate than on the comparable filters without the impactors. The ratio of loss was higher with the sodium chloride-coated filters than carbonate-coated ones, but the amount of reduction was higher with the carbonate-coated filters. If the nitrate on the NaCl-coated filters is indicative of nitric acid, then the impactors are removing a significant amount of nitric acid and a smaller percentage of the nitrogenous species causing the high collection of nitrate by the carbonate-coated filters.

Results for denuders

Denuders were tested with four types of coatings: carbonate and sodium chloride, with and without glycerol. Figure 3-4 summarizes the results of the nitrate collected with these denuder combinations compared with the 2.67 µg/m^3 mean nitrate for the daily nylon front filters, shown by the horizontal line. In this case, the carbonate-coated denuder nitrate average was nearly the same as the mean from the nylon filters. Of interest is that the carbonate-coated denuders were the only substrates that also collected a significant amount of nitrite. It appears that these denuders were not as efficient at collecting the non-nitric acid nitrogenous species as the carbonate-coated filters, and that which was collected was only partially oxidized to nitrate. As with the sodium chloride-coated filters, the nitrate on the sodium chloride-coated denuders was much less than the nitrate mean of the daily nylon filters. In this case it was more than 50 percent lower, possibly indicating that the collection by sodium chloride denuders was less efficient than similarly coated filters.

Given the variability of the nitrate between replicates, one cannot determine whether glycerol had any effect on the collection efficiency.

3.1.3 Field Evaluation: Claremont Substrate Testing with Filtered Air

The second phase of field testing was done in Claremont, California for the two-week period beginning August 29, 1995. Simultaneous measurements of nitric acid by TDLAS, FTIR, CADMP and South Coast Air Quality Management District (SCAQMD) samplers provided additional measurements of ambient nitric acid concentrations during this measurement period.

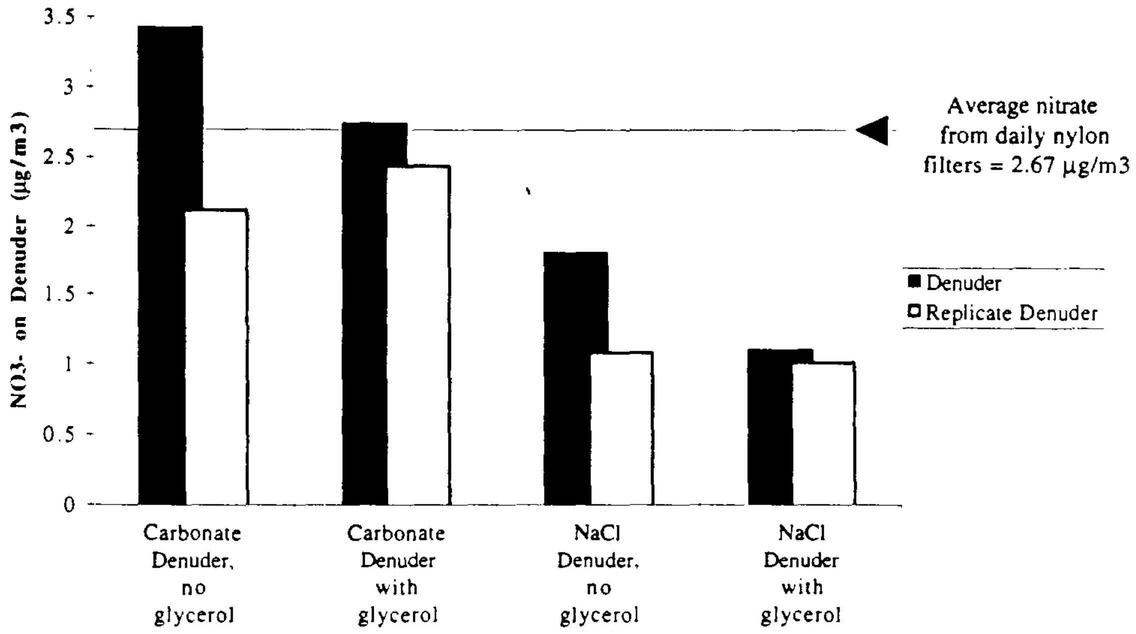

Figure 3-4 Nitrate measured in substrate testing system in Riverside for glass honeycomb denuders coated with sodium carbonate and sodium chloride, both with and without glycerol

The Two-Week Sampler substrates tested in these experiments are listed in Table 2-2. These included three types of filters: carbonate-coated quartz filters, sodium chloride-coated quartz filters and nylon filters. Four types of denuder coatings were tested: carbonate and sodium chloride, with and without glycerol. Each of these substrate combinations was tested in duplicate. Each was operated for two weeks at near 0.4 ℓ/min, and results are compared to a double nylon filter which was changed daily. Nitrate and sulfate concentration data from all substrates, and nitrite concentration data from the carbonate substrates and nylon filters are given in Table 3-7. The nitrate results are summarized in Table 3-8.

Table 3-7 Species Concentration Data from Substrate Testing System: Claremont Two-Week Values

ID	Substrate (Denuder#)†	Leg	Pos.	Volume (m^3)	Ambient Concentrations ($\mu g/m^3$) NO_2^-	NO_3^-	$SO_4^=$	Comment
095	Cb-Q filter	1	- 1	7.33	0.06	21.13	5.14	
096	Cb-Q filter	1	- 2	7.33	-0.05	3.24	0.10	
097	Cb-Q filter	1	- 3	7.33	-0.08	1.92	0.04	
101	NaCl-Q filter	2	- 1	6.98		12.41	-0.09	Cl^- high
102	NaCl-Q filter	2	- 2	6.98		3.50	-0.16	Cl^- high
103	NaCl-Q filter	2	- 3	6.98		1.85	-0.56	Cl^- high
107	CbDo denuder (#114)	3	- 1	6.89	0.14	14.28	2.86	
108	Na-Q filter	3	- 2	6.89		2.01	0.01	Cl^- high
109	Cb-Q filter	3	- 3	6.89	0.12	7.18	1.28	
113	NaDo denuder (<#100)	4	- 1	7.08		7.77	-0.03	approx. 1400 µg Cl-
114	NaCl-Q filter	4	- 2	7.08		5.96	-0.29	Cl^- high
115	NaCl-Q filter	4	- 3	7.08		1.30	-0.15	Cl^- high
119	NaDg denuder (#109)	5	- 1	6.67		9.71	0.31	approx. 1100 µg Cl-
120	NaCl-Q filter	5	- 2	6.67		3.68	-0.48	Cl- high
121	NaCl-Q filter	5	- 3	6.67		0.52	-0.71	Cl- high
125	CbDg denuder (#91)	6	- 1	7.07	0.16	12.11	2.07	
126	Cb-Q filter	6	- 2	7.07	0.24	9.92	2.60	
127	Cb-Q filter	6	- 3	7.07	-0.02	3.86	0.16	
131	Nylon filter	7	- 1	7.11	0.05	15.31	1.39	
132	Nylon filter	7	- 2	7.11	0.06	1.01	1.27	
133	Nylon filter	7	- 3	7.11	0.08	0.96	0.95	
137	CbDo denuder (<#100)	8	- 1	6.77	1.60	10.74	2.64	
138	Teflo filter	8	- 2	6.77	0.00	-0.01	0.07	
139	Cb-Q filter	8	- 3	6.77	0.07	4.10	0.16	
098	Cb-Q filter	9	- 1	6.75	0.21	23.90	5.24	
099	Cb-Q filter	9	- 2	6.75	-0.08	2.81	0.09	
100	Cb-Q filter	9	- 3	6.75	-0.09	2.23	0.08	
104	NaCl-Q filter	10	- 1	8.88		9.95	-0.17	Cl- high
105	NaCl-Q filter	10	- 2	8.88		1.52	-0.20	Cl- high
106	NaCl-Q filter	10	- 3	8.88		0.21	-0.25	Cl- high
110	CbDo denuder (#92)	11	- 1	7.95	0.04	14.58	2.73	
111	Cb-Q filter	11	- 2	7.95	0.15	8.79	1.49	
112	Cb-Q filter	11	- 3	7.95	-0.07	2.40	0.09	
116	NaDo denuder (#31)	12	- 1	7.89		8.95	0.24	approx. 380 µg Cl-
117	NaCl-Q filter	12	- 2	7.89		5.62	0.00	Cl- high
118	NaCl-Q filter	12	- 3	7.89		0.74	-0.32	Cl- high
122	NaDg denuder (#108)	13	- 1	8.01		9.50	0.14	approx. 1300 µg Cl-
123	NaCl-Q filter	13	- 2	8.01		4.03	-0.50	Cl- high
124	NaCl-Q filter	13	- 3	8.01		0.47	-0.58	Cl^- high
128	CbDg denuder (#93)	14	- 1	7.90	0.00	11.67	1.82	
129	Cb-Q filter	14	- 2	7.90	0.18	11.82	3.08	

Table 3-7 Species Concentration Data from Substrate Testing System: Claremont Two-Week Values

				Volume	Ambient Concentrations (µg/m3)			
ID	Substrate (Denuder#)†	Leg	Pos.	(m^3)	NO_2^-	NO_3^-	$SO_4^=$	Comment
130	Cb-Q filter	14	- 3	7.90	-0.05	2.75	0.06	
134	Nylon filter	15	- 1	7.81	0.00	16.05	1.30	
135	Nylon filter	15	- 2	7.81	0.00	1.02	1.26	
136	Nylon filter	15	- 3	7.81	0.06	0.95	0.98	
140	CbDo denuder (#119)	16	- 1	8.30	0.50	10.59	2.77	
141	Teflo filter	16	- 2	8.30	0.00	0.00	0.06	
142	Cb-Q filter	16	- 3	8.30	0.20	6.55	1.24	
Average of daily nylon front filter		17	- 1	-	0.05	16.03	0.35	*see Table 3-13 for*
Average of daily nylon back filter		17	- 2	-	0.05	0.47	0.05	*individual filter results*

† Substrate Codes:

Cb-Q filter: Pallflex quartz filter impregnated with 1 mL of 0.5% sodium carbonate.

NaCl-Q filter: Pallflex quartz filter impregnated with 1 mL of 0.5% sodium chloride.

Nylon filter: Gelman nylasorb filter.

CbDo denuder (#nn): honeycomb serial no "nn", coated with sodium carbonate, without glyecerol.

CbDg denuder (#nn): honeycomb serial no "nn", coated with sodium carbonate, with glyecerol.

NaDo denuder (#nn): honeycomb serial no "nn", coated with sodium chloride, without glyecerol.

NaDg denuder (#nn): honeycomb serial no "nn", coated with sodium chloride, with glyecerol.

Note: All of the glass honeycomb denuders are 8 mm long with approximately 200 parallel sintered glass tubes. Those with serial numbers below 150 are used in Two-Week Sampler network.

	First	Repli-		NO_3^- Values ($\mu g/m^3$)			Ratio‡ of Pos. 1 to	Ratio‡ of Leg Sum to
Substrate†	Leg	cate	Pos.	from First Leg	from Replicate	Average	Daily Nylon	Daily Nylon
Cb-Q filter	1	9	- 1	21.13	23.90	22.51	1.40	1.72
Cb-Q filter	1	9	- 2	3.24	2.81	3.02		
Cb-Q filter	1	9	- 3	1.92	2.23	2.07		
NaCl-Q filter	2	10	- 1	12.41	9.95	11.18	0.70	0.92
NaCl-Q filter	2	10	- 2	3.50	1.52	2.51		
NaCl-Q filter	2	10	- 3	1.85	0.21	1.03		
CbDo denuder	3	11	- 1	14.28	14.58	14.43	0.90	1.54
Na-Q, Cb-Q ¥	3	11	- 2	2.01	8.79	5.40		
Cb-Q filter	3	11	- 3	7.18	2.40	4.79		
NaDo denuder	4	12	- 1	7.77	8.95	8.36	0.52	0.95
NaCl-Q filter	4	12	- 2	5.96	5.62	5.79		
NaCl-Q filter	4	12	- 3	1.30	0.74	1.02		
NaDg denuder	5	13	- 1	9.71	9.50	9.61	0.60	0.87
NaCl-Q filter	5	13	- 2	3.68	4.03	3.85		
NaCl-Q filter	5	13	- 3	0.52	0.47	0.49		
CbDg denuder	6	14	- 1	12.11	11.67	11.89	0.74	1.63
Cb-Q filter	6	14	- 2	9.92	11.82	10.87		
Cb-Q filter	6	14	- 3	3.86	2.75	3.30		
Nylon filter	7	15	- 1	15.31	16.05	15.68	0.98	1.10
Nylon filter	7	15	- 2	1.01	1.02	1.02		
Nylon filter	7	15	- 3	0.96	0.95	0.96		
CbDo denuder	8	16	- 1	10.74	10.59	10.66	0.67	1.00
Teflon filter	8	16	- 2	-0.01	0.00	0.00		
Cb-Q filter	8	16	- 3	4.10	6.55	5.33		
Average of front daily nylon filter:						16.03		

† See Table 3-7 for explanation of substrate codes.

¥ Leg 3 position 2 had Na-Q filter, Leg 11 position 2 had Cb-Q filter.

‡ Ratios calculated from Leg average

Table 3-8 Summary of Nitrate Results from Substrate Testing System: Claremont Two-Week Values

Precision

Precision of the measurements is shown in Figure 3-5, which compares the sum of nitrate values from tandem substrates on the primary and replicate legs. With the exception of the measurement on the tandem sodium chloride filters, the differences in nitrate between the primary and replicates was less than 10%. In general, the variation among substrate types was much greater than between replicates.

Reference Value

The reference values to which the two-week samples are compared are those from the first of the two tandem nylon filters which were changed daily. The nitric acid concentration from the first of these filters averaged 16.0 $\mu g/m^3$ over the two-week period. The second, backup filter averaged 0.5 $\mu g/m^3$, and was always less than 4% of the front filter value. Precision of this measurement was checked on two days by operating a duplicate nylon filter pack on the One-Day Sampler Leg (Leg 18). The nitrate concentrations from the front nylon filters differed by 0.2% and 0.6%, which is better than the precision for flow rate measurement.

Results for Filter Substrates

Results for filter substrates operated for two weeks are compared to the daily nylon filter in Figure 3-6. The two-week filters were operated with three of the same type in series, and the nitrate concentration from each filter is shown. The horizontal line shows the average nitric acid concentration of 16.0 $\mu g/m^3$ measured by nylon filters changed daily. Carbonate impregnated quartz filters yielded the largest values, with an average of 22.5 $\mu g/m^3$ on the first filter, or 40% higher than the daily nylon. The second and third carbonate filters had comparable levels of nitrate. Nitrate levels on sodium chloride-coated filters were lower than the daily nylon filter, with the nitrate levels dropping sharply on one set of successive substrates, but not on the replicate set. While the first pattern indicates efficient collection, that from the replicate does not. It should be noted that the filters were coated with a 0.47 percent solution of sodium chloride for this study, while a 2 percent solution was used for the Riverside collection. The sum of the three tandem sodium chloride filters averaged 13.7 $\mu g/m^3$, or 86% of the daily nylon filter value. The two-week nylon filters were the closest to the daily nylon filter value, with an average of 15.7 $\mu g/m^3$ for the first filter, or 98% of the daily nylon. Backup nylon filters operated for two weeks were comparable, with no decrease from the second to the third filter. Values for the two-week operation ranged from 0.95 to 1.02 $\mu g/m^3$ nitrate, which is higher than those from the one-day operation.

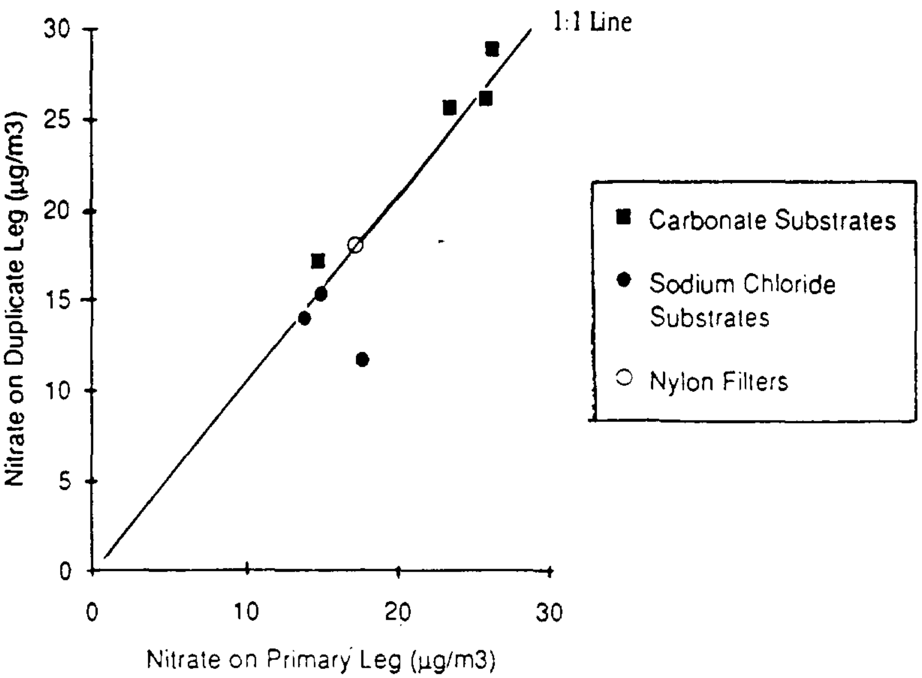

Figure 3-5 Comparison of sum of nitrate from tandem substrates on the primary leg of the Substrate Testing System in Claremont to that on the replicate leg

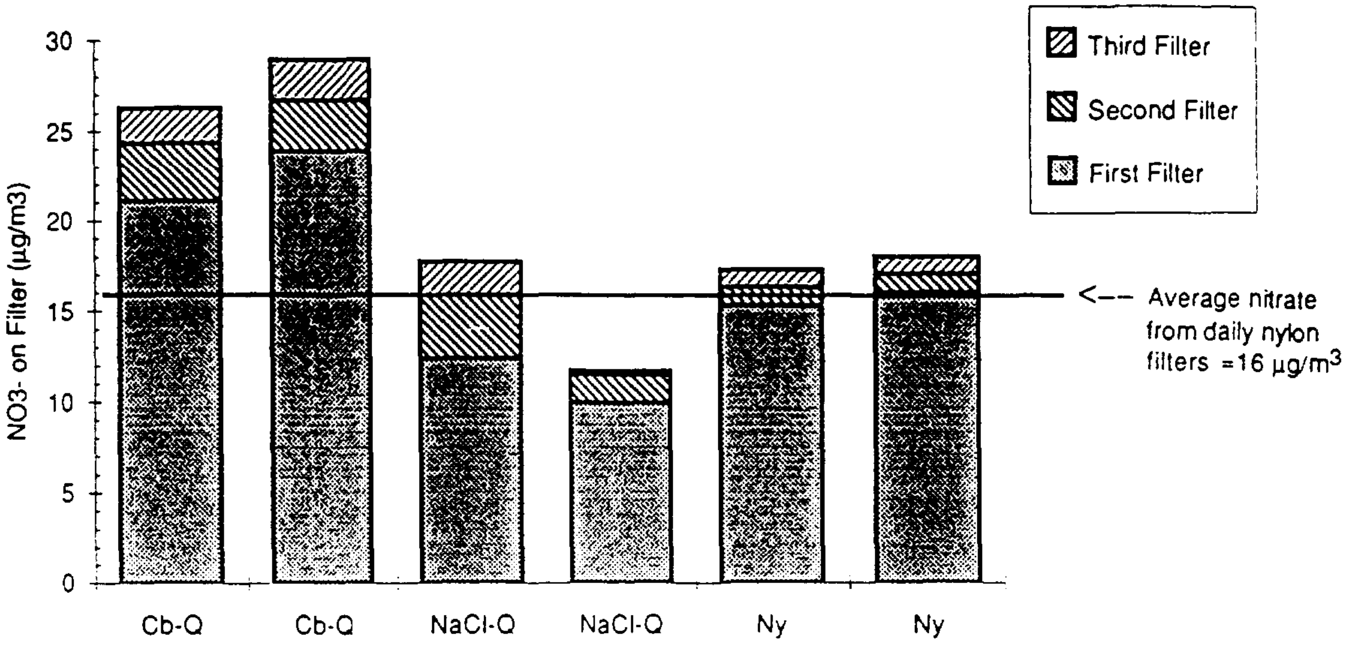

Figure 3-6 Nitrate measured in Substrate Testing System in Claremont for sodium carbonate-coated quartz filters (Cb-Q), sodium chloride-coated quartz filters (NaCl-Q) and Gelman Nylon filters (Ny); each operated in series of three

Results for Denuders

Denuders were operated with four types of coatings: carbonate and sodium chloride, with and without glycerol. Results for the two-week operation of the denuders are compared to the reference daily nylon filter value, indicated by the horizontal line, in Figure 3-7. As with the filter substrates, carbonate-coated denuders yielded higher nitric acid values than the NaCl coated denuders. The average value from the carbonate denuders without glycerol was 14.4 μg/m^3, (values from legs 8 and 16 were not used as they were preceded by an impactor) or 90% of the reference daily nylon value. Previous studies in Pasadena showed that HNO_3 measured by the glass denuder was 15% higher than that measured by the daily nylon filter. The carbonate denuder with glycerol averaged 11.9 μg/m^3, lower than that without glycerol. Nitrite values for carbonate denuder coatings with glycerol and those without glycerol were less than 0.2 μg/m^3, indicating that the difference in the conversion of captured nitrous acid to nitrate was not the reason for the difference between the two denuder coatings. This result differs from the Pasadena study (Luhrman et al., 1994) for which no difference was observed between carbonate denuders with and without glycerol coatings. The sodium chloride-coated denuders gave an average value of 9.0 μg/m^3, or 56% of the reference daily nylon filter value. This is consistent with the laboratory testing, described below, which showed that the sodium chloride denuders are not as efficient for the capture of nitric acid as are the carbonate-coated denuders.

3.2 Evaluation of the Organic Acids Leg of the Two-Week Sampler

3.2.1 Laboratory Evaluation

These experiments were performed in order to determine whether PAN is a potential sampling artifact using the Organic Acids Leg of the Two-Week Sampler. Synthetically generated PAN was used to expose a sampling cassette consisting of a pair of potassium hydroxide-coated quartz filters. The filters were coated using the protocol in the EPI program. It should be noted that the Teflon filter normally used in the Two-Week Sampler's Organic Acids Leg was omitted, since PAN adsorption was not expected on this filter.

Table 3-9 presents the results obtained by measuring the PAN input concentration with a NO-NO_x analyzer and extracting and measuring the acetate and formate on the filter extracts. The blank data, shown at the bottom of the table, were obtained by exposing the sampling cassette to pure air alone for the same time and at the same flow rates used for the PAN exposure tests.

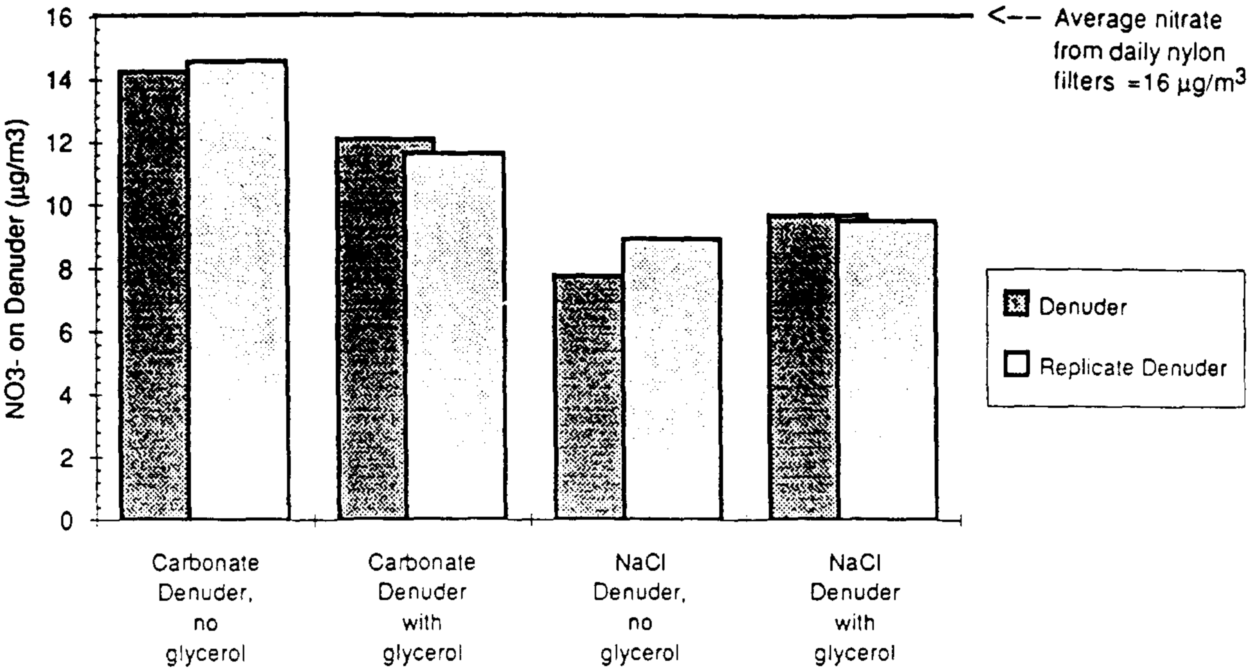

Figure 3-7 Nitrate measured in Substrate Testing System in Claremont for glass honeycomb denuders coated with sodium carbonate and sodium chloride, with and without glycerol

Table 3-9 PAN Acetate and Formate Deposition to Substrates of the Organic Acids Leg of the Two-Week Sampler

Exp	Start Date	Temp °C	RH	PAN μg/m^3	O$_3$ ppm	HONO μg/m^3	HCl ppm	Samp Vol	Front Filter $CH_3CO_2^-$ μg/m^3	Front Filter $CH_3CO_2^-$ % Converted	Front Filter HCO_2^- μg/m^3	Front Filter HCO_2^- % Converted	Back Filter $CH_3CO_2^-$ μg/m^3	Back Filter $CH_3CO_2^-$ % Converted	Back Filter HCO_2^- μg/m^3
1a	28-Apr	20	low	31	none	none	none	4.03	11.2	74%	<0.6	0%	8.46	56%	<0.6
1b	21-Apr	40	low	37	none	none	none	4.03	6.48	36%	<0.6	0%	11.1	62%	<0.6
2a	19-May	20	high	29	none	none	none	4.01	12.2	86%	<0.5	0%	11.4	81%	<0.5
3a	24-Mar	20	low	120	none	none	none	3.45	>41.4*	ND*	1.72	4%	11.2	19%	<0.6
3aR	21-Jul	20	low	164	none	none	none	4.01	20	25%	<0.5	0%	20.7	26%	<0.5
3b	30-Mar	40	low	78	none	none	none	3.45	45.2	119%	1.35	5%	24.8	65%	<0.6
4a	5-May	20	high	235	none	none	none	3.98	179	156%	7.34	8%	28.8	25%	<0.5
4b	6-Apr	40	high	44	none	none	none	4.03	8.19	38%	1.69	10%	10.7	50%	<0.6
5	12-May	40	low	100	0.2	none	none	3.96	3.84†	8%	<0.5	0%	8.54	18%	<0.5
5.5	13-Apr	40	low	42	none	0.01	none	4.03	13.1	64%	3.08	19%	13.5	66%	<0.6
6	7-Jul	40	low	89	none	none	0.05	3.86	29.3	68%	12	35%	24.7	57%	<0.5
Blank	30-Jun	40	low	0	none	none	none	4.6	<0.3		<0.5		<0.3		<0.5
Blank	30-Jun	40	low	0	none	none	none	4.6	<0.3		<0.5		<0.3		<0.5
Blank	30-Jun	40	low	0	none	none	none	4.6	<0.3		<0.5		<0.3		<0.5
* Column capacity exceeded, insufficient sample for reanalysis † Large peak eluting before acetate															
Means (w/o 3a,5,5.5 or 6)															
High Temperature										64%		5%		59%	
Low Temperature										85%		2%		47%	
High RH										94%		6%		52%	
Low RH										63%		1%		52%	
Overall Mean										76%		3%		52%	

All blanks were below the detection limit; therefore corrections of the data were not necessary. The data exhibit the following characteristics for this type of filter pack:

- The PAN measured with the NO-NO_X analyzer was consistently lower than the sum of the acetate measured on the filters.
- The overall filter removal efficiency was approximately 60% based on the ratio between the front and back filter acetate. The results show high variability which is generally consistent with previous studies conducted by Grosjean and Parmar (1990).
- Low temperature and high RH resulted in greater PAN removal efficiency
- The addition of ozone caused a large peak to elute before the acetate when the front filter was analyzed. This peak caused greater uncertainty in the quantification of the acetate concentration for this sample; neither the magnitude nor direction could be estimated. This effect was not observed on the back filter.
- Traces of formate were observed in the front filter while concentrations in the back filter were below the detection limit in all cases. The origin of the formate is not known. The single experiment with added hydrochloric acid showed the highest formate on the front filter, while the addition of nitrous acid gave the third highest. The addition of acid would be expected to lower the amount of formate trapped if it was to have any effect. The formate may also be due to impurities in the PAN preparation.

3.2.2 Field Evaluation

Collection Interval Artifacts

The objective of this study was to determine whether composited, daily potassium hydroxide filter packs would yield the same formate and acetate results as a single two-week sample. If these data sets were inequivalent, a sample collection artifact would be suspected for the Organic Acids Leg of the Two-Week Sampler. The daily sample used two collocated filter packs while the two-week sample consisted of four collocated samplers. During four of the days, the collocated daily sampler was loaded with sodium carbonate-coated filters to determine whether this material made a difference in the formate or acetate collected.

Table 3-10 presents the results of the formate and acetate analyses of the front and back coated filters. The filters collected on October 30th 1995 were believed to be uncoated as a result of an error committed by the back-up technician.

Table 3-10 Acetate and Formate Collected on the Organic Acids Leg of the Two-Week Sampler at Riverside (blank corrected)

Daily Filter Samples (Sampler1)					**Daily Filter Samples (Sampler2)**				
Date Started	Front Filter $CH_3CO_2^-$ μg/m^3	Front Filter HCO_2^- μg/m^3	Back Filter $CH_3CO_2^-$ μg/m^3	Back Filter HCO_2^- μg/m^3	Front Filter $CH_3CO_2^-$ μg/m^3	Front Filter HCO_2^- μg/m^3	Back Filter $CH_3CO_2^-$ μg/m^3	Back Filter HCO_2^- μg/m^3	Comments
10/21	10.41	5.16	2.00	0.00	10.84	4.68			
10/22	10.62	5.93	1.82	0.00	12.33	5.85			
10/23	13.82	8.11	3.49	0.00	16.47	8.29			
10/24	13.09	7.29	2.24	0.00	12.01	5.31			
10/25	7.85	5.51	1.18	0.00	8.41	4.98			
10/26	7.52	4.39	1.05	0.00	9.69	4.92			
10/27	14.36	8.25	2.92	0.00	14.87	7.34			
10/28	9.03	4.91	1.24	0.00	9.30	4.72			
10/29	9.00	5.47	1.67	0.00	11.07	5.54			
10/30	-0.59	0.00	7.69	1.41	-0.69	0.00			May not be coated filters
10/31	12.35	7.30	2.18	0.00	8.23	5.05	3.56	0.00	CO$_3$ Coated
11/01	8.36	3.72	1.38	0.00	9.47	3.89	1.45	0.00	CO$_3$ Coated
11/02	3.15	1.04	0.85	0.00	3.77	1.14	1.47	0.00	CO$_3$ Coated
11/03	3.30	1.43	1.51	0.00	4.54	1.19	1.67	0.00	CO$_3$ Coated
Mean w/0	**9.45**	**5.27**	**1.81**	**0.00**	**11.67**	**5.74**			KOH period
10/30					**6.50**	**2.82**	**2.04**	**0.00**	CO$_3$ period
Two-Week Filter Samples									
10/21	11.22	4.41	1.94	0.15					
10/21	14.37	4.96	2.94	0.23					
10/21	9.54	3.32	2.77	0.47					
10/21	8.98	3.03	2.31	0.21					
Mean	**11.03**	**3.93**	**2.49**	**0.27**					
Blanks:									
Mean KOH	3.11	1							Formate Bk 1/2 Det. Lim.
Mean CO$_3$	2.76	1							Formate Bk 1/2 Det. Lim.

The laboratory results supported this belief, and these data were not included in further data analyses. The mean filter blank for acetate was 3.11 μg/filter with a standard deviation of 1.9 for six hydroxide-coated filters, while that for formate was below the detection limit of 2 μg/filter. Data were corrected for these blanks values for all statistical calculations and plots (1 μg/filter was used for the formate blank).

Figure 3-8 is a scatterplot of the front filter acetate concentration of one daily sampler compared to the other. Application of the Wilcoxan Ranked Sum Test resulted in the conclusion that the two data sets cannot be assumed to be equivalent (the R+ value, 19, was only slightly smaller than the $T_{critical}$, 21). A linear regression was performed (less one point which was considered an outlier) yielding a regression coefficient squared of 0.92 with a slope of 0.99 and an intercept of 1.21. The regression equation indicates a slight positive bias of sampler #2 relative to sampler #1.

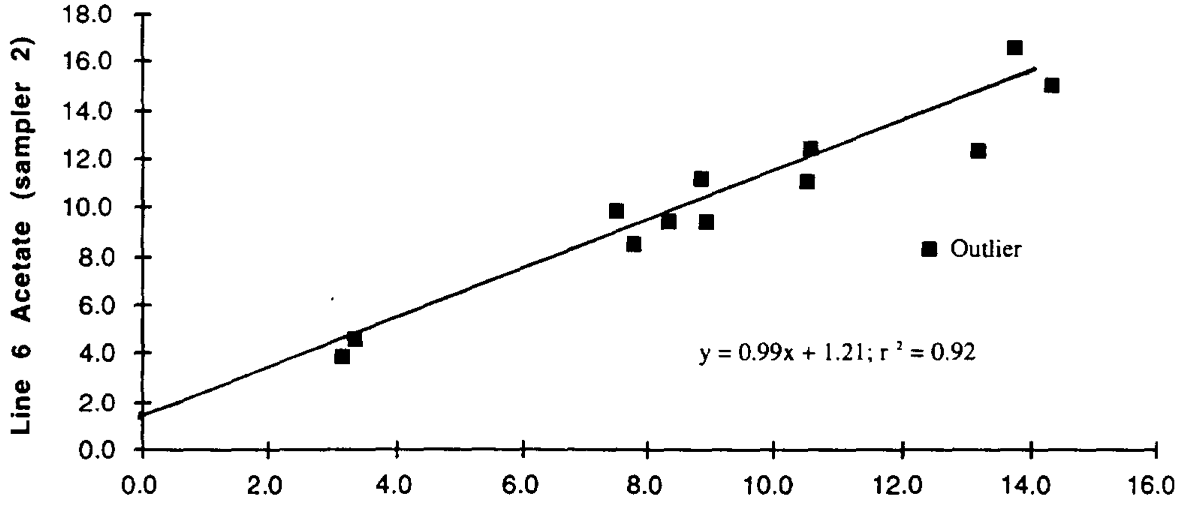

Figure 3-8 Line 1 (sampler 1) acetate vs Line 6 (sampler 2) acetate, front filters (blank corrected)

Figure 3-9 is a scatterplot of the front filter formate of one daily sampler compared to the other. Application of the Wilcoxan test in this case supports the hypothesis that the data sets are equivalent (R+ was 64.5 and R- was 26.5, both above the $T_{critical}$ of 21). Precision of the acetate and formate sampling was calculated using the collocated daily samples and by calculating the standard deviation of the percentage difference between the pairs and dividing by the square root of two (since both measurements must be considered equally imprecise). For acetate the precision was 18%, while for formate it was 13%. These values are somewhat higher than the two major sources of uncertainty, the flow rate (estimated 5% uncertainty) and analytical quantification (less than 6% uncertainty based on network operations).

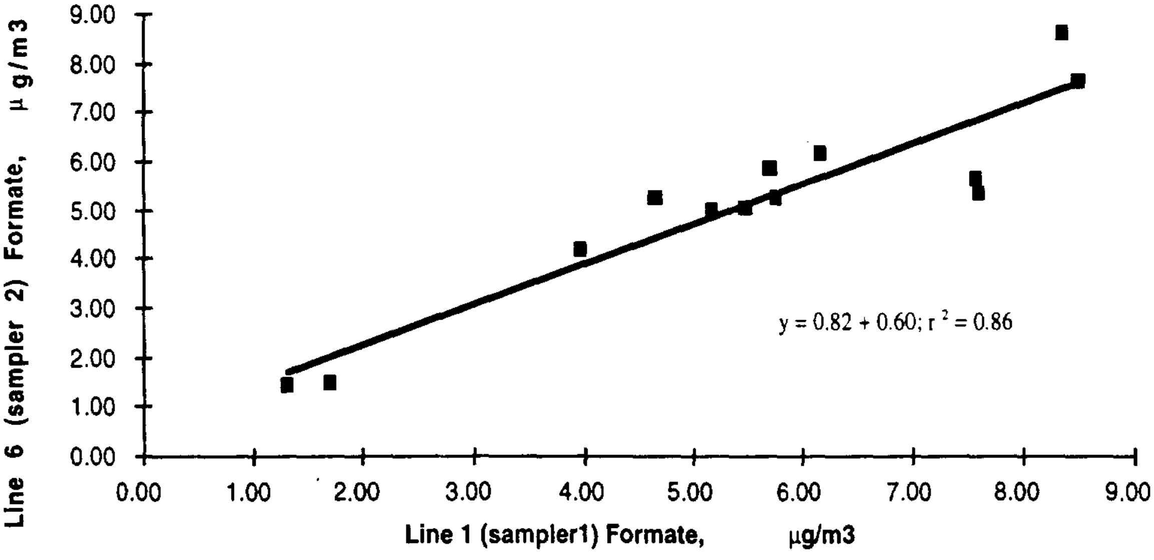

Figure 3-9 Line 1 (sampler 1) Formate vs Line 6 (sampler 2) Formate, front filter (blank corrected)

The relative standard deviation of the four two-week collections was 22 percent for acetate and 23 percent for formate. The daily composited acetate concentration on the front filter was 9.5 ± 1.7 $\mu g/m^3$ (only sampler #1 was used for compositing results since sampler #2 used a carbonate coating during four collection periods) while the mean acetate for the four two-week samples was 11.0 ± 2.4 $\mu g/m^3$ Since these are within the experimental uncertainty, a sampling interval-based collection artifact is therefore unlikely. Similarly, the daily composited formate concentration on the front filter was 5.3 ± 0.7 $\mu g/m^3$ compared to 3.9 ± 0.9 $\mu g/m^3$ mean of the four two-week samples.

The acetate on the back filter was consistently about 20% of that on the front filter for both the daily and the two-week sampling intervals. Figure 3-10 is a plot of this data.

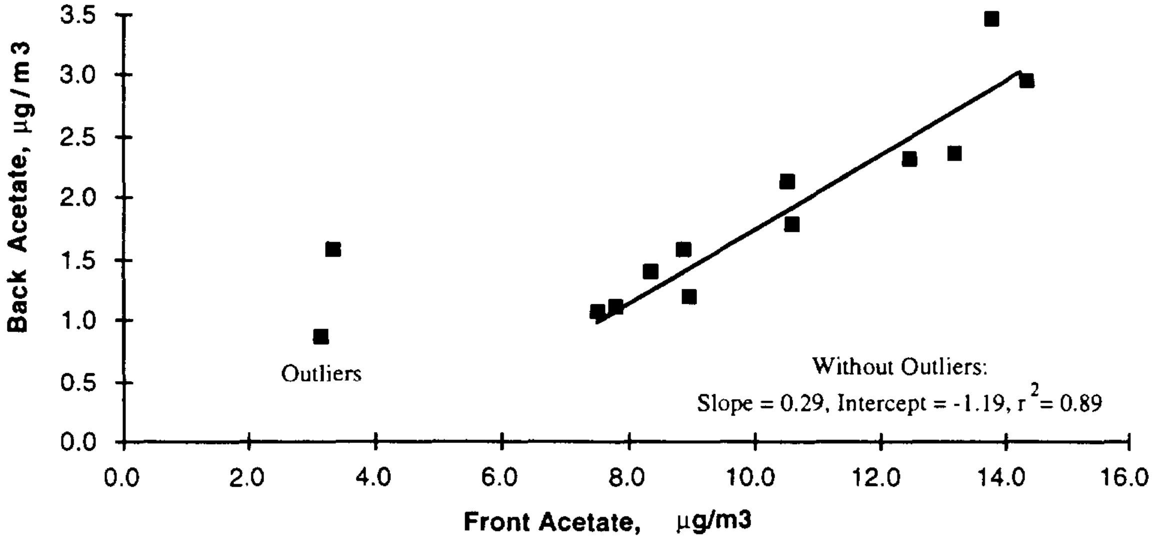

Figure 3-10 Scatter Plot of Front Filter vs Back Filter Acetate (blank corrected)

By comparison, no significant formate was observed for any of the back filters. This result differs from that of Kawamura et al., (1985) who showed the collection efficiency of formic acid to be approximately 80% on the first of two filters. The front and back acetate concentrations appear to be linearly related, with a correlation coefficient of 0.82, a slope of 0.17 and an intercept of 0.2 $\mu g/m^3$, as shown in the figure. It should be noted that the two lowest acetate concentrations appear to be outliers. Without these two pairs, the correlation coefficient increased to 0.94, the slope to 0.28 and the intercept to -1.08. These results are in reasonable agreement with laboratory studies that showed the collection efficiency for acetic acid to be approximately 80% for hydroxide-coated filters (Kawamura et al., 1985). The intercept could either indicate a change in collection efficiency with concentration or that both acetic acid and PAN are being removed, but with different efficiencies (the laboratory tests suggested a PAN efficiency of 60%). Without knowing an accurate PAN concentration, the amount of the interference cannot be determined, but it is likely to be significant since PAN concentrations are generally in a similar concentration range (Williams and Grosjean, 1990).

The data from Table 3-10 also show that the carbonate-coated filters yielded similar results to those from the hydroxide-coated filters. Due to the limited data set, meaningful statistical comparisons were not possible. In addition, two of the days were the low acetate days for which the fraction on the back filter was not in agreement with the rest of the data set. Since carbonate-coated filters showed little affinity for PAN in laboratory testing, the acetate on these back filters would most likely be due to acetic acid penetrating the front filter, whereas with the hydroxide-coated filters the origin of the acetate is more likely to be a combination of PAN and acetic acid.

Biogenic Degradation

The objective of this study was to determine whether biodegradation of formate or acetate occurred during or after sample collection. Three Organic Acids Leg sampling cassettes (Teflon filter followed by a front and back potassium hydroxide-coated quartz filter) of the Two-Week Sampler were run collocated. One back filter was spiked with formate and acetate before collection, one was spiked after collection, and the third was not spiked at all. Three such sample collections were made, one in the winter of 1994, one in the spring of 1995 and the final one in the summer of 1995. Due to a communication error, the same spiking solution was used for all three tests. It was stored at room temperature but sealed.

Table 3-11 summarizes the results of the acetate and formate analyses for this sampling. Several features of this data set are immediately apparent. First, the spike was not fully recovered in any of the samples. Second, the formate and acetate on the 'spiked-before' filter in the third study appear to be anomalously low. The acetate recovered was even less than the acetate expected from the sampling as shown by the unspiked sample. The quality of the data can be estimated from evaluating the values for acetate and formate on the front filter for each study since these are essentially triplicate collocated samples. While the spread among each triplicate is about 20%, (the average relative standard deviation was 12% for acetate and 25% for formate) several outliers are observed. The most prominent is filter number three in the second study, which has twice the formate of the other two filters, but approximately the same amount of acetate.

Table 3-11 Summary of Formate and Acetate Analysis for the Biodegradation Study

Filter Use	Sample Vol, m^3	Formate µg	Formate µg/m^3	Acetate µg	Acetate µg/m^3	Comments
Organic Acid Decomposition Study #1				Formate Spike = 33 µg		
Start Date February 3, 1995				Acetate Spike = 72 µg		
#1-Front	8.00	21.00	2.62	46.30	5.78	
#1-Back	8.00	2.31	0.29	6.49	0.81	Not Spiked
#2-Front	8.00	15.30	1.91	34.60	4.32	
#2-Back	8.00	33.20	4.15	54.80	6.85	Spiked Before
#3-Front	8.18	13.50	1.65	33.00	4.03	
#3-Back	8.18	30.00	3.67	49.80	6.08	Spiked After
Blank-Front		<2		5.79	0.72	Blank
Blank-Back		<2		2.08	0.26	Blank
Mean, Front			**2.06**		**4.71**	
Standard Deviation,Front			**0.50**		**0.94**	
Formate % Recovery = 94 before,84 after;Acetate % Recovery= 67 before, 60 after						
Organic Acid Decomposition Study #2						
Start Date April 13, 1995						
#1-Front	8.10	14.70	1.81	35.40	4.37	
#1-Back	8.10	<2	<0.25	15.20	1.88	Not Spiked
#2-Front	8.04	13.90	1.73	32.90	4.09	
#2-Back	8.04	13.00	1.62	39.50	4.91	Spiked Before
#3-Front	7.98	28.70	3.59	36.10	4.52	
#3-Back	7.98	17.00	2.13	32.40	4.06	Spiked After
Blank-Front		<2		<1.5		Blank
Blank-Back		<2		<1.5		Blank
Mean, Front			**2.38**		**4.33**	
Standard Deviation,Front			**1.05**		**0.22**	
Formate % Recovery = 39 before,50 after;Acetate % Recovery= 34 before, 24 after						
Organic Acid Decomposition Study #3						
Start Date July 18, 1995						
#1-Front	7.82	46.50	5.94	64.30	8.22	
#1-Back	7.82	<2	<0.25	42.20	5.39	Not Spiked
#2-Front	7.98	54.60	6.84	79.80	10.00	
#2-Back	7.98	7.70	0.96	33.20	4.16	Spiked Before
#3-Front	7.86	53.40	6.79	81.30	10.34	
#3-Back	7.86	24.50	3.12	103.80	13.20	Spiked After
Blank-Front		<2		<1.5		Blank
Blank-Back		<2		<1.5		Blank
Mean, Front			**6.53**		**9.52**	
Standard Deviation,Front			**0.50**		**1.14**	

A sampling error is therefore unlikely. Since the blank values are near the detection limit, contamination is also unlikely. The most probable cause of the error is therefore the laboratory analysis.

In order to assess the potential for laboratory error, we spiked three identical filters with the spiking solution (originally expected to deliver 33 µg formate and 72 µg acetate to the filters) and had them analyzed by the laboratory. The results are shown below in terms of µg/filter:

	Sample 1	**Sample 2**	**Sample 3**
Acetate	32.8	30.8	32.5
Formate	15.5	6.8	14.4

The results are consistent except for the formate of sample #2, which was unexpectedly low. There is no rationalization for this result. This experiment showed that significant formate and acetate remained in solution in spite of the many months of storage, although the concentrations of the spiking solution may have dropped by approximately half. Since random outliers are probable, in addition to a rather large precision value, (as shown by the standard deviation of front filter analyses) further statistical treatment of the limited ambient data set would not be conclusive. For the first two experiments the 'spiked before' and 'spiked after' formate and acetate were within the measurement precision based on the front filters (25% and 12% respectively). The overall conclusion is that laboratory uncertainties are probably larger than any biogenic degradation. Biogenic degradation, based on these experiments, cannot be assessed until the analytical method precision and data quality are better quantified and improved.

Claremont Comparison Study

Ambient samples were collected from three replicate Organic Acids Legs during the second two-week period of a special study conducted at Claremont under separate ARB funding. During this study formic acid was measured with an FTIR during the daytime periods only. Concentrations were significant at the time measurement periods were started and stopped. Therefore it was not possible to compare the formic acid measured using the FTIR directly with that determined from the two-week sampling period. During this period the mean formic acid determined by analyzing the first KOH-coated back filter from the Two-Week Sampler was 9.7 µg/m^3, with a standard deviation of 0.1 µg/m^3 (based on the triplicate sample). No formate was detected on the second back filter.

3.3 Design and Evaluation of a One-Day Sampler Based on a High Flow Rate Adaption of the Two-Week Sampler

For many applications, 24-hour sampling rather than two-week sampling is needed. Therefore, the all-glass honeycomb denuder used in the Two-Week Sampler was adapted to the higher flow rates needed for collection of 24-hour samples. Results are given below for theoretical and experimental analysis of denuder and inlet performance. It was not the objective of these studies to produce a final sampler, but to the test the feasibility of one-day sampling using this technology.

3.3.1 Configuration of the One-Day Sampler

The configuration of all of the One-Day Samplers tested in this study followed the design shown in Figure 3-11. Analogous to the Two-Week Sampler, the One-Day Sampler employs a Teflon impactor mounted in the inlet of a Savilex Teflon filter holder. The Teflon impactor is similar in design to that of the Two-Week Sampler, with a single jet impinging onto a glass frit; however, the jet diameter was enlarged to 0.226 cm to accommodate the larger flow rate. The impactor is followed by two glass honeycomb denuders and an adsorbing backup-filter operated in series. The second denuder is added to determine break-through of nitric acid. These all-glass honeycombs are 8 mm in length, and consist of approximately 200 sintered tubes. The length of the denuder was evaluated on the basis of theory and on laboratory studies described below. These tests included both sodium carbonate and sodium chloride coatings for the denuders. In field tests described below, four different sampler configurations were tested, using two types of denuders and two types of coatings. Only one type of impactor was tested.

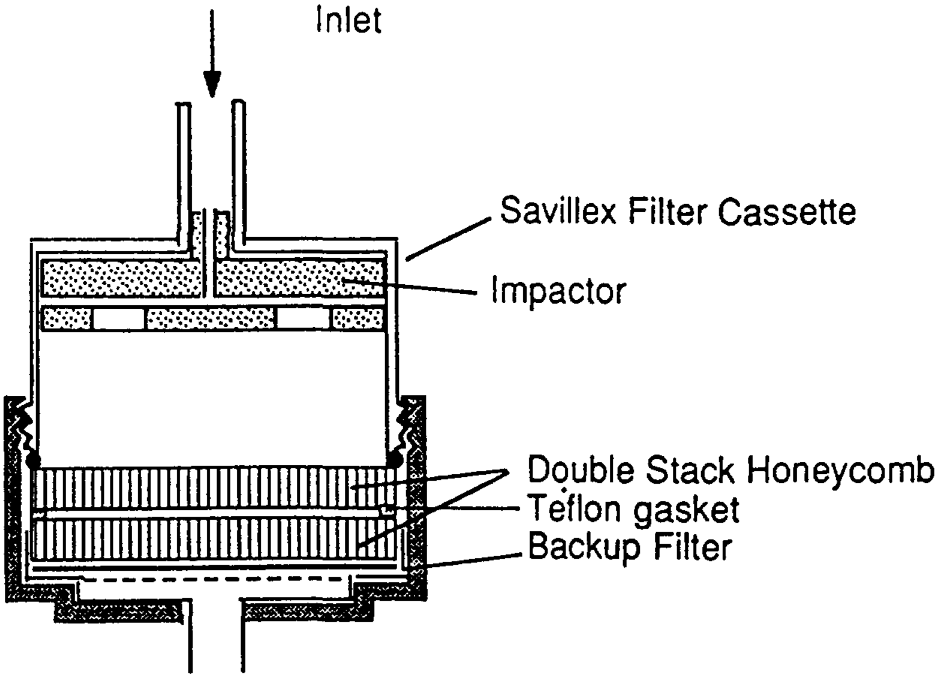

Figure 3-11 Schematic of the One-Day Sampler showing impactor precutter, tandem denuders and backup filter housed in Teflon filter cassette

3.3.2 Theoretical Considerations for the One-Day Sampler Denuder

The required length of the denuder for the One-Day sampler was estimated using diffusion theory. For laminar flow, the collection efficiencies in the honeycomb denuders depend on the number of tubes, overall length, flow rate, and diffusion coefficient. Using the Gormley-Kennedy relationship (Gormley and Kennedy, 1949), collection efficiencies were calculated for nitric acid using the geometry of the glass honeycomb used in the Two-Week Sampler, as shown in Table 3-12.

Table 3-12. Theoretical HNO_3 Collection Efficiencies for Honeycomb Denuder

Honeycomb Length	Flow Rate		
	3 ℓ/min	4 ℓ/min	5 ℓ/min
8 mm	99.4	97.9	95.6
14 mm	99.98	99.9	99.5

These calculations show that the collection efficiency at 3 ℓ/min for the 8 mm honeycomb may be sufficient to capture nitric acid adequately. In practice, actual collection efficiencies can differ from theoretical values because adsorption efficiency of the reactive gas may not be 100%, and because theory does not account for collection on the top surface of the honeycomb. The first effect tends to decrease collection efficiencies, while the second effect increases it. Thus, experimental evaluation is needed. It should be noted that particles are not collected by diffusion in the denuder because of their low diffusion coefficient. The Gormley-Kennedy relationship shows less than 1% capture of 0.05 µm diameter particles, and less than 0.2% capture for particles above 0.2 µm, for the conditions outlined in Table 2-3.

3.3.3 Laboratory Evaluation of Denuder Nitric Acid Penetration

This laboratory experiment was conducted to determine the efficiency of a single carbonate or chloride-coated honeycomb denuder prior to initiating field evaluations. The experiment was conducted at room temperature and used matrix air at both 10 and 50 percent relative humidity. The synthetically generated nitric acid was added to obtain a nominal concentration of 35 ppb. This should be the highest concentration that the denuder would be subjected to while sampling ambient air, and this is therefore the most severe test of the denuder's efficiency in removing nitric acid. A NO-NO_X analyzer was used to determine nitric acid concentrations before and after the honeycomb in order to determine the penetration through the denuder. The flow rates were varied from 0.6 to 5.6 ℓ/min.

Figure 3-12 is a graphical summary of the results. This graph shows several features of the denuder:

- The denuder penetration does not drop to zero, but appears to plateau around five percent. This does appear to be real, although small drifts of the analyzer from zero or minor leakage could prevent the air exiting the denuder from reaching zero NO_X concentrations. Since the air in the laboratory generally contained 50-100 ppb of NO_X, this plateau could be caused by a ten percent leakage of the filter holder.

- Nitric acid penetration is low at the design flow rate. At about 3 ℓ/min the penetration starts to increase as predicted by the Gormley-Kennedy expression.

- The scrubbing efficiency for NaCl is much more flow dependent, with the penetration increasing rapidly after 2ℓ/min. This is consistent with results obtained from an ARB-sponsored project to develop a new acidic species sampler (Fitz 1996).

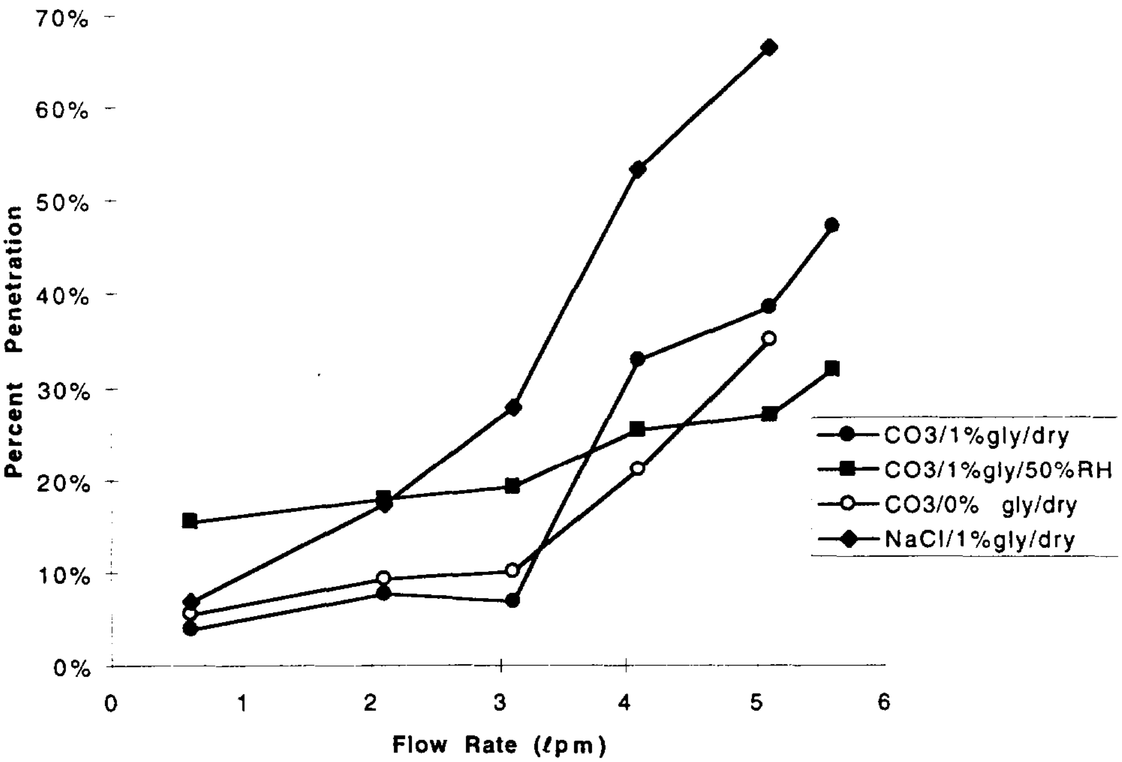

Figure 3-12 Penetration of Nitric Acid through Honeycomb Denuders

3.3.4 Redesign and Evaluation of the Impactor

Based on the laboratory testing of denuder performance, a flow rate of 2.5 ℓ/min was selected for the evaluation of the One-Day Sampler prototype. For this flow rate, a fine particle precut was designed using an impactor with the same geometry as for the Two-Week Sampler, but with a larger jet. The jet diameter, 0.226 cm, was calculated from the Stokes number, as described by Marple and Rubow (1986) and others. The collection efficiency of the impactor was measured in the laboratory using polystyrene latex spheres. As shown in Figure 3-13, the measured 50% collection efficiency cutpoint for the impactor is 2.1 µm at a flow rate of 2.5 ℓ/min. This compares with the 2.35 µm cutpoint of the Two-Week Sampler.

3.3.5 Evaluation of Particle Losses

The One-Day Sampler uses Teflon surfaces to minimize deposition of nitric acid in the inlet; however, Teflon readily carries an electric charge, and may be a sink for particles due to electrostatic deposition. Particle losses were evaluated by measuring the penetration of room air particles through the cassette, impactor, and denuder. Particle losses by number count (determined by the OPC) as a function of flow rate are shown in Figure 3-14. At 2.5 ℓ/min flow the losses are less than 5% by particle number. At 0.4 ℓ/min losses are 15% by particle number, as observed earlier (Hering, 1993). When charged particles were removed by an electrostatic precipitator, the particle losses were eliminated. Thus, those losses observed are attributed to electrostatic deposition. Electrostatic losses preferentially affect the smaller, more mobile particles. When these losses are evaluated as a percentage of particle mass, rather than as a percentage of particle number, the losses are smaller because the mass median diameter is larger than the number median diameter. The larger particles, which account for the majority of the particle mass, are not lost as readily as the smaller particles, which account for the majority of the particle number. For the Two-Week Sampler, the 15-20% loss by particle number at 0.4 ℓ/min corresponded to a 5% loss of particle mass. Correspondingly, the 5% loss of particle number at 2.5 ℓ/min is expected to lead to a loss of less than 2% of the particle mass.

3.3.6 Field Evaluation

3.3.6.1 Initial Riverside One-Day Denuder Testing

The feasibility of using the standard 8 mm denuder at higher flow rates was tested during the Riverside sampling tests as leg 17 of the filtered-air testing apparatus. Samples of denuders followed by a nylon back filter were run for two consecutive days at a nominal flow rate of 2 ℓ/min.

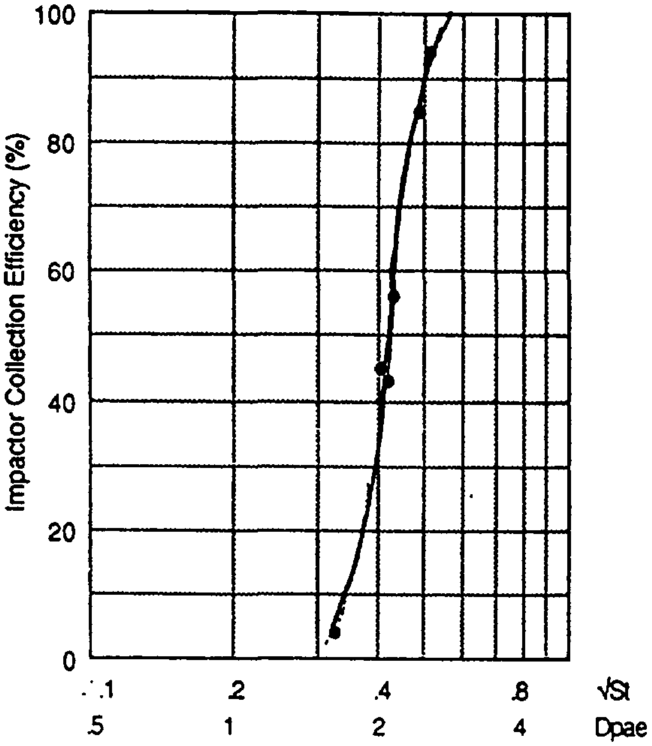

Figure 3-13 Collection efficiency for the impactor precutter of the One-Day Sampler, shown as a function of Stokes number, and particle diameter at a flow rate of 2.5 ℓ/min

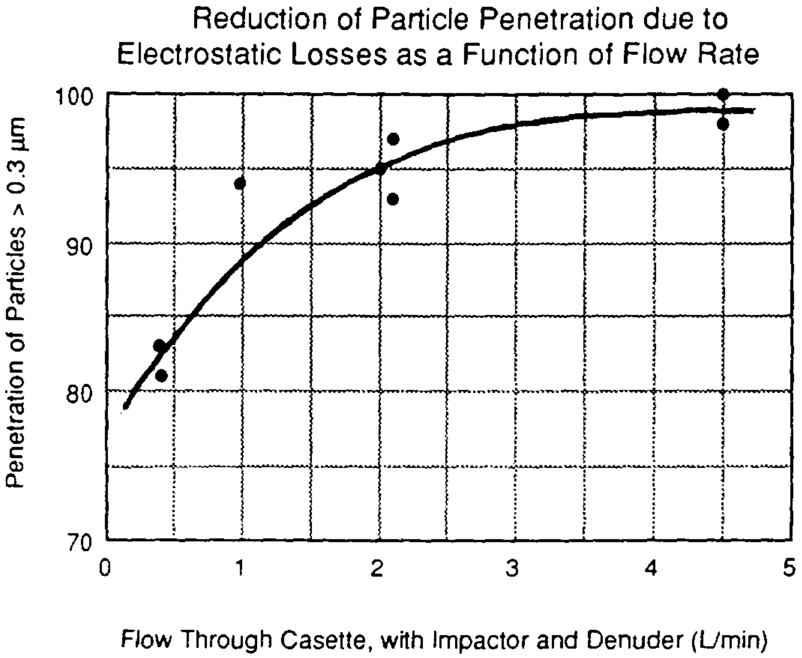

Figure 3-14 Particle penetration through the One-Day Sampler cassette

Table 3-13 shows the nitrite, nitrate, and sulfate data. Since the nylon back filters from dual nylon filter packs were found to contain a significant amount of nitrate, the amount of nitrate on the nylon filter behind the denuder cannot be used as a measure of denuder efficiency.

		Blank Corrected Concentrations,µg/m^3		
Substrate	Period	NO_2	NO_3	SO_4
NaCl Denuder with gly	1	0.00	0.69	0.91
Nylon Back Filter	1	0.01	0.77	0.41
CO_3 Denuder with gly	2	0.75	1.16	1.26
Nylon Backfilter	2	0.02	0.47	0.09
NaCl Denuder	3	0.00	1.05	0.56
Nylon Back Filter	3	0.09	1.25	0.77
CO_3 Denuder	4	1.41	2.46	3.48
Nylon Back Filter	4	0.63	1.20	0.30
NaCl Denuder with gly	5	0.00	1.40	0.56
Nylon Back Filter	5	0.11	1.31	1.39
CO_3 Denuder with gly	6	1.69	2.66	3.43
Nylon Backfilter	6	0.23	1.47	0.24
Nylon	1	0.13	1.97	1.05
Nylon Back Filter	1	0.19	0.87	0.32
Nylon	2	0.08	1.85	0.80
Nylon Back Filter	2	0.03	0.66	0.26
Nylon	3	0.04	1.72	0.54
Nylon Back Filter	3	0.04	0.59	0.30
Nylon	4	0.08	2.01	0.75
Nylon Back Filter	4	0.15	0.64	0.43
Nylon	5	0.10	2.26	0.90
Nylon Back Filter	5	0.28	0.66	0.71
Nylon	6	0.27	2.66	0.97
Nylon Back Filter	6	0.21	0.56	0.67

Table 3-13 Summary of measurements made with the One-Day Sampler denuders operated at Riverside for two days at 2 ℓ/min

Table 3-14 summarizes the nitrate data and shows ratios to the nylon/nylon filter pack collected daily and averaged for two days (denuder vs front nylon filter from nylon/nylon filter pack; denuder back nylon filter vs nylon back filter from nylon/nylon filter pack). It also shows the ratio of the denuder nitrate to its nylon filter nitrate. The ratio of the nitrate on the carbonate denuder to that of the front nylon filter of the nylon/nylon filter pack (0.95) was in good agreement with the samples collected for two weeks at 0.4 ℓ/min (1.00). In addition, the ratio on the sodium chloride denuder to that of the front nylon filter (0.53) was also in good agreement with the two-week data (0.47). It can therefore be concluded that the denuder efficiency does not significantly change when the flow rate is changed from 0.4 to 2ℓ/min in agreement with the theoretical calculations.

Substrate	Period	NO_3 µg/m^3	Ratio to front nylon of Nylon/Nylon Filterpack	Ratio to back nylon of Nylon/Nylon Filterpack
NaCl Denuder with gly	1	0.69	0.35	
Nylon Back Filter	1	0.77		0.89
CO_3 Denuder with gly	2	1.16	0.63	
Nylon Backfilter	2	0.47		0.71
NaCl Denuder	3	1.05	0.61	
Nylon Back Filter	3	1.25		2.12
CO_3 Denuder	4	2.46	1.22	
Nylon Back Filter	4	1.20		1.88
NaCl Denuder with gly	5	1.40	0.62	
Nylon Back Filter	5	1.31		1.98
CO_3 Denuder with gly	6	2.66	1.00	
Nylon Backfilter	6	1.47		2.63
Chloride Denuder Average			0.53	
Carbonate Denuder Average			0.95	

Table 3-14 **Summary of nitrate measurements made with the One-Day Sampler denuders operated at Riverside for two days at 2 lpm**

3.3.6.2 Claremont Field Evaluation of the One-Day Sampler

Two types of field evaluations were conducted in the Claremont study. First, substrates for the One-Day Sampler were compared against daily nylon filters for sampling of filtered ambient air. These tests were done as part of the multi-legged Teflon substrate testing system used to test the Two-Week Sampler substrates. Second, a prototype One-Day Sampler was operated on 12 of the 14 sampling days directly on ambient air. Several different denuders and filter substrates were tested in both systems. To the greatest extent possible, the same type of denuder or filter substrate was tested in the substrate testing system as was used in the sampler.

Sample Integrity Checks

As part of the field quality assurance procedures, field technicians were directed to simultaneously read the flow rate at the inlet and exit of each sample cassette. For the substrate testing cassettes on Legs 17 and 18, these readings were done before each cassette was installed. For the One-Day Sampler, these readings were done at the beginning and end of every sample. The simultaneous readings were done to provide a check for leaks in the sample cassettes and these readings are presented in Figure 3-15. For all but one sample, the flow rate downstream of the filter cassette was approximately the same as upstream, indicating no significant leaks. The data for the one sample which showed a much higher downstream flow than at the inlet was discarded.

Substrate Evaluation

Substrates for the One-Day Sampler were evaluated in the multi-legged Teflon substrate testing system shown in Figure 2-2. At Claremont, Legs 17 and 18 were used for tandem nylon filters and for One-Day Sampler substrates respectively. Denuders were always operated with two of the same type, with the same coating, in tandem. The ion concentrations for each of the substrates for Legs 17 and 18 are given in Table 3-15.

The nitric acid value from each set of denuders is calculated assuming equal collection efficiencies on each denuder, as follows:

$$[\mathrm{HNO3}] = \frac{[\mathrm{D1}]}{1-\frac{[\mathrm{D2}]}{[\mathrm{D1}]}} \qquad (1)$$

where [D1] and [D2] are the nitrate concentrations for the first and second denuder, respectively. This approach was compared to that obtained by summing all three substrates for this Leg of the sampler, and the results agreed within 8%, with no systematic difference between the two approaches. The method of Equation (1) was used because it can be applied universally to ambient sampling by the One-Day Sampler, and to cases where the backup filter was mistakenly not installed. Nitrate results are summarized in Table 3-16.

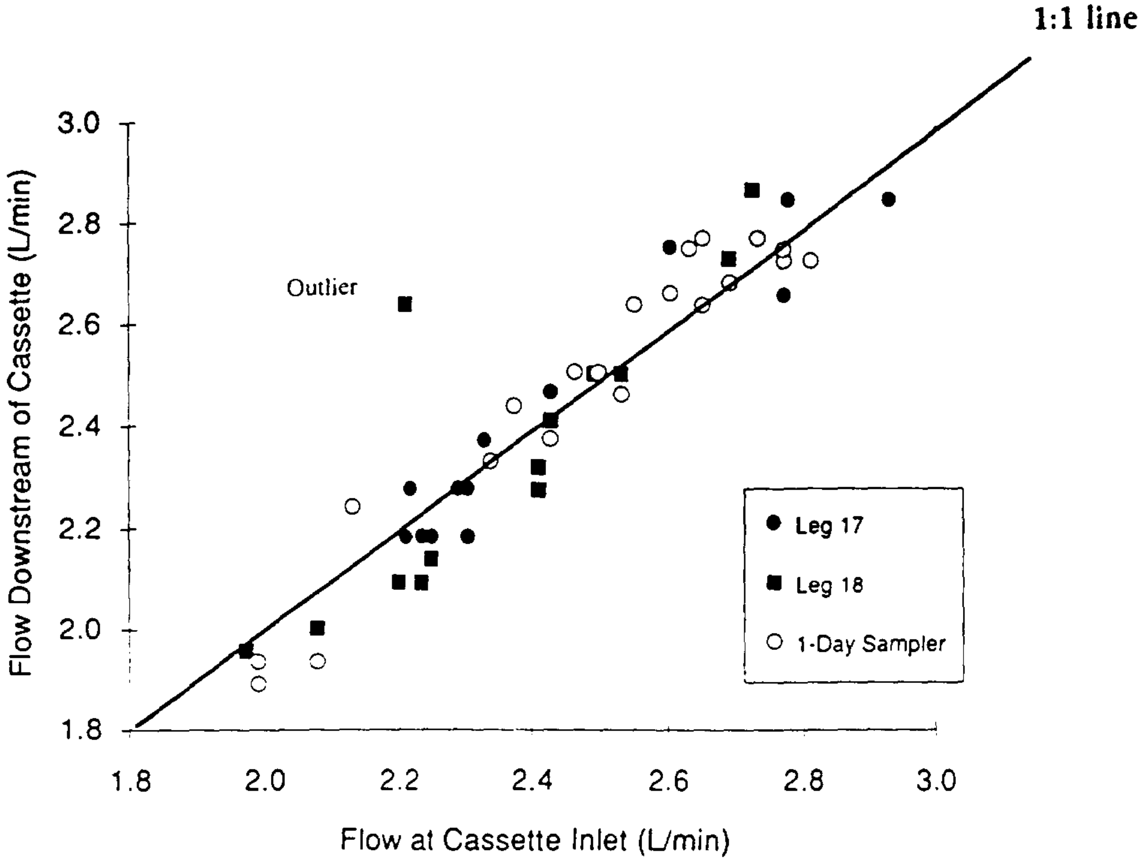

Figure 3-15 Results of inlet and inline flow checks done as part of the field quality assurance procedures at Claremont, showing one outlier

Table 3-15 Species Concentration Data from Daily Samples on Substrate Testing System at Claremont (Legs 17 and 18)

Leg	Start Date	Substrates, Positions 1 & 2	Vol. (m^3)	Results ($\mu g/m^3$) for First Filter ID	NO_2^-	NO_3^-	$SO_4^=$	Results ($\mu g/m^3$) for Second Filter ID	NO_2^-	NO_3^-	$SO_4^=$	
17	8/29	Tandem nylon filters	3.46	001	0.15	14.00	0.43	002	0.28	0.35	0.44	
17	8/30	Tandem nylon filters	2.37	009	0.21	32.84	0.88	010	0.32	0.83	1.02	
17	9/09	Tandem nylon filters	3.73	075	0.00	11.75	0.67	076	0.20	0.44	0.61	
17	9/10	Tandem nylon filters	4.07	081	0.12	12.26	0.58	082	0.22	0.56	0.60	
17	9/03	Tandem nylon filters	3.51	035	0.00	18.84	0.61	036	0.16	0.48	0.69	
17	9/05	Tandem nylon filters	3.58	050	0.14	12.92	0.42	051	0.27	0.35	0.47	
17	8/31	Tandem nylon filters	3.63	017	0.14	18.91	0.48	018	0.26	0.45	0.55	
17	9/01	Tandem nylon filters	3.68	024	0.12	19.49	0.60	025	0.14	0.59	0.72	
17	9/02	Tandem nylon filters	3.70	031	0.10	24.49	0.57	032	0.18	0.61	0.67	
17	9/04	Tandem nylon filters	3.89	043	0.14	16.18	0.58	044	0.19	0.48	0.64	
17	9/06	Tandem nylon filters	3.51	058	0.19	7.57	0.77	059	0.29	0.31	0.79	
17	9/11	Tandem nylon filters	3.76	089	0.15	20.91	0.44	090	0.30	0.47	0.52	
17	9/07	Tandem nylon filters	3.70	065	0.12	10.17	0.68	066	0.18	0.33	0.68	
17	9/08	Tandem nylon filters	3.84	069	0.11	10.19	0.77	070	0.23	0.39	0.75	
Leg	Start Date	Substrates, Positions 1 & 2	Vol. (m^3)	Results ($\mu g/m^3$) for First Denuder ID	NO_2^-	NO_3^-	$SO_4^=$	Results ($\mu g/m^3$) for Second Denuder ID	NO_2^-	NO_3^-	$SO_4^=$	Comment
18	8/29	CbDg denuders, #450, #449	3.26	003	-0.08	9.81	1.34	004	0.33	3.72	0.85	
18	8/30	CbDg denuders, #121, #106	3.02	011	0.02	17.45	2.30	012	0.01	4.90	1.70	
18	9/09	CbDg denuders, #457, #458	3.46	077	0.32	9.02	1.93	078	0.88	1.60	0.39	
18	9/10	CbDg denuders, #11, #73	3.46	083	2.35	12.79	3.65	084	0.79	1.15	0.60	
18	9/03	NaDg denuders, #115, #116	4.20	037		5.49	-0.13	038		4.49	0.30	A
18	9/05	NaDg denuders, #453, #454	4.14	052		7.77	0.09	053		0.92	0.04	A
18	8/31	Tandem NaCl-Q filters	4.27	019		12.85	-1.14	020		6.05	-1.06	H
18	9/01	Tandem NaCl-Q filters	4.28	026		15.86	-1.07	027		3.15	-0.87	H
18	9/02	Tandem NaCl-Q filters	4.22	033		21.46	-1.02	034		3.80	-0.99	H
18	9/04	Tandem NaCl-Q filters	3.80	045		13.97	1.22	046		3.78	0.89	H
18	9/06	Tandem NaCl-Q filters	3.45	060		7.47	1.34	061		0.39	2.31	H
18	9/11	Tandem NaCl-Q filters	3.27	091		18.02	1.29	092		4.09	1.21	H
18	9/07	Tandem nylon filters	3.23	067	0.14	10.15	0.77	068	0.21	0.34	0.78	
18	9/08	Tandem nylon filters	3.23	071	0.14	10.13	0.88	072	0.22	0.41	0.84	
Leg	Start Date	Pos. 3 Substrate	Vol. (m^3)	Results ($\mu g/m^3$) for Position 3 Filter ID	NO_2^-	NO_3^-	$SO_4^=$					
18	8/29	Nylon filter	3.26	005	0.29	1.11	0.19					
18	8/30	Nylon filter	3.02	013	0.24	3.53	0.35					
18	9/10	NaCl-Q filter	3.46	085		0.32	0.67					
18	9/03	NaCl-Q filter	4.20	039		2.39	0.62					
18	9/05	NaCl-Q filter	4.14	054		2.00	0.12					
Comments:		A: approx. 775-1000 µg Cl^-										
		H: high chloride										

Table 3-16 Summary of Nitrate Results from One-Day Substrate Testing at Claremont

Leg	Start Date	Substrates, Positions 1 & 2¥	Substrate Nitrate ($\mu g/m^3$) Pos. 1	Substrate Nitrate ($\mu g/m^3$) Pos. 2	Substrate Efficiency (%)	Denuder HNO_3 ($\mu g/m^3$ NO_3)	Sum of Leg 18 NO_3^- ($\mu g/m^3$)	Daily Nylon† NO_3^- ($\mu g/m^3$)
18	8/29	CbDg denuders, #450, #449	9.81	3.72	62%	15.82	14.65	14.00
18	8/30	CbDg denuders, #121, #106	17.45	4.90	72%	24.26	25.88	32.84
18	9/09	CbDg denuders, #457, #458	9.02	1.60	82%	10.96	10.62	11.75
18	9/10	CbDg denuders, #11, #73	12.79	1.15	91%	14.06	14.26	12.26
18	9/05	NaDg denuders, #453, #454	7.77	0.92	88%	8.82	10.69	12.92
18	8/31	Tandem NaCl-Q filters	12.85	6.05	53%	-	18.89	18.91
18	9/01	Tandem NaCl-Q filters	15.86	3.15	80%	-	19.01	19.49
18	9/02	Tandem NaCl-Q filters	21.46	3.80	82%	-	25.26	24.49
18	9/04	Tandem NaCl-Q filters	13.97	3.78	73%	-	17.75	16.18
18	9/06	Tandem NaCl-Q filters	7.47	0.39	95%	-	7.86	7.57
18	9/11	Tandem NaCl-Q filters	18.02	4.09	77%	-	22.11	20.91
18	9/07	Tandem nylon filters	10.15	0.34	97%	-	10.49	10.17
18	9/08	Tandem nylon filters	10.13	0.41	96%	-	10.54	10.19

¥ substrate codes given in Table 3-7

† from Leg 17 of Substrate Testing System, first nylon filter only.

Nitric acid was measured by tandem denuders operated for 24 hours at 2.5 ± 0.5 ℓ/min, which is calculated by Equation (1), and is compared to 24-hour nylon filter values in Figure 3-16. Four tests were done with carbonate-coated denuders. The ratio of the tandem carbonate denuder nitric acid to that from the nylon filter ranged from 0.74 to 1.14, with an average of 0.99 ± 0.12.

Denuder collection efficiencies, shown in Table 3-16 were more variable, ranging from 62% to 91% (mean = 77%). Only one successful test was completed with the tandem sodium chloride denuders, yielding 67% of the nylon filter nitric acid value. Results for the sum of tandem sodium chloride impregnated filters operated at the same flow rates of 2.5 ± 0.5 L/min, are also shown in Figure 3-16. The ratio of nitrate on the sum of the two tandem sodium chloride filters to that on the nylon filters ranged from 0.97 to 1.09, with an average of 1.03 ±.04.

One-Day Sampler Prototype Evaluation

The One-Day Sampler consists of a Teflon impactor to remove coarse particles, followed by two denuders of the same type to remove nitric acid, and then followed by an adsorbing filter to collect fine particles. An adsorbing filter is used to prevent the loss of particulate nitrate. Nitric acid values are obtained from the One-Day Sampler by correcting for denuder efficiency using Equation (1). Nitrate found on the follow-up filter is assumed to be particulate nitrate.

Concentrations measured in the One-Day Sampler are given in Table 3-17. Denuder collection efficiencies, calculated for nitric acid from the relative amount of nitric acid collected on the two tandem denuders (efficiency = 1-[D2]/[D1]), are given in Table 3-18. The carbonate denuder efficiencies for ambient sampling range from 91% to 100% with an average of 95 ± 4%, which is higher on the whole than for the denuders in the substrate testing system.

On five of the measurement days, denuders of the same type that were used in the One-Day Sampler were operated simultaneously in Leg 18 of the substrate testing system. The nitric acid values from these two systems are compared in Figure 3-17. The data are highly correlated, but nitric acid values from the One-Day Sampler are systematically lower than from the testing system. Because a portion of the nitric acid in the testing system is derived from volatilized particle nitrate from the Teflon prefilter, higher nitric acid values are expected in the substrate testing system. However, One-Day Sampler results would also be low should there be nitric acid losses in the inlet system.

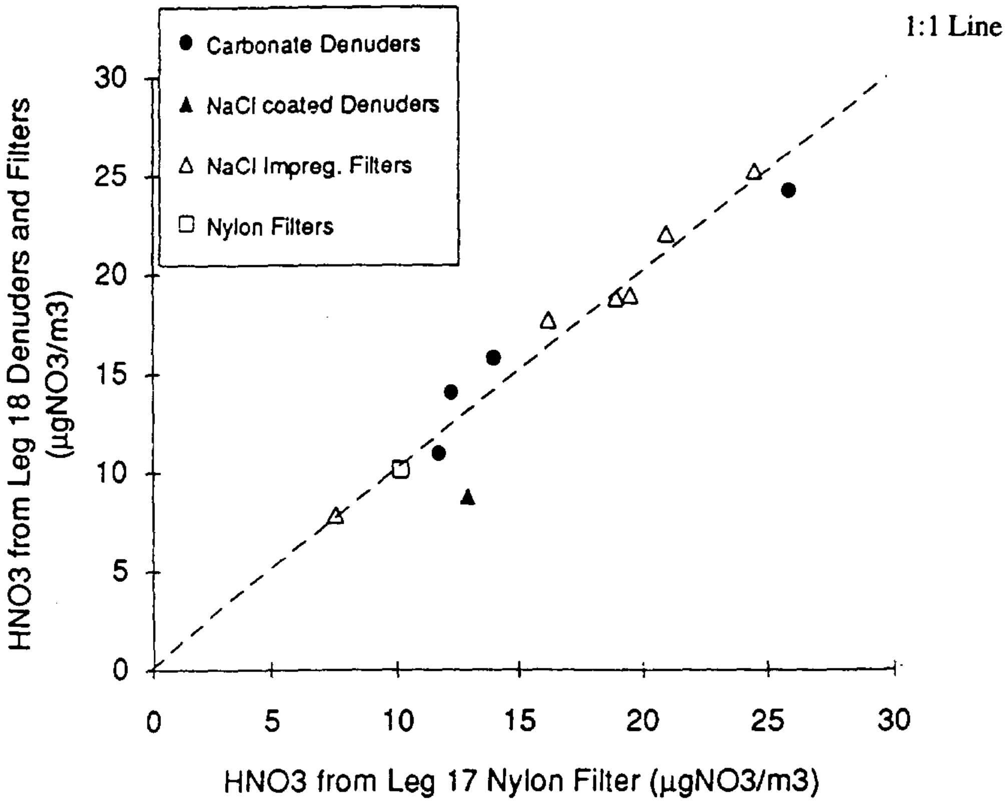

Figure 3-16 Nitric acid measured by the daily nylon filters and by the One-Day denuder pairs operated at 2.5 ± 0.5 ℓ/min in the substrate testing system at Claremont. (For the 8/30 sample, the sum of the denuders and after filter was substituted for the nylon filter value)

Table 3-17 Concentrations from One-Day Sampler at Claremont

	Start		Stop		Denuder	Flow	Vol	$SO_4^{=}$ ($\mu g/m^3$)			NO_2^- ($\mu g/m^3$)			NO_3^- ($\mu g/m^3$)			HNO_3
ID	Date	Time	Date	Time	Type†	(ℓ/min)	(m^3)	Den#1	Den#2	Filter	Den#1	Den#2	Filter	Den#1	Den#2	Filter	Efficiency
1Dy01	29-Aug	1242	30-Aug	0904	CbDg	2.57	3.14	1.65	-0.03	1.43	0.05	-0.14	0.34	9.81	0.14	2.03	99%
1Dy02	30-Aug	0907	31-Aug	1033	CbDg	2.51	3.83	2.31	1.74	2.25	0.08	0.11	0.18	13.47	1.23	4.91	91%
1Dy03	31-Aug	1043	1-Sep	1025	NaDg	2.55	3.63	-0.20	-0.31	0.49				9.26	0.73	6.95	92%
1Dy04	1-Sep	1025	2-Sep	0910	NaDg	2.51	3.42	0.62	-0.06	1.79				12.28	0.57	6.33	95%
1Dy05	3-Sep	1004	4-Sep	0947	NaDg	2.73	3.88	-0.02	0.08	3.21				5.72	1.40	4.58	76%
1Dy06	4-Sep	0949	5-Sep	1018	NaDg	2.75	4.04	-0.17	-0.17	1.64				8.02	1.61	8.12	80%
1Dy07	5-Sep	1019	6-Sep	1015	NaDg	2.69	3.87	-0.21	-0.25	2.41				4.25	0.61	4.47	86%
1Dy08	6-Sep	1345	7-Sep	1051	NaDg	2.74	3.47	-0.18	-0.26	2.98				2.82	-0.71	2.94	100%
1Dy09	8-Sep	1026	9-Sep	1047	CbDg	2.30	3.36	4.78	1.35		2.11	1.33		7.23	0.27		96%
1Dy10	9-Sep	1050	10-Sep	0928	CbDg	1.91	2.60	4.00	-0.35		3.71	0.03		5.95	-0.06		100%
1Dy11	10-Sep	0930	11-Sep	0948	CbDg	2.39	3.48	4.58	0.98	3.94	2.14	0.76		7.14	0.66	5.98	91%
1Dy12	11-Sep	0949	12-Sep	0901	CbDg	2.31	3.21	3.89	0.01		1.44	1.38		13.42	1.08		92%

† Codes for Denuder types given in Table 3-7.

					Ambient Nitric Acid Values as $\mu g/m^3$ NO_3^-			
		Start	Denuder	Denuder	Ambient HNO_3		HNO_3 in Substrate Testing System	
ID	Date	Time	Type†	Efficiency	One-Day	TDLAS ¥	Nylon filter	Denuder Pair ‡
1Dy01	29-Aug	1242	CbDg	99%	9.95	18.27	14.00	15.82
1Dy02	30-Aug	0907	CbDg	91%	14.83	21.06	32.84	24.26
1Dy03	31-Aug	1043	NaDg	92%	10.05	23.04	18.91	
1Dy04	1-Sep	1025	NaDg	95%	12.88	26.04	19.49	
1Dy05	3-Sep	1004	NaDg	76%	7.58	18.50	18.84	
1Dy06	4-Sep	0949	NaDg	80%	10.04	14.98	16.18	
1Dy07	5-Sep	1019	NaDg	86%	4.96	11.37	12.92	8.82
1Dy08	6-Sep	1345	NaDg	100%	2.82	7.25	7.57	
1Dy09	8-Sep	1026	CbDg	96%	7.51		10.19	
1Dy10	9-Sep	1050	CbDg	100%	5.95	8.99	11.75	10.96
1Dy11	10-Sep	0930	CbDg	91%	7.87	9.40	12.26	14.06
1Dy12	11-Sep	0949	CbDg	92%	14.59	17.19	20.91	

† Codes for denuder types given in Table 3-7.

¥ Reported nitric acid values in ppb, multiplied by 2.385

‡ Nitric acid from Leg 18 denuders. For each day the same type of denuder was used in Leg 18 as in the One-Day Sampler.

Table 3-18 Summary of One-Day Denuder Results for Nitric Acid at Claremont

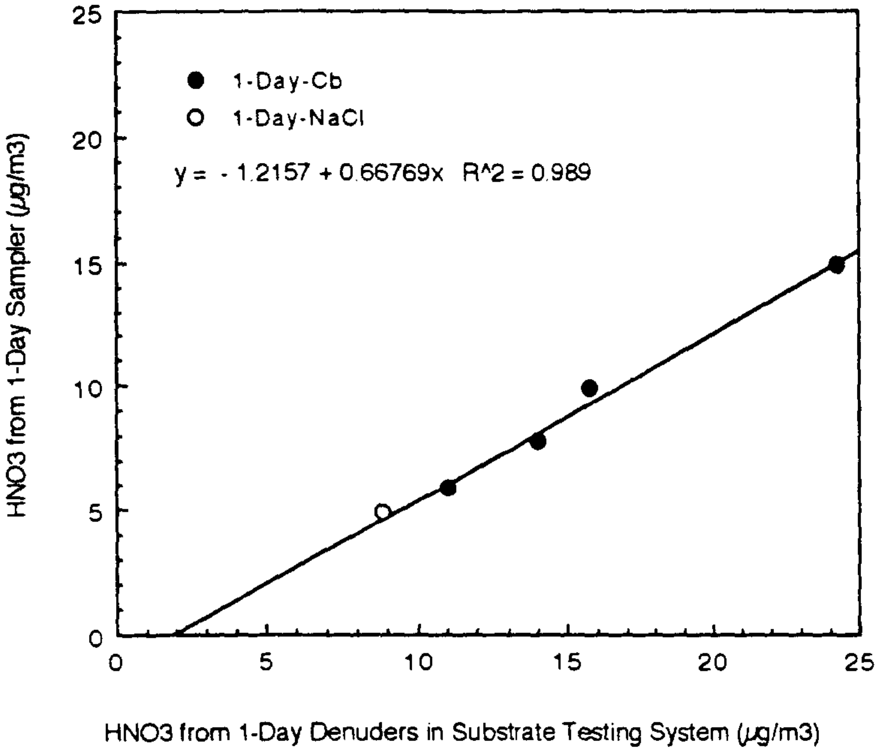

Figure 3-17 Nitric acid measured by One-Day Sampler compared to that measured by One-Day denuder pairs of the same type and on the same day from the substrate testing system at Claremont

One-Day Sampler values for nitric acid are compared to those reported for the TDLAS measurements at Claremont in Figure 3-18. The data are fairly well correlated, with values of $R^2 = 0.75$ and 0.83 for carbonate and sodium chloride denuders, respectively. Values from the carbonate denuder are systematically higher than from the sodium chloride denuders, in agreement with results from the substrate testing system. However, overall, the nitric acid values from the One-Day Sampler are significantly lower than those from the TDLAS. The average of the One-Day Sampler nitric acid from carbonate and sodium chloride-coated denuders is lower than the average TDLAS over the same time period by 29% and 52% respectively. Interestingly, the TDLAS values tend to agree (the correlation coefficients indicate a significant scatter of the data) with the daily nylon filter from the substrate testing system, as shown in Figure 3-19. On average, the daily nylon filter operated downstream of Teflon filters is only 6% lower than that from the TDLAS.

A limited amount of FTIR nitric acid data is available for periods which were above the detection limit of approximately 4 ppb. Figure 3-20 is a composite diurnal profile of nitric acid for eight days when data from both spectroscopic methods are available. Note that the TDLAS is lower in late morning but higher most of the afternoon and 28 percent higher than the FTIR for this period. This may be caused by capture of ammonium nitrate on the Teflon prefilter of the instrument, which begins to volatilize in the early afternoon, releasing HNO_3.

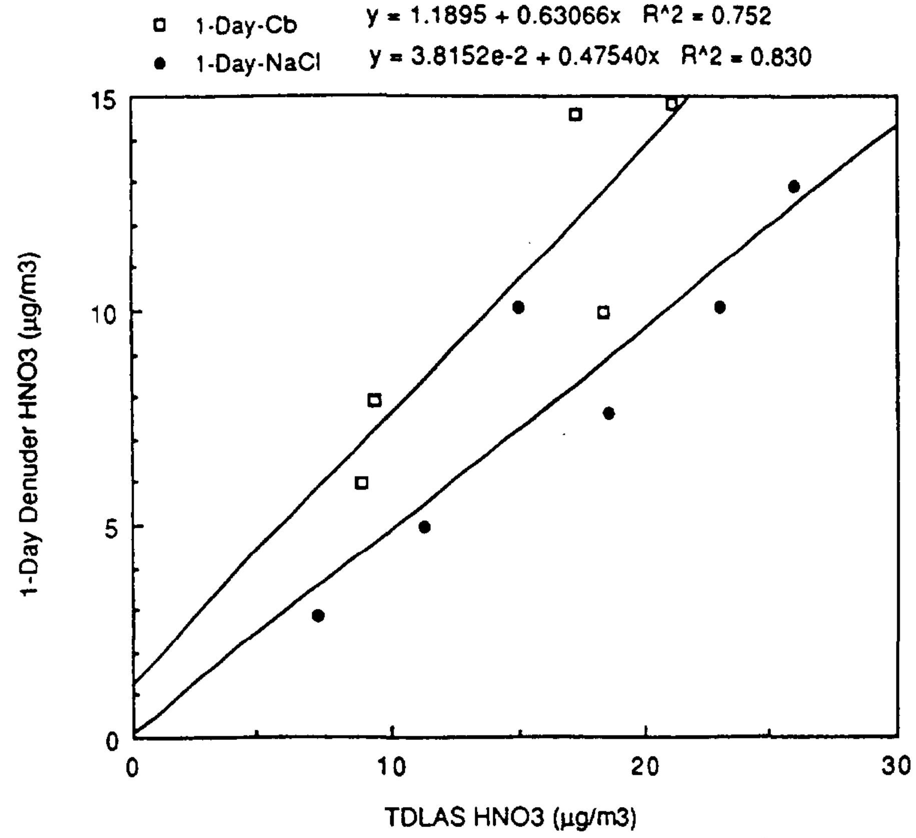

Figure 3-18 Nitric acid measured at Claremont by One-Day Sampler compared to that measured by the TDLAS

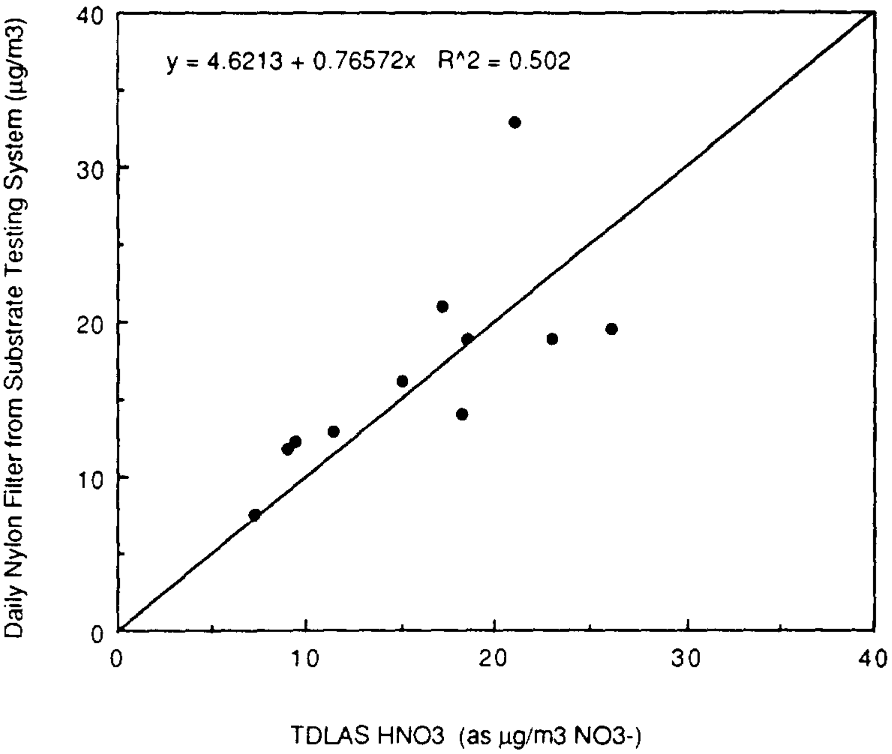

Figure 3-19 Nitric acid measured at Claremont by daily nylon filters in the substrate testing system compared to that measured by the TDLAS

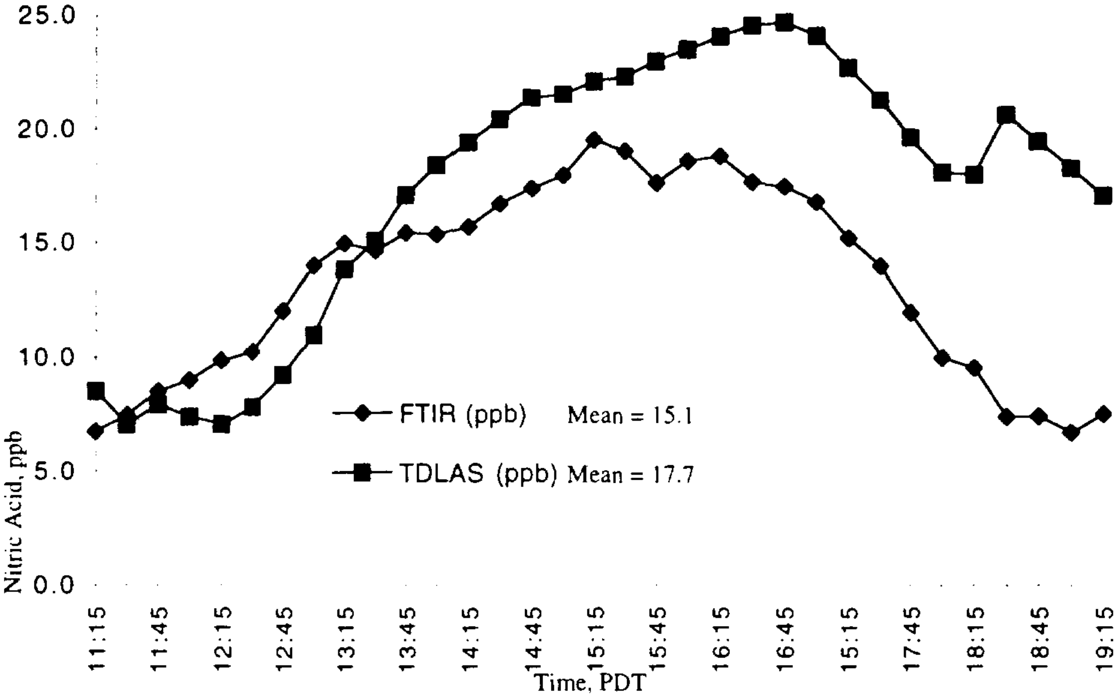

Figure 3-20 Comparison of nitric acid by TDLAS FTIR at Claremont for eight composited days in September 1995

4.0 SUMMARY AND CONCLUSIONS

4.1. Summary of Experimental Results

4.1.1 Evaluation of the Main Leg of the Two-Week Sampler

- *Laboratory Evaluation*

Laboratory experiments with synthetically-generated nitric acid showed that penetration through the carbonate-coated honeycomb denuder was approximately 10 percent at worst case high nitric acid concentrations (35 ppb). NaCl-coated denuders were as efficient as carbonate in removing nitric acid at the design flow rate of the Two-Week Sampler, but the efficiency dropped more quickly as a function of flow rate. Adding glycerol to the denuder coating solution did not have a significant effect during the field evaluation.

For the main leg of the Two-Week Sampler, interferences due to PAN decomposition on either the carbonate-coated denuder or quartz back filter have been shown in the laboratory to be generally low. On the other hand, the laboratory testing showed that carbonate-coated denuders had the potential to remove 50-100% of the nitrous acid (carbonate-coated filters approximately 50%), resulting in nitrite deposits when ozone was not present and nitrate deposits under high concentrations of ozone (200 ppb). A single laboratory test showed that a NaCl-coated denuder had no affinity to collect nitrous acid while over thirty percent of the PAN was removed.

- *Field Evaluation*

Nylon filters appeared to collect artifact nitrate during the field test in Riverside, since significant amounts of nitrate were found on back filters and more nitrate was consistently found on nylon filters compared to their chloride-coated counterparts. Nitrous acid is a likely interferent for nylon filters based on previously reported studies (Sanhueza et al., 1984 and Sickles and Hodson, 1989). There was no evidence of this phenomenon during the Claremont study. It is possible that either the interferent is found at higher concentrations in Riverside and/or that this was caused by photochemistry occurring during this time of year. Since the Riverside site was in an area of light manufacturing, it is possible that the interferent was due to local emissions. It is not clear what type of industrial nitrogenous species could be adsorbed by both nylon filters and carbonate substrates.

Field testing of the Main Leg substrates over a two-week period showed that the nitric acid values from nitrate on the carbonate-coated denuders agree with the nitrate values found for nylon filters changed daily, although at Riverside there appeared to be a significant interferent for both. The field testing also indicated that there is a positive artifact for the carbonate-coated backup filters. These tests show that the carbonate-coated filters were more efficient at removing the sampling artifact gas than were the similarly coated denuders. The denuders were less efficient than filters in allowing the oxidation of nitrite to nitrate. While these denuders used in Riverside did apparently collect significant artifact nitrate compared to similar NaCl-coated substrates, they allowed major amounts (approximately 70 percent) of this nitrogenous gas to pass through, only to be trapped efficiently (approximately 60 percent efficiency) by the carbonate-coated filter below. This filter is therefore of limited use in measuring volatilized particulate nitrate, and the Main Leg will invariably over-estimate the amount of particulate nitrate. The reason that the nitrate on the nylon filters and the carbonate-coated denuders compared favorably is because the nitrite was only partially oxidized to nitrate. Sodium chloride-coated filters showed higher nitric acid collection efficiency in Riverside than Claremont. The difference could be either due to different environmental conditions or the lower strength coating mixture used in Claremont (0.47 percent compared to 2 percent).

It could not be determined whether the nitric acid penetration was greater with Teflon or Kevlar impactors due to the apparent nitric acid artifact when using carbonate-coated back filters. Both impactors appeared to remove nitric acid. When sodium chloride denuders were used, slightly more nitric acid appeared to penetrate the Teflon impactor. With the limited data available, it is not possible to say whether or not this was significant.

4.1.2 Evaluation of the Organic Acids Leg of the Two-Week Sampler

Laboratory Evaluation

Laboratory evaluation confirmed that PAN is collected by the KOH-coated filters used for measuring formic acid and the upper limit value for acetic acid. Especially under conditions of low temperature and high relative humidity, PAN is collected as acetate, and contributes to the upper limit value of acetic acid. The conversion on the KOH-coated filters used for sampling organic acids was greater than the carbonate-coated substrates of the Main Leg of the Two-Week Sampler. This difference indicates that the hydroxide does not rapidly convert to carbonate by the reaction with water vapor and carbon dioxide as would be expected from a bulk sample. It should be noted that the Aadco pure air generator only partially removes carbon dioxide.

Field Evaluation

The large percentage of acetate found on the back filter of the ambient air collections is in agreement with the laboratory results that PAN is readily collected by the KOH-coated filter. No such formate was observed on the second coated filter.

Long sampling intervals did not appear to cause significant sample deterioration for the Organic Acids Leg of the Two-Week Sampler in either the sampling interval experiment or the biodegradation experiment.

4.1.3 Design and Evaluation of a One-Day Sampler

Design

The design was the same as the Two-Week Sampler with the exception of changes in the impactor jet diameter and the use of two 8mm honeycomb denuders. Calculations showed that the 8mm honeycomb denuder has a high theoretical collection efficiency for nitric acid at up to 3 ℓ/min. Two such denuders were used so that breakthrough could be measured. The Teflon impactor was redesigned for the higher flow rate of 2.5 ℓ/min.

Laboratory Evaluation of Denuder Nitric Acid Penetration

The carbonate-coated denuder was found to effectively remove nitric acid at up to 3ℓ/min. With a NaCl coating the removal efficiency starting dropping at 2 ℓ/min.

Laboratory Evaluation for Particle Penetration

Particle penetration characteristics were evaluated with test aerosols. The cutpoint of the redesigned impactor was measured to be 2.1μm at 2.5 ℓ/min. Fine particle losses through the denuder and Teflon cassette were measured as a function of flow rate and were found to decrease with increasing flow rate. At the One-Day sampling rate of 2.5 ℓ/min losses were less than five percent by number count and estimated to be less than two percent of fine ambient particulate mass. These losses were attributed to electrostatic deposition.

Field Evaluation

Tandem carbonate-coated denuders operated at 2.5 ℓ/min give consistent results for nitric acid. In the testing of substrates, the systematic difference with respect to nylon filters was 4%. The positive artifacts seen for two-week sampling were not apparent for 24-hour sampling with the carbonate-coated denuders. When these denuders were incorporated within a sampler, single denuder efficiencies were always greater than 90%; thus indicating that flow rates up to 5 ℓ/min are feasible if tandem denuders are used However, reported nitric acid concentrations were lower, on average, than from the TDLAS system. By comparison, sodium chloride-coated denuders showed more variable and lower efficiency than the carbonate-coated denuders. The results for this prototype system show high potential for the possibility of a higher flow-rate, compact system using the glass honeycomb denuders. Results indicate that flow rates above 2.5 ℓ/min would be possible with this tandem denuder system. Further testing is needed, including measurements of collection efficiencies under a variety of conditions, and measurements of the nitric acid penetration through the impactor and cassette inlet.

4.2 Conclusions

The following conclusions may be drawn from this study:

- The carbonate-coated denuder collects nitric acid from particle free air in good agreement with nylon filters. Interferences from PAN and, more likely, nitrous acid may be expected depending on the environmental conditions. The high temperatures at Claremont compared to Riverside, may have inhibited the collection of nitrous acid as shown by the laboratory study The agreement with nylon filters could also be due to a nitrous acid collection artifact of similar magnitude for these filters.

- There is an indication of loss of nitric acid with both the Teflon and Kevlar impactors.

- The carbonate-coated filters have a high affinity for collecting nitrous acid, and a lesser one for PAN. Their use as a backup for the Teflon filter is likely to cause a significant positive bias in the measurement of particulate nitrate.

- As expected, the KOH-coated filters used to measure the upper limit of acetic acid were found to collect PAN, and thus would give a positive bias if the data were interpreted as acetic acid. These values should continue to be reported as upper limits of acetic acid concentrations.

- No evidence of biogenic degradation of analytes was observed for either the Main or the Organic Acids Leg of the Two-Week Sampler.

- Sodium chloride coatings have the potential of reducing interferences due to nitrous acid, but as currently used, are not highly efficient for collection of nitric acid. The collection efficiency for nitric acid was lower than for carbonate-coated substrates and was somewhat inconsistent, perhaps due to the physical inconsistencies of the coating process. The coated filters showed a higher retention efficiency compared to the denuders.

- The use of a single carbonate-coated denuder for 24-hour sampling is feasible at a flow rate of 2.5 ℓ/min and could be pursued to provide a simple sampler for daily nitric acid and fine particle measurements. If lower detection limits are required, the use of tandem carbonate-coated denuders at a flow rate up to 5 ℓ/min may be practical.

In general, the nitric acid measurements are thought to be as accurate as can be expected for this difficult to measure species. There may be some positive artifact due to collection of nitrous acid by the carbonate-coated denuder, and some losses of nitric acid in the impactors which may tend to cancel one another out. Nitric acid measured with the prototype One-Day Sampler was about 30 percent lower than the TDLAS in Claremont; nitric acid measured with the FTIR was also about 30 percent lower during this period.

Since the carbonate-coated filter used to trap volatilized nitrate in the Two-Week Sampler was shown to adsorb both nitrous acid and PAN, particulate nitrate for the Children's Health Study will be biased high. The magnitude of this bias is difficult to assess since little data on nitrous acid and PAN concentrations are available; temperature and humidity may also affect the collection efficiency.

The PAN interference will cause assays for acetic acid from the Organic Acids Leg of the Two-Week Sampler to be biased high. This is again difficult to assess since the PAN concentration data are not available and the magnitude of the interference will be dependent on other variables such as humidity and temperature. The acetic acid data for the Children's Health Study should therefore continue to be considered an upper limit. The acetate on the back filter may be used to correct for this interference. The acetate on the back filter (which should be subtracted from the front filter acetate if due solely to PAN) may underestimate the adsorption of PAN (since PAN was partially removed by the front filter). On the other hand, this acetate may be due to acetic acid also penetrating the front filter (in which case it should be <u>added</u> to the front filter acetate) since Kawamura et al. (1985) reported a collection efficiency of 80 percent at a much higher flow rate (10 ℓ/min). Thus there are two opposing potential sampling artifacts that would tend to cancel the errors in subtracting the acetate on the back filter from that of the front. This could be applied to the Children's Health Study data with a caveat of the risks involved.

The potential sampling artifacts for species measured by the Two-Week Sampler have been shown to be dependent on environmental parameters, which differ with time of year, location and most probably other variables. Thus data collected routinely for the Children's Health Study cannot directly be assessed based on our observations. What we have conclusively shown is a lack of sample degradation during the collection interval when compared to daily samples.

5.0 RECOMMENDATIONS

Based on the experimental results, the following recommendations are proposed:

- The carbonate-coated glass honeycomb denuder now used for the Two-Week Sampler gave better overall performance for removing nitric acid (with nylon filters as a reference) than similar denuders coated with sodium chloride. Its use should therefore be continued with recognition that there is a potential positive artifact due to nitrous acid and PAN. While sodium chloride-coated honeycomb denuders appeared to be more specific for nitric acid removal, their collection efficiency, based on the nitrate collected by sodium chloride-coated back filters, appeared satisfactory in Riverside sampling, but low in Claremont.

- Consideration should be given to replace the carbonate-coated back filter of the Main Leg of the Two-Week Sampler with either a nylon filter or a sodium chloride coated (minimum of 2 percent coating strength) quartz filter. Additional work is needed to optimize the sodium chloride coating process.

- The retention of nitric acid by the impactors should be better quantified. It is possible, based on our studies of the CADMP sampler, that the retention may vary with temperature, humidity, and concentration history.

- Sodium chloride denuders have the potential to reduce nitric acid collection artifacts, but collection efficiencies were shown to be variable and sometimes low under our test conditions. Additional work is needed to optimize a coating mixture which would provide consistent and high efficiency for the removal of nitric acid.

- If all of the acetic acid is removed by the front filter of the Organic Acids Leg, then the back filter will be a lower limit of the bias. The efficiency of this front filter in removing acetic acid at the Two-Week Sampler's flow rate should be determined in order to estimate the level of this bias in correcting and better estimating the accuracy of past data. If high acetic acid capture efficiency is shown, a third KOH-coated back filter should be investigated for evaluating the interference.

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APPENDIX A

STANDARD OPERATING PROCEDURE
TWO-WEEK SAMPLER

LAREI STANDARD OPERATING PROCEDURE
Page: OF
Date: 4/5/94
Title: Two-week Sampler
Revision: 2

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1. PURPOSE

This method describes the procedures for preparation, extraction, and analysis of the two-week sampler.

2. APPARATUS AND MATERIALS

2.1 Filter Media

Teflon - Gelman R2PL047, Teflo with ring 47 mm, 1 μm

tissuquartz - 2500 QAT-UP 47 mm (Pallflex, Putnam, Ct)

Teflon membrane, 47 mm (Savillex, Minnetonka, MN)

2.2 Q-tips

2.3 Dow 704 silicon oil

2.4 disposable pipette

2.5 powder-free Latex gloves

2.6 Kimwipes

2.7 aluminum foil

2.8 flat-tipped tweezers

2.9 Chemicals

Fisher certified:

- HCL, concentrated
- KOH
- methanol
- sodium acetate
- sodium bicarbonate
- sodium carbonate
- sodium formate
- sodium hydroxide

sulfuric acid

TBAOH, 55% aqueous solution, (Sachem, Austin, Tx)

2.10 shaker table

2.11 Eppendorf micropipetter, 100 µl

2.12 Dispensers, 10 ml

2.13 Deionized (DI) water

2.14 furnace

2.15 sample vials

2.16 Standards (SPEX Industries, Edison, NJ)

2.17 ultra-sonic bath

2.18 balance (Cahn electrobalance)

3. PROCEDURES

3.1 Sampler preparation

3.1.1 Wear powder-free Latex gloves at all times when handling sampler parts. Filter holders must be washed and dried between each use. Remove the particle collection plate, wipe it with a Q-tip wetted with alcohol, and sonicate in a beaker of DI water for 10 minutes. Place on Kimwipes and allow to air dry.

3.1.2 Nuts may be washed in a dishpan. Fill pan with tap water and a small amount of detergent. Agitate for one minute and soak for 5 minutes. Transfer nuts to rinse dishpan and fill with DI water. Agitate for 1 minute and soak for 5 minutes. Drain pan, refill with DI water and repeat. Remove nuts, place on Kimwipes and allow to air dry.

3.1.3 Place all other filter holder parts in an ultra-sonic bath with DI water and a small amount of detergent. Sonicate for 15 minutes. Rinse each part with DI water in a squirt bottle. Empty ultra-sonic bath, rinse and refill with DI water. Return parts to ultra-sonic bath and sonicate for 15 minutes. Wearing gloves, rinse each part with alcohol in a squirt bottle. Lay the parts out on Kimwipes. Shake screens to remove excess liquid. Cover with Kimwipes and allow to air dry.

3.1.4 Honeycombs are sonicated in a beaker of DI water for 10 minutes. Drain, refill with DI water and repeat. Remove from ultra-sonic bath, and rinse with alcohol in a squirt bottle.

3.1.5 Teflo filters will be pre- and post-weighed in a room with stable temperature and humidity. Gravimetric analysis is done on a Cahn Model 4700 Automatic Electrobalance which weighs to the nearest 0.001 mg. Balances are serviced twice a year under contract to Precision Instrument Repair and certified to be accurate to within 0.5%. Balances are calibrated daily by laboratory personnel prior to use. Static electricity is discharged from filters by use of a Kr-85 source. Using flat-tipped tweezers, remove filters from containers and place in a Petri dish. The cover should be slightly raised so that air can circulate while the filters are protected from contamination. Allow the filters to equilibrate for at least two weeks prior to pre-weighing. Using flat-tipped tweezers, remove Teflon filters from the container and inspect for tears or pinholes. Allow each filter to rest on the Static Eliminator for one minute. Gently place the appropriate tare weight on the right-hand balance pan. Gently place the filter on the left-hand pan. Wait until the reading is stable and record the weight and tare weight on a log sheet. Place each filter in a petri dish and write its weight on the cover.

Also weigh the "lab blank" which is kept near the balance. It is weighed on both the 20 mg range with a 150 mg tare weight, and on the 200 mg range without a tare weight. This is done as a check on the balance performance.

3.1.6 Using a disposable pipette, add one drop of mineral oil to each glass frit, then wipe with a dry Q-tip.

3.1.7 Honeycombs are coated by dipping in a solution of 2% carbonate in 50/50 water/methanol. (Weigh out 2 grams of Na_2CO_3, quantitatively transfer to a 100 ml volumetric flask, and dissolve in 50 ml of DI water. Bring to volume with methanol.) Slid honeycomb into a beaker filled with coating solution. Swirl beaker several times, turn honeycomb over with forceps and repeat three times. Place honeycombs on Kimwipes, blot, and let air dry.

3.1.8 Quartz filters are cleaned by baking in a furnace at 550°C for 4 to 10 hours. Filters for organic sampling are impregnated with 0.1 M KOH (0.561 g KOH in 100 ml water) by laying filters out on an aluminum foil covered oven rack and pipetting 1 ml of solution onto each. Filters for the main leg are impregnated with 0.46% carbonate (0.23 g Na_2CO_3 in 25 ml water and 25 ml methanol) as above. They are dried in an oven at 80 to 120 °C for about 30 minutes. After 15 to 20 minutes, slightly move each filter with forceps. This prevents them from sticking to the foil and tearing. Treated filters are stacked and stored in petri dishes.

3.2 Assembly

3.2.1 Main leg -- Use yellow cassettes. Wearing gloves and using forceps, assemble in the following order. Hold bottom piece with support screen in one hand, add sodium carbonate coated quartz filter, thin (030) O-ring, support grid, Teflo filter with polycarbonate ring facing up, thin o-ring, honeycomb (make sure it is seated inside support ring), top piece with impactor, and thicker o-ring (130). Use care when assembling teflon impactor as teflon threads are easily stripped by the stainless steel screws. Do not crossthread or tighten excessively.
See figure 1.

3.2.2 Organic acid leg -- Use grey cassettes. Wearing gloves and using forceps, assemble in the following order. Hold bottom piece in one hand, add KOH quartz filter, thin o-ring, support grid, KOH filter, thin o-ring, support grid, Teflon membrane, thin o-ring, and plain top piece, without impactor.
See figure 2.

3.2.3 Fine particle leg -- Use green cassettes. Wearing gloves and using forceps, assemble in the following order. Hold bottom piece in one hand, add uncoated, baked quartz filter, and top piece.
See figure 3.

3.3 Sample extraction

3.3.1 Teflo filters are equilibrated for 24 hours prior to post-weighing. After post-weighing, Teflo filters are placed in clean, labelled vials. Vials and tubes are washed by triple rinsing in DI water, placing upside-down on a Kimwipe and allowing to air dry overnight. Clean vials and tubes are capped and stored in zip-lock bags. Using an Eppendorf micropipetter, place 200 μl of ethanol on the face of each filter. With a calibrated dispenser, add 10 ml DI water to each sample. Sonicate for 30 minutes, rotating a quarter turn every 10 minutes. Add ice cubes to the bath to keep the water near room temperature.

3.3.2 Sodium carbonate coated filters are placed in pre-cleaned, labelled 20 ml sonication vials and 10 ml of DI water is added using a calibrated dispenser. They are sonicated for 30 minutes, rotating vials a quarter turn every 10 minutes.

3.3.3 Honeycombs should be handled only with gloved hands and tweezers. Remove from sampler stacks and place in pre-cleaned, labelled 6 ounce Savillex Teflon containers. Tip the beaker and slide honeycomb into it to reduce risk of breakage. Add 25 ml of DI water to each beaker and snap on lid. Place on shaker table and shake for 30 minutes at speed 9.. Place containers in refrigerator and allow to stand overnight. The next morning, again shake on shaker table for 30 minutes and analyze by IC. Swirl each container just prior to drawing up sample into the syringe. One day later, repeat analysis of two samples. If the results of the replicate analysis are not within 10%, re-analyze all the samples.

3.3.4 Organic filters are placed in pre-cleaned, labelled 20 ml sonication vials and 10 ml of DI water is added by calibrated dispenser. They are placed on a shaker table for two hours at full speed.

3.3.5 Quartz filters from the fine particle leg (leg C) are placed in annealed aluminum foil petri dishes (prepared by Cal Tech). Each petri dish is sealed with Teflon tape and placed in the freezer until they can be transported to Cal Tech.

3.4 Analysis by ion chromatography

3.4.1 Cation analysis is done on the Dionex model 2000i ion chromatograph with a CS 12 analytical column, a CG3 guard column, a CMMS-II suppressor, TBAOH regenerant (140 mL in 4 L DI water), and HCL eluent (5 ml concentrated HCl in 2 L DI water). Eluant must be degassed prior to use. Sonicate in side-arm flask under vacuum until no more bubbles form. Slowly pour degassed eluent into reservoir to avoid reintroducing gas into the liquid.

Turn on nitrogen tank and ensure that pressure is at least 80 psi. Start eluent pump and pressurize regenerant reservoir. Allow sufficient time for columns to equilibrate; this is indicated by a stable, low-noise baseline. Reset auto zero as necessary.

Shake each sample vial prior to loading it in to the IC. Draw up about 0.25 ml of sample into a plastic 3 ml syringe. Pointing tip up, draw plunger down to the end of the syringe. Expel syringe into waste container. Repeat rinse once. Fill syringe with about 1 ml of sample, expel air and load into sample port. Use a Gelman Acro-disc 0.45 µm filter to remove particulate that could clog the column. Start recorder (Shimadzu C-RIA) at the same time the inject toggle switch is activated.

Initially, a standard is run at least twice to show reproducibility. When an acceptable chromatogram has been produced, the recorder is recalibrated.

When all the samples have been analyzed, switch the pump from eluent to water. When conductance has dropped to less than 4 us, shut off pump, depressurize regenerant, and turn off cell.

3.4.2 Anion analysis is done on the DX 100 ion chromatograp with an AS4A analytical column, an AG4A guard column, an AMMS suppressor, and Na2CO3/NaHCO3 eluent. For operation, see ion chromatograph section of passive ozone badge SOP.

3.4.3 Organic acid analysis is done on the DX 300 ion chromatograph with an AS5A analytical column, an ASRS suppressor, and sodium hydroxide eluent.

3.4.3.1 Eluent preparation. Prepare a 95.8 mM NaOH eluent by sparging 1 liter of water with helium for 10 minutes. Add 5.0 ml of 50% NaOH (Fisher Scientific) by graduated pipette. The aliquot should be taken from the middle of the bottle. Swirl the eluent to mix it. Sparge this solution with helium for another 10 minutes. The eluent reservoir is then pressurized and kept under helium. This eluent should be used no longer than two weeks.

Prepare a 2.4 mM NaOH eluent by sparging 975 ml of water with helium for 10 minutes. Add 25 ml of the 95.8 mM NaOH eluent and mix. Sparge this solution for another 10 minutes. The eluent reservoir is then pressurized and kept under helium. This eluent should be used no longer than 1 week.

The water eluent is prepared as needed by sparging it with helium for 10 minutes. The eluent reservoir is then pressurized and kept under helium.

3.4.3.1 Standard preparation. Dry reagent-grade sodium acetate and sodium formate (Fisher Scientific) overnight in an oven and store covered in a desiccator. Prepare a stock standard of approximately 500 ppm acetate and formate by weighing 0.17 g of sodium acetate and 0.19 g of sodium formate, quantitatively transferring to a 250 ml volumetric flask and bringing to volume with DI water. Mix well. Transfer to HDPE bottles and store in the refrigerator. It has shelf-life of 6 months.

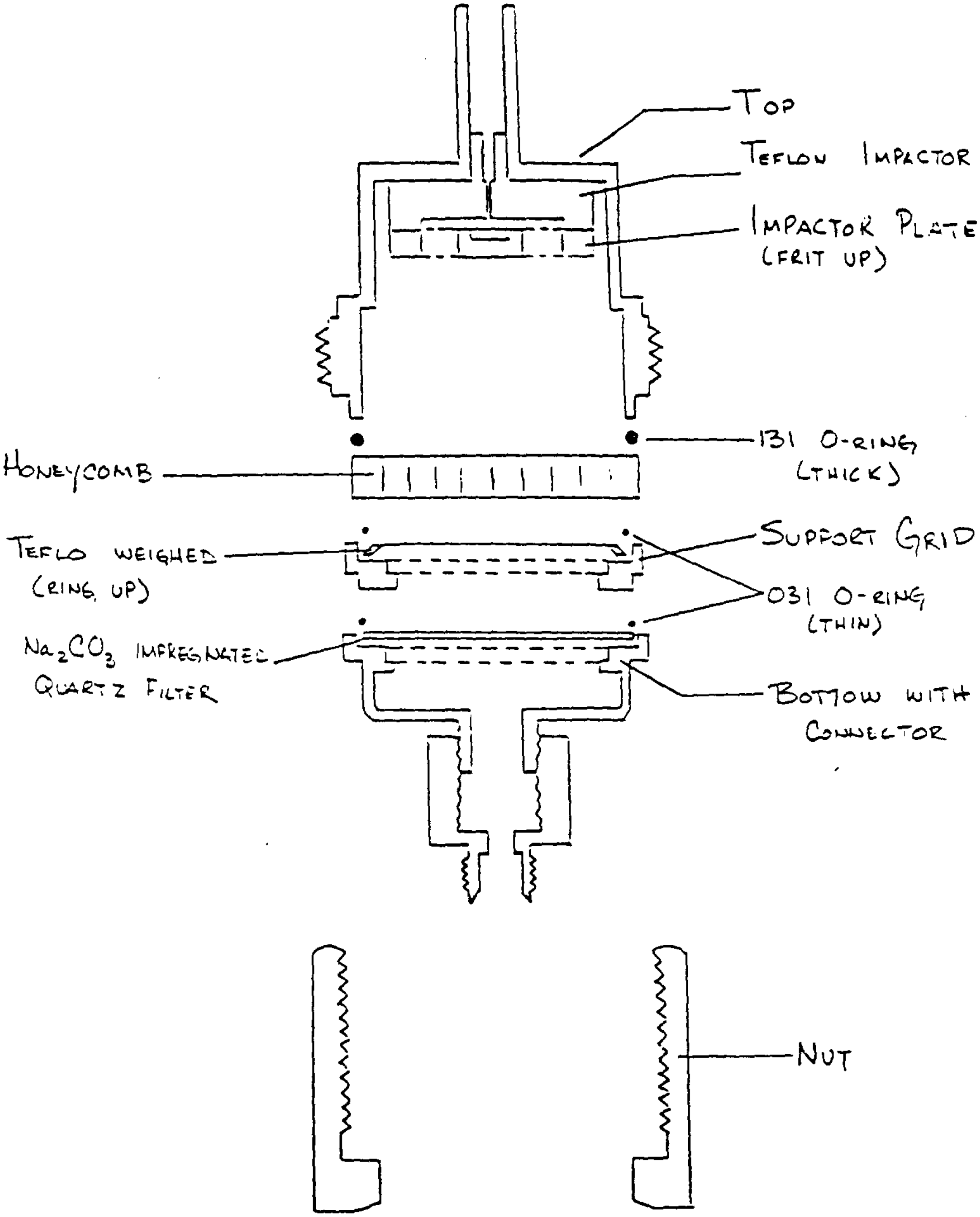
Working standards are prepared by diluting the stock standard with 3 mM Na2CO3. Weigh 0.15 g of Na2CO3, quantitatively transfer to a 500 ml volumetric flask and bring to volume with water. These standards are stored in HDPE bottles in the refrigerator for up to one week.

3.4.3.3 Sample storage and extraction. Sample filters are stored in vials in the freezer until extraction. The samples are extracted in 10 ml of DI water and placed in the shaker bath for 2 hours. They are extracted and analyzed the same day with the remaining sample being stored in the refrigerator.

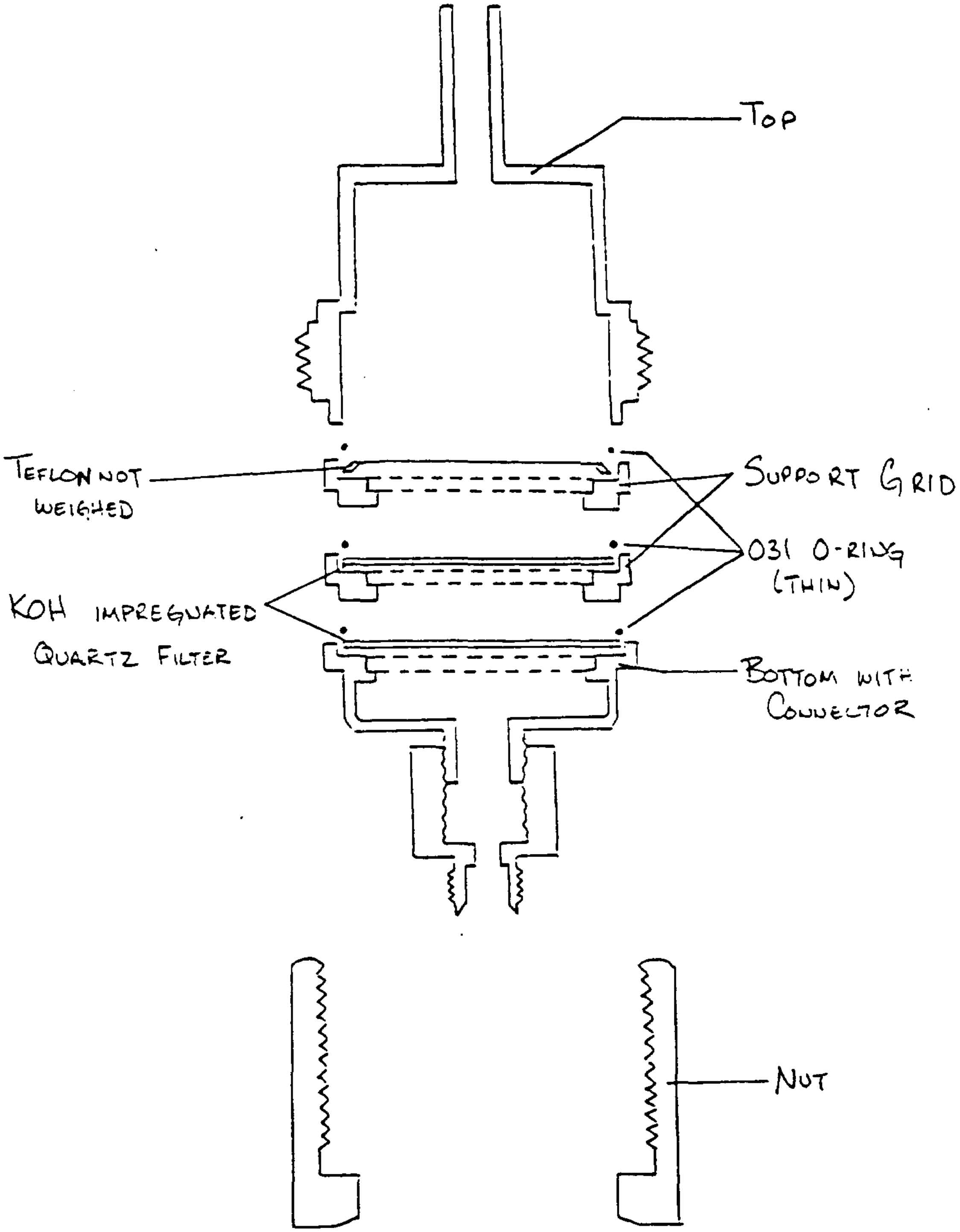
3.4.3.4 IC analysis. The samples are analyzed on a DIONEX DX-300 ion chromatograph using the DIONEX AI-450 automation software. The samples are first filtered through a 0.45 μm filter

(Fisher Scientific) while being placed in the IC sample vials and loaded into the autosampler. A copy of the method used, "org-acid.met", is provided.

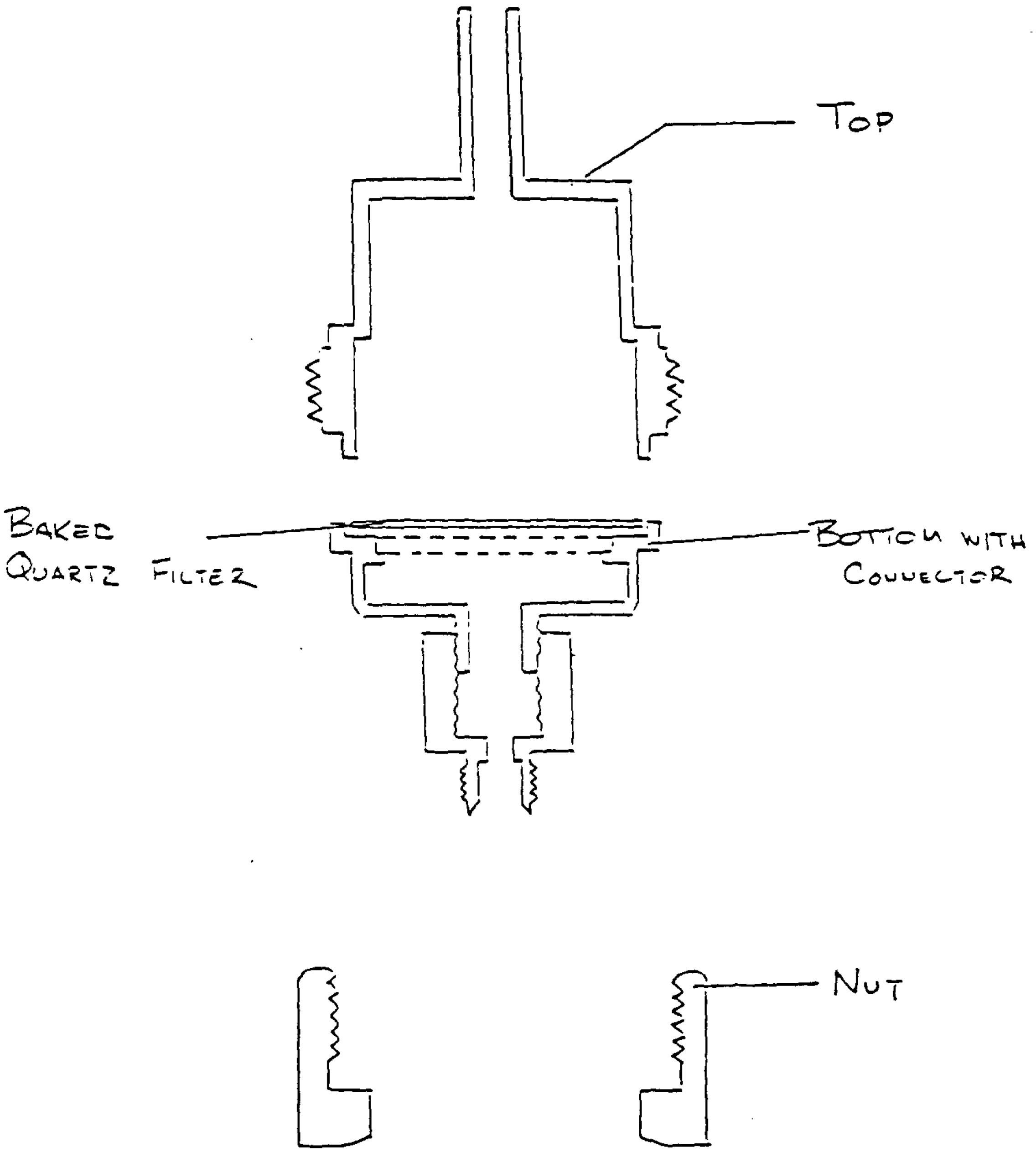
MAIN LEG - #A YELLOW



Organic Acids Leg - #B Gray



FINE PARTICLE LEG - #C GREEN



APPENDIX B

ADI CLAREMONT STUDY WORKPLAN

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ADI Sampling Systems for Claremont Nitric Acid Study, Sept 1995
Measurement Protocol -- Sept 1, 1995

Blue Box Experiment

The purpose of this experiment is to compare the collection characteristics of various types of substrates for nitric acid under ambient conditions. Of interest are the extent of positive interferences and overall collection efficiencies under ambient sampling conditions.

The experiment arrangement consists of 18 sampling legs to allow simultaneous sampling from a common Teflon manifold. Ambient air is drawn into the manifold at 12 L/min through a pair of 47mm Teflon filters (Gelman Zeflor __ µm pore size, Lot no. ___). The Teflon filters remove airborne particles while passing nitric acid and other ambient constituents (such as nitrous acid and ozone).

Legs labeled 1 through 16 are used to test substrates for the Two-Week Sampler. Each of these legs is operated at 0.4 L/min over the two-week period without changing substrates. Legs 17 and 18 sample from the same manifold at 3 L/min and the substrates on these legs are changed daily. Leg 17 consists of a double nylon filter changed daily serves as a reference. Leg 18 is used to test various substrates and denuders for 24-hr sampling. Leg 18 test substrates parallel those for the One-Day sampler, as described below.

One-Day Sampler

The One-Day Sampler is based on the sampling methodology developed for the two-week sampler. It has been adapted for a higher flow rate of 3 L/min to accommodate 24-hour measurement periods for assessment of ambient nitric acid and fine particle inorganic ions. It employs a Teflon impactor mounted in the inlet of a Savilex Teflon filter holder followed by two glass honeycomb denuders and an adsorbing backup-filter operated in series. The jet diameter of the Teflon impactors is 0.089 inches.

In this experiment four configurations of the 1-Day sampler are being tested. There are two types of denuders. Those with ID numbers below 130 are etched with HF, as are two-week sampler denuders. Those with ID numbers above 400 have been etched first with the HF, and then etched again with the same commercial etching solution used on the Harvard denuder systems. In addition, two types of coatings are being tested, 2% Na_2CO_3 in 50/50 water/methanol with 1% glycerol, and 2% NaCl in 50/50 water/methanol with 1% glycerol. The NaCl denuders are always operated with a quartz filter impregnated with 1 mL of 0.5% NaCl in 50/50 water/methanol. The Na_2CO_3 coated denuders are operated with either a Nylasorb backup filter or a NaCl impregnated quartz filter. These same configurations, without the Teflon impactor, are operated on Leg 18. The One-Day Sampler and Leg 18 configurations are summarized in Table 1 below.

Table 1. Description of Leg 18 and the 1-Day Sampler Configurations

Config Name	No. of Denuders	Type of Denuder	Denuder Coating	Type of Backup Filter
Both Leg 18 and the 1-Day Sampler:				
Na100	2	S/N<130	2% NaCl	NaCl imprg quartz
Na400	2	S/N>400	2% NaCl	NaCl imprg quartz
Cb100	2	S/N<130	2% Na_2CO_3	Nylasorb
Cb400	2	S/N>400	2% Na_2CO_3	Nylasorb
CbNa100	2	S/N<130	2% Na_2CO_3	NaCl imprg quartz
Leg 18 only:				
$NaCl_f$	0			Double NaCl imprg quartz filters
Ny-Ny	0			Double Nylasorb filters

Sampling Schedule and Change-out Protocol

Legs 1 - 16 of Blue Box run for entire 2-week period with original substrates. They are shut down temporarily each morning when the Blue Box is stopped to change Legs 17 and 18. Flows are recorded each day before and again after sample changes on Legs 17 and 18.

Legs 17 and 18 are changed each day. One-day sampler will operate 12 of the 14 days. The substrates tested vary from day to day. The planned schedule isgiven in Table 2.

Table 2. Scehdule for Samples Changed Daily

Start Day	Leg 17	Leg 18 (denuder nos.)	One-Day (denuder nos.)
Tues, 8/29	Ny-Ny	Cb 00 ?	Cb 00 ?
Wed, 8/30	Ny-Ny	$NaCl_f$?	Na 00 ?
Thur, 8/31	Ny-Ny	Cb 00 ?	Cb 00 ?
Fri, 9/1	Ny-Ny	$NaCl_f$?	Na 00 ?
Sat, 9/2	Ny-Ny	$NaCl_f$	not run
Sun, 9/2	Ny-Ny	Na100 (115,116)	Na100 (117,95)
Mo, 9/3	Ny-Ny	$NaCl_f$	Na400 (443,445)
Tues, 9/4	Ny-Ny	Na400	Na400
Wed, 9/5	Ny-Ny	$NaCl_f$	Na400
Thurs, 9/6	Ny-Ny	Ny-Ny	not run
Fri, 9/7	Ny-Ny	Ny-Ny	Cb100 (101,118)
Sat, 9/8	Ny-Ny	Cb400 (453,454)	Cb400 (455,456)
Su, 9/9	Ny-Ny	CbNa100	CbNa100
Mo, 9/10	Ny-Ny	$NaCl_f$	CbNa100

Tues, sampling ends.

Substrate Descriptions and Substrate Preparation

Glass Honeycombs

Description: The glass honeycomb substrates are 47 mm diameter, 8 mm thick all-glass honeycombs manufactured by Adams and Chittenden Scientific Glass (Berkeley, CA). Each honeycomb consists of approximately 200 glass tubes, 2 mm in diameter. Honeycombs with serial numbers below 130 are etched for 5 minutes using a 25% solution of HF so that they may be coated. Those with serial numbers above 400 have been etched with the commercial etching solution used on the Harvard denuder systems.

Preparation: Cover working surface with aluminum foil, cleaned with alcohol or water. Clean honeycombs in doubly distilled in an ultrasonic cleaner for 10 minutes, then rinse with alcohol. Let air dry on Kim-wipes, covered with a Kim-Wipe. Once dry, coat honeycombs by dipping in a glass beaker containing enough coating solution to cover honeycomb. For "Cb100" and "Cb400" honeycombs the solution of is 2% Na_2CO_3, 1% glycerol in 50/50 water/methanol. For "Na100" and "Na400" honeycombs the solution of is 2% NaCl, 1% glycerol in 50/50 water/methanol. Blot honeycombs with Kim-wipes to remove excess, and let air dry under clean Kim-Wipe for 1 or more hours. Honeycombs may be handled with gloved hands. Powderless gloves are best. If only powdered gloves are available, rinse gloved hands with water to remove powder which transfers to outside of glove.

NaCl Impregnated Quartz Filters

Description: The substrates are quartz filters from Pallflex Products Corp. (Putman, CT), product number 2500QAT-UP. To ensure cleanliness, substrates are baked in an oven at 550°C for 4 to 10 hours. *(Toni - this has already been done for the quartz filters you were sent)*

Preparation: Cover working surface with aluminum foil, cleaned with alcohol or water. Lay out opened plastic petri dishes edge up on work surface. The petri dishes used for denuders are easiest for this. Using blunt forceps lay out individual filters using the edges of the petri dishes for support so the filters are suspended above the work surface but do not touch each other. Impregnate by pipeting 1 mL of 0.5% NaCl in 50/50 water/methanol onto each filter. Make aluminum foil tent to cover filters without touching them, and let air dry for 4 or more hours. (In clean environments, no noticeable contamination is seen for 24 hour drying times.).

General Instructions for Changing Cassettes Substrates

Cassette Descriptions

Cassettes refer to the filter holder assembly used for the denuders and filters during sampling. There are several pieces:

Top: Milky white Teflon piece with threads which is inlet.

Regular Tops have a thick lower lip and no provision for an O-ring. These are used for cassettes with filters only, that is no denuders.

Machined tops have been machined to hold the thicker of the two types of o-rings (no. 131). This o-ring presses against the denuder surface to provide a seal.

Spacer: Teflon support grid used to separate stacked filters.

Bottom: Outlet piece with 1/4 inch swage connection which attaches to Tygon tubing line.

Nuts: Colored piece which slips over bottom piece and threads to top piece to hold cassette together.

Black O-rings: two sizes: thick and thin, both are viton.

Teflon O-ring: No. 223 O-ring made of hard Teflon.

Flat Teflon Washer : No. 223 flat washer.

Unloading - All Cassettes

Cover working surface with aluminum foil, cleaned with alcohol or water. Layout and label petri dishes with a consecutive sample number, leg or "1-day" number, substrate type, sample start and stop dates. Use snap petri dishes (provided by Dennis) for filters, and loose covered petri dishes (provided by ADI) for denuders. One substrate per dish.

To unload cassette, grasp between thumb and first (or second) finger. With swage piece pointing upward, unthread nut and remove. Turn over with inlet facing up and unload into petri dishes. Handle denuders with gloved hands, filters with cleaned blunt forceps. Denuders are put in petri dishes with 1 Kim-wipe, and the dish is then wrapped in aluminum foil to hold together. Stack petri dishes with samples together, wrap in aluminum foil and then place in plastic bag. Label bag with "ADI" sample dates and place in refrigerator.

Leg 17 Cassette - Loading Instructions

All Leg 17 cassettes have two Nylasorb filters, as shown in lab notebook figure for Leg 17. The top is a regular top. The nut is a short green nut. No o-rings are used. Wrap threads on top with Teflon Tape Assemble as shown except for nut. Holding assembled pieces together between thumb and first or second finger, turn upside down with swage fitting facing upward, slip nut over this piece with swage and tighten against top piece while holding assembly together.

Leg 18 Cassettes with Carbonate Denuders and Nylasorb AF - Cb100, Cb400

Reference lab notebook figure for Leg 18 with denuders. Wrap threads on top with Teflon tape. Holding bottom piece, load Nylasorb after filter, then thick Teflon o-ring, then two stacked carbonate denuders separated by flat Teflon gasket and then machined top piece with thick black O-ring. Holding assembled pieces together between thumb and first or second finger, turn upside down with swage fitting facing upward, slip nut over this piece with swage and tighten against top piece while holding assembly together. Try to keep top and bottom pieces from rotating. Do not over tighten. Final tightening is done during leak testing described below.

Leg 18 Cassettes with Carbonate Denuders and NaCl AF - CbNa100

Follow the same instructions as above for Cb100 and Cb400, only load NaCl impregnated quartz after filter in place of Nylasorb. The loading order is: NaCl quartz, thick Teflon o-ring, then two stacked carbonate denuders separated by flat Teflon gasket and then machined top piece with thick black O-ring. Threads on top shold be wrapped with Teflon tape. Assemble and leak test as described above.

Leg 18 Cassettes with NaCl Denuders - Na100, Na400

Reference same lab notebook figure as for carbonate denuder configuration. Wrap threads on top with Teflon tape. Holding bottom piece, load NaCl impregnated quartz filter, then thick Teflon o-ring, then two stacked NaCl coated denuders separated by flat Teflon gasket and then machined top piece with thick black O-ring. Holding assembled pieces together between thumb and first or second finger, turn upside down with swage fitting facing upward, slip nut over this piece with swage and tighten against top piece while holding assembly together. Try to keep top and bottom pieces from rotating. Do not over tighten. Final tightening is done during leak testing described below.

Leg 18 Cassettes with Double NaCl Filters - NaCl$_f$

Reference lab notebook figure for Leg 18 with filters only. Wrap threads on top with Teflon tape. Holding bottom piece, load NaCl impregnated quartz filter, then thin viton o-ring, spacer, then second (top) NaCl quartz filter and regular top piece . Holding assembled pieces together between thumb and first or second finger, turn upside down with swage fitting facing upward, slip nut over this piece with swage and tighten against top piece while holding assembly together. Try to keep top and bottom pieces from rotating. Do not over tighten. Final tightening is done during leak testing described below.

One-Day Sampler Cassette - Loading Instructions

This cassette differs from Leg 18 cassette in that a Teflon impactor is mounted in the "Top" piece of the cassette. These are a simple press fit. The impaction plate needs to be wiped clean when new substrates are installed, otherwise the procedure is as for Leg 18.

Clean Impaction Plate: With phillips screw driver, remove impaction plate of each impactor. The top of the impactor stays with the holder top and need not be removed. Wipe fritted glass surface with a Q-tip to remove build up of particles. Reinstall. Caution is needed because Teflon threads are easily stripped by the stainless-steel screws, so be especially careful not to cross thread and do not tighten excessively.

Load Cassettes: Follow the same instructions as for Leg 18 cassettes with denuders, i.e. Cb100, Cb400, Na100 and Na400.

Leak testing

Cassettes are individually leak tested. Use One Day Sampling pump. Disconnect before valve so that this will not require readjustment. Use rotameter with valve at outlet, connected to pump. Set flow at 1 L/min. Test cassettes by connecting to inlet of rotameter, block flow at inlet with gloved finger or crimped Tygon. (the Tygon which fits is in box with rotameter for daily changes). Flow should go to less than 200 cc/min. If not, tighten cassette by hand or with wrenches until leak stops. Do not over tighten.

Storage of Loaded Cassettes before Sampling

Cap cassettes with black caps, group by days in plastic bag and store at room temperature. (Cold storage tends to create leaks in the cassette).