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Monitoring for Acidic Pollutants in Support of Epidemiological Studies in the South Coast Air Basin of California

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

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Final Report

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EXECUTIVE SUMMARY

Particulate and gaseous constituents of air pollution were measured in downtown Los Angeles during daylight hours (0730 to 1930 PDT) from August 1 through October 30, 1993. Atmospheric acids were quantified as strong acidity in $PM_{2.5}$ (particles with aerodynamic diameters <2.5 µm) and as gaseous nitric acid. $PM_{2.5}$ mass, nitrate, chloride, sulfate and ammonium were also measured. Collocated measurements with a Harvard HEADS sampling system were acquired from October 9 through October 20, 1993. The following conclusions are drawn from these measurements:

- Strong acid concentrations in the particulate phase were generally low. For nearly all of the samples, hydrogen ion concentrations (derived from the difference in pH before and after sample extraction) were lower than 10 nmole/m^3, and the highest value of ~60 nmole/m^3 was accompanied by a high sulfate concentration (>40 µg/m^3) which was more than 90% neutralized. Significant levels of aerosol strong acidity were not found during the study period.

- Nitric acid concentrations ranged from <1 to 18 µg/m^3. Nitric acid concentrations were moderately correlated with particulate nitrate levels, but they were often lower than particulate nitrate concentrations when the latter were at their highest levels.

- More than 50% of the average $PM_{2.5}$ was composed of secondary aerosol, specifically sulfate, nitrate, and ammonium, during the study period. The highest $PM_{2.5}$ concentrations were measured during the fall, and the highest sulfate, nitrate, and ammonium concentrations were also found during this period.

- Medvol and HEADS measurements were comparable, within ±20%, for particulate nitrate and sulfate. Total nitrate (sum of particulate nitrate and nitric acid) concentrations were comparable below about 10 µg/m^3, but Medvol total nitrate was less than half of HEADS total nitrate for several of the concentrations measured above this level. Since nitric acid concentrations for the Medvol are calculated from the difference between total nitrate and particulate nitrate, the Medvol showed nitric acid concentrations to be less than half of the corresponding HEADS nitric acid levels for many of the twelve collocated samples.

ACKNOWLEDGEMENTS AND DISCLAIMER

Ms. Hazel Braxton-Owens, Ms. Alba Martinez, and other staff at the Los Angeles Children's Asthma Project, are recognized for their assistance in the sampling aspects of this project. The assistance and cooperation of Sam Mai and other South Coast Air Quality Management District staff in arranging for use of the sampling site is greatly appreciated. Dr. Nehzat Motallebi of the California Air Resources Board and Drs. Judith Chow, Alan Gertler, and John Watson of DRI provided careful review and constructive recommendations for the presentation of data in this report.

The results and conclusions presented in this report do not necessarily reflect the position and policies of the California Air Resources Board.

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1.0 INTRODUCTION

1.1 Background

The relationship of ambient air concentrations of atmospheric pollutants to observable health effects in normal and "sensitive" groups of human subjects has been of great interest and the subject of a variety of investigations (Koenig et al., 1989; Ostro et al., 1991). One sensitive group of concern--asthmatics--have been the subject of several studies, in connection with one of which we monitored the concentrations of acidic pollutants in gaseous and aerosol phases along with associated ions and $PM_{2.5}$ mass for a 3-month period, August-October, 1993.

Sulfates, formed by gas-to-particle conversion from SO_2, constitute a large fraction of fine-particulate mass in the atmosphere, and thus play a major role in atmospheric visibility degradation. Since these facts were recognized in the mid-1970's, major efforts to improve methods for determination of sulfur in ambient atmospheric particles have been conducted by measurement scientists. The chemical nature of airborne sulfate was found to be of significance in aerosol growth processes, and the fraction present as sulfuric acid or other acidic sulfate species was deemed potentially significant for health effects reasons as well. Thus, measurement scientists sought to distinguish sulfuric acid and bisulfate from other sulfate species in atmospheric aerosols with as short a time resolution as possible. The principal means found to accomplish this involved either solvent extraction of filter samples, or various schemes based on the differing thermal properties of the principal sulfur compounds in ambient particles--sulfuric acid, ammonium bisulfate, letovicite ($[NH_4]_3H[SO_4]_2$), ammonium sulfate, and alkali and alkaline earth sulfates. These extraction and thermal analysis schemes have been reviewed by Tanner (1989).

The use of a conventional filter pack (Teflon/nylon), with or without a denuder device to remove acidic and basic gases prior to the filter, to determine airborne sulfate and its associated strong acidity, is hampered by the relatively long collection times (6-24 hr) needed at conventional flows of 10-30 L/min to collect enough sample at ambient concentration to analyze for strong acid. Use of an acid-treated quartz filter enables much higher linear flow velocities to be used (up to 500 L/min for a 102-mm diameter filter), and indeed, strong acid determinations for samples collected in as little as one hour were reported by Tanner et al., 1977). However, there are problems with a high-volume sampling approach, principally the difficulty in using denuders to remove ammonia in incoming air, leading to the potential for neutralization of acidic particles to occur if the ammonia gas concentration increases during the sampling period. In addition, there are further possibilities for neutralization during handling operations prior to laboratory analysis. Clearly, 6- to 12-hr sampling of aerosols including analysis for strong acidity is achievable (Koutrakis et al., 1988), although it would be best to extract and analyze the sample at the location where it was collected, and as soon after collection as possible, to minimize the neutralization of acidic particles and reduce other sampling artifacts.

Gaseous nitric acid has not to date been associated with adverse health effects (Aris et al., 1991). It is formed during daylight hours primarily by reaction of nitrogen dioxide with OH radicals. This is the same path by which gas-phase conversion of SO_2 to sulfuric acid occurs, and for equivalent concentrations of NO_2 and SO_2, the rate of formation of nitric acid is about 5 times faster than for sulfuric acid. In contrast to sulfuric acid, however, nitric acid is found predominantly in the gas phase under most atmospheric conditions unless ammonia concentrations are sufficiently large to convert it to ammonium nitrate aerosol. In this study we have made 12-hr daytime measurements of nitric acid by the denuder difference technique (Shaw et al., 1982; Spicer et al., 1982; Forrest et al., 1982) employing a medium volume sampler and an aluminum denuder similar to that used by Wall et al. (1988).

Previous studies have found that acidic aerosols occur in higher concentrations during daylight hours (Spicer et al., 1982; Hering et al., 1988); indeed, few occurrences of episodic acidic aerosol concentrations at night have been documented. In addition, daytime concentrations of nitric acid and ozone are much higher than at night in urban areas. Therefore we sampled aerosols and nitric acid only during 12-hr daytime periods for the 3-month monitoring period of this study.

Monitoring for $PM_{2.5}$ mass, and sulfate, nitrate, and ammonium was conducted in addition to direct measurement of aerosol strong acidity. This has provided data on the fraction of major inorganic constituents in the fine particle mass. Thus, in addition to the actual concentration of strong acid (usually calculated as nmoles/m^3 of H^+ or $\mu g/m^3$ of sulfuric acid), the relative acidity of the aerosol as equivalent ratio of H^+ to the sum of sulfate and nitrate can also be calculated from our data. The additional diagnostic of the fine-particle inorganic cation-anion balance has been provided by the measurement of ammonium concentrations.

1.2 Objectives

The objectives of this study are:

- Acquire summertime and fall daytime measurements of fine particles, acidic species, and related chemical concentrations in downtown Los Angeles.
- Identify periods with high concentrations of particulate and gaseous acid concentrations in ambient air and the degree to which these vary together with time.
- Examine the equivalence of measurements acquired with two different monitoring methods over a fraction of the summertime monitoring period.

To accomplish these objectives, a medium volume sampling system (Medvol) was located at the South Coast Air Quality Management District's (SCAQMD) Downtown Los Angeles monitoring site at the Los Angeles Division of Water and Power building on N. Main Street. This site has been the subject of intensive aerosol studies in prior monitoring programs (Solomon et al., 1989; Chow et al., 1994). Daytime samples of twelve-hour duration were acquired each day between 0800 and 2000 PST from August 1 through October 30, 1993 for $PM_{2.5}$ (particles with aerodynamic diameters <2.5 µm), particulate sulfate, nitrate and ammonium, particulate strong acidity, and gaseous nitric acid. A Harvard HEADS sampler, with pump and flow control provided by DRI, was collocated with the Medvol from October 9 through October 20, 1994 to evaluate the equivalence between these two measurement systems for selected chemical species.

2.0 EXPERIMENTAL PROCEDURES

2.1 Field Operations

The downtown Los Angeles site is near the intersection of major freeways at the LA Department of Water and Power location at 1630 N. Main St., and represents a site exposed to a combination of fresh and partially aged emissions. The Medvol sampler was located on the roof of building #3. Sampling commenced on August 1, 1993 and continued through October 30, 1993, after which the Medvol was removed and the site was restored to its prior condition. Filter packs were changed each day for sampling between 0730 and 1930 hr PST. The Harvard HEADS sampler was operated over the same daily period from October 9 through October 20. 1993.

Volunteer field operators were provided with written procedures and training prior to and during the monitoring period. Filter packs were shipped monthly and maintained under refrigeration prior to and after their exposure in the sampler. Flow rates through the filter packs were measured with a calibrated rotameter before and after each sampling period.

Daily samples were obtained except for the periods of August 3 through 5, August 14, and August 31 through September 9, 1993. No valid samples were taken on August 3rd through 5th due to a power problem; a dedicated 20-A, GFI line was installed for the DRI sampler and no subsequent problems with power were encountered. The loss of the August 14 sample was caused by a sampler failure. A labor dispute at Los Angeles Department of Water and Power prevented access to the site from August 31 through September 9, 1993, and samples could not be acquired during this period.

The Harvard HEADS sampler was collocated with the Medvol from October 9 through 20, 1993. Pre-loaded denuders (one carbonate-coated denuder for acid gases and one citric acid-coated denuder for basic gases) and filter packs were provided by the Harvard School of Public Health. At the entrance to the first denuder is a fritted glass impactor plate that excludes particles >2.5 µm diameter, at 10 L/min flow. Samples acquired with the Medvol and with the HEADS samplers were submitted to the same laboratory analysis methods.

2.2 Sampler Configuration and Analysis

Figure 2-1 shows a schematic diagram of the measurement system applied in this study. The Medvol consists of a PFA Teflon-coated aluminum plenum to which a Bendix 240 Teflon-coated cyclone inlet is attached. This inlet has an aerodynamic cut-point of 2.5 µm at a flow rate of 113 L/min. Prior to deployment, the interior of the plenum and cyclone had been cleaned, treated with dilute nitric acid, rinsed and dried, as described by Watson et al. (1989a).

Air was drawn into the plenum through this inlet at the prescribed flow rate. Three Savillex PFA filters holders were located at the bottom of the plenum and air was drawn through these at 20 L/min. The remaining 53 L/min of make-up flow was drawn through empty filter holders, and measured before and after each sampling period with a magnehelic gauge against a pressure drop determined with a calibrated rotameter. The three filter holders contained the following combinations of filters:

- Filter Pack 1 (FP1) was directly connected to the plenum and contained a Teflon membrane filter for-mass, sulfate, nitrate, chloride and ammonium measurements, followed by a nylon filter to collect nitric acid and any particulate nitrate which volatilized from the Teflon filter during sampling. The sum of nitrate concentrations from the two filters represents total nitrate in both gaseous and particulate phases.

- Filter Pack 2 (FP2) contained a nylon filter and was located downstream from an anodized aluminum annular denuder which removed nitric and hydrochloric acids. This filter was analyzed for nitrate to determine particulate nitrate. For samples taken on and after August 30th, it was also analyzed for chloride to determine particulate chloride.

- Filter Pack 3 (FP3) contained a Teflon membrane filter located after a citric acid-coated tubular denuder to remove basic gases such as ammonia. Measurements of pH were made on extracts from this filter to quantify the hydrogen ion content, which represented strong acidity in suspended particles.

The collocated annular denuder (HEADS) sampler (Figure 2-2), operated 9-20 October, consisted of a carbonate-coated acid gas denuder with an glass impactor frit on the inlet (to remove coarse particles), followed by a citric acid-coated basic gas denuder. Downstream of the denuders was a filter pack consisting of a Teflon filter followed by a pair of carbonate-impregnated cellulose filters and a pair of citric acid-impregnated filters. The flow through the denuders was maintained at 10 L/min (±5%) with a pump and needle valve and the flow recorded before and after each sampling period. The acid gas denuder was extracted and analyzed by IC for chloride and nitrate to quantify HCl and HNO_3, respectively. The basic gas denuder was extracted and analyzed for ammonium by automated colorimetry to quantify gaseous ammonia. The Teflon filter was bisected and one half analyzed as per FP1 of the DRI MedVol sampler. The other half was analyzed for aerosol strong acidity as per FP3 of the Medvol (see below). The carbonate filters were analyzed for chloride and nitrate to quantify "volatilized" particulate chloride and nitrate. The citric acid-impregnated filters were not analyzed. Particulate fine mass was not determined on the HEADS samples.

Chow et al. (1993) describe the laboratory analysis procedures in detail. The Teflon filter in FP1 was weighed on a calibrated microbalance before and after sampling to obtain mass concentrations. It was then extracted in deionized distilled water, and a portion of this extract was analyzed by ion chromatography for sulfate, chloride and nitrate, and by automated colorimetry for ammonium. Nylon filters from FP1 and FP2 were extracted in sodium carbonate eluent and were analyzed by ion chromatography for nitrate. Hydrogen ion was quantified by extracting the Teflon filter from FP3 in dilute sulfuric acid (pH=4.0), then measuring the pH of the extract with a combination pH electrode, standardized with a pH=4.00 buffer. The pH of the sample extract was converted to hydrogen ion concentration, and the hydrogen ion content of the eluent was subtracted to obtain the concentration of hydrogen ion associated with strong aerosol acidity in the sample.

Replicates, standards, and blanks were analyzed for approximately ten percent of all analyses, and samples were re-run when performance tolerances were exceeded. Laboratory data were combined with measured flow rates and sample durations to determine ambient concentrations for the specified observables. As a data validation check, cation/anion balances were calculated and were found to be in agreement for samples in which sulfate and nitrate levels were higher than the mean, **and** in which strong aerosol acidity levels were positive. Data have been assembled with graphical representations in an EXCEL 5.0 workbook which is available from DRI.

Tables 2-1 and 2-2 summarize the average precisions estimated for the Medvol and HEADS measurements, as determined by propagating individual precisions for flow rates and chemical analyses. Flow rate precisions are based on the standard deviation of repeated measurement taken with the calibration rotameter. Analysis precisions are estimated from replicate and field blank analyses. Watson et al. (1989a) describe the error propagation methods.

Table 2-1
Estimated precisions of measured quantities[*] for the Medvol sampler

Measured Species	*Flow Precision*	*Mean Blank Precision*	*Mean Analytical Precision*	*Overall Mean Precision*
Mass	±5%	±4.6%	±1.0%	±6.9%
H^+	±5%	----	----	est ±10% or ±5nmole/m3
NH_4^+	±5%	±0.30%	±4.7%	±6.9%
$SO_4^=$	±5%	±0.21%	±3.4%	±6.0%
Cl^-	±5%	±20%	±8.6%	±22%
NO_3^-	±5%	±2.5%	±2.1%	±6.0%
HCl(g)	±5%	±9.0%	±17.3%	±20%
HNO_3(g)	±5%	±5%	±7%	±10.0%

[*] Mean uncertainties of individual measurements, expressed in % except where noted.

Table 2-2
Estimated precisions of measured quantities[*] for the HEADS sampler

Measured Species	*Flow Precision*	*Mean Blank Precison*	*Mean Analytical Precision*	*Overall Mean Precision*
H^+	±5%	-----	-----	est ±10% or ±10 nmole/m^3
NH_4^+	±5%	est[1] ±6.5%	±7.0%	±10.9%
$SO_4^=$	±5%	est ±6.0%	±4.5%	±9.0%
Cl^-	±5%	est ±18%	±30%	±36%
NO_3^-	±5%	est ±6.0%	±6.8%	±10.4%
HCl(g)	±5%	est ±9%	±5%	±12.4%
HNO_3(g)	±5%	est ±4.0%	±2.1%	±6.8%

[*] Mean precisions of individual measurements, expressed in % except where noted.

[1] Estimated since only one HEADS field blank was taken.

3.0 CONCENTRATIONS OF ACIDIC SPECIES

3.1 Statistical Summary

Table 3-1 provides a statistical summary of measurements taken over the monitoring period. Total nitrate refers to the sum of particulate nitrate and nitric acid concentrations. Particulate ammonium is determined from the sum of measured ammonium plus "volatilized ammonium", the latter caused by volatilization of ammonium nitrate from the Teflon filter in FP1 during sampling. All units are in $\mu g/m^3$ except hydrogen ion which is expressed in $nmole/m^3$. Volumes reflect local temperatures and pressures that occurred during sampling.

Table 3-1
Statistical summary of measurements at downtown Los Angeles from August 1 through October 30, 1993

	$PM_{2.5}$[a]	*Ammonium*[a]	*Sulfate*[a]	*Nitrate*[a]	*Chloride*[a]	*Nitric Acid*[a]	*Hydrogen*[b]	*Total Nitrate*[a]
Mean	40.82	6.65	6.09	10.20	0.34	7.10	-0.49	17.30
Median	32.66	6.41	5.25	9.22	0.23	6.72	4.10	16.87
Std. Dev.	32.47	3.70	5.43	5.47	0.40	3.25	21.81	7.67
Minimum	4.48	1.17	1.18	0.38	0.00	0.00	-82.36	2.37
Maximum	208.68	27.74	46.02	25.64	2.11	18.32	62.98	43.96
Count	77	77	77	77	77	77	77	77

[a] Units of $\mu g/m^3$
[b] Units of $nmole/m^3$

Several of the hydrogen ion concentrations are negative, meaning that measured pH exceeded that of the extraction solvent (pH=4.0). These values are real and indicate that the amount of soluble basic material in $PM_{2.5}$ exceeded, on an equivalent basis, the amount of hydrogen ion associated with sulfate for those samples.

There was a large variation in concentrations for all measured quantities during the study period. The maximum $PM_{2.5}$ concentration of 209 $\mu g/m^3$ occurred on September 23, 1993. All measured species (except particulate chloride and gaseous HCl) attained their maxima on this date, regardless of the filter media used. No sampling anomalies were found for this sample, so this extreme is believed to be real. This value by itself exceeds the federal twenty-four average PM_{10} (particles with aerodynamic diameter < 10 μm) standard of 150 $\mu g/m^3$, and far exceeds the California state PM_{10} standard of 50 $\mu g/m^3$. The average concentration of 41 $\mu g/m^3$ approaches the annual average PM_{10} standard of 50 $\mu g/m^3$, and far exceeds the annual average state standard of 30 $\mu g/m^3$. The measured mass on the Teflon filter actually under-estimates the total $PM_{2.5}$ concentration because some of the ammonium nitrate originally captured by this filter volatilized during sampling and was captured on the nylon backup filter.

Nitrate and nitric acid were the most abundant chemical species measured during the study period. On average, particulate nitrate constituted 25% of the mass measured on the Teflon filter. Ammonium and sulfate were the next most abundant species, each constituting approximately 15% of the average mass measured on the Teflon filter. Average sulfate, nitrate, and ammonium constituted more than half of the average $PM_{2.5}$ mass measured on the Teflon filter during the study period. This is consistent with results from prior $PM_{2.5}$ measurements in Los Angeles (Gray et al. 1986; Solomon et al., 1989; Chow et al., 1994) which have found the remaining mass to be composed of organic and elemental carbon, crustal material, and marine aerosol, in that order of abundance.

The sulfate maximum of 46 $\mu g/m^3$ on September 23, 1993 is among the highest measured on 24-hour average samples in recent years in southern California. The maximum nitrate concentration of 26 $\mu g/m^3$ is lower than maxima found in other studies during the same season in prior years. This may reflect the fact that higher temperatures during daytime samples shift ammonium nitrate toward the gaseous nitric acid and ammonia phases, resulting in lower particulate nitrate levels than would be found for samples which are acquired over daytime and nighttime hours (Chow et al., 1994).

Particulate chloride values are small, which is also consistent with other measurements taken in Los Angeles. Chow et al. (1994) show from Southern California Air Quality Study (SCAQS) data that sodium chloride from marine aerosol reacts quickly with nitric acid to create sodium nitrate. The chloride is converted to gaseous hydrochloric acid by this process. This confirms results of Wall et al. (1988) concerning the origin of gaseous and particulate chloride in this near-coastal area.

The average hydrogen ion concentration was low, indicating that most of the particulate strong acid was already neutralized, presumably by atmospheric ammonia. Russell and Cass (1984) show that there are sufficient ammonia emissions in the Los Angeles area to cause this neutralization and Chow et al. (1994) found a good relationship for summer and fall SCAQS samples between measured ammonium ion and that calculated assuming that all sulfate and nitrate are present as ammonium sulfate and ammonium nitrate. These results are consistent with the low particulate strong acidity levels found by Lioy et al. (1980) in the New York City area.

3.2 Temporal Variations

Figures 3-1 through 3-3 show the temporal variation for particle mass, chemical composition, and hydrogen ion concentrations. Figure 3-1 shows that mass concentrations were less than 50 $\mu g/m^3$ prior to September except for the sample taken on August 26. The majority of high mass concentrations occurred after the September 23 episode, with mass concentrations exceeding 50 $\mu g/m^3$ from 9/23 through 9/25, 9/27 through 9/30, 10/21 through 10/23, and 10/25 through 10/30. The final episode occurred at almost exactly the time period during which Solomon et al. (1989) measured high PM$_{10}$ during 1986 and Chow et al. (1992) measured high PM$_{10}$ during 1988.

Figure 3-2 shows that particulate nitrate was the most abundant component of PM$_{2.5}$ during all of these episodes except for the 9/23 sample, in which sulfate attained its highest concentration of the study. Nitric acid concentrations generally tracked the particulate nitrate concentrations, but there was a substantial decrease in concentrations during the PM$_{2.5}$ episodes. The final 10/25 through 10/30 episode is illustrative because it shows nitric acid levels decreasing as the particulate nitrate levels increase. It is probable that ammonia concentrations and relative humidities were higher, and/or temperatures were lower, during this period. Both conditions would shift the equilibrium between nitric acid, ammonia, and ammonium nitrate toward the particulate phase.

Figure 3-2 shows that most of the chemical species measured during this study rise and fall in conjunction with each other. The exception is particulate chloride, which increases when PM$_{2.5}$ and its chemical constituents decrease. This is most notable over the 9/11 through 9/13, 9/15 through 9/17, and 10/3 through 10/8 periods, and it is consistent with the well-documented intrusion inland of the relatively clean, but chloride-rich marine layer (Watson et al., 1993). The relatively clean air from the ocean displaces the polluted air that normally accumulates during prolonged periods of stagnation.

Figure 3-3 shows that hydrogen ion concentrations are generally low and often negative. This is consistent with results from previous studies in southern California (Solomon et al., 1992) that show the most important component of aerosol acidity, sulfuric acid, to be almost entirely neutralized. For perspective, hydrogen ion concentrations of 200 to 300 nmoles/m^3 are commonly measured at non-urban sites in the eastern United States (c.f., Lioy et al. (1980). The only event that indicated significant acidity, within a few times the uncertainty intervals reported in Section 2, occurred during the 9/23 episode. Even during this event, more than 90% of the sulfate was present as neutral ammonium sulfate.

Figure 3-4 compares the temporal distribution of the hydrogen ion to sulfate mole ratio with nitric acid concentrations for the study period. The charge ratio does not significantly deviate from zero except during high PM$_{2.5}$ episodes after 9/23. This plot shows only a weak relationship between nitric acid and the mole ratio indicator of particulate strong acidity. Indeed, if any relationship exists, nitric acid appears to be higher during late September and late October when strong acidity is highly neutralized. Figure 3-5 shows no consistent relationship between corresponding measurements of nitric acid and aerosol strong acidity.

3.3 Correlation Coefficients

Table 3-2 lists the paired correlation coefficients for the seventy-seven valid samples obtained during the study period. These coefficients reflect the qualitative relationships shown in Figures 3-1 through 3-3. The largest correlation coefficients are found between ammonium, sulfate, and nitrate, indicating that the majority of ammonium is associated with the sulfate and nitrate anions. This is consistent with the low values of particulate strong acidity shown in Figure 3-4, implying the absence of sulfuric acid and low quantities of hydrogen bisulfate in the majority of samples. The most abundant neutralized sulfate compound is ammonium sulfate. As noted above, ammonium nitrate is the most abundant nitrate compound in southern California.

Hydrogen ion concentrations are most highly correlated with ammonium and sulfate concentrations. The low correlations with nitric acid and nitrate further confirm the lack of co-occurrence of aerosol strong acidity and nitric acid.

Table 3-2
Paired correlation coefficients for measured chemical concentrations

	$PM_{2.5}$	Ammonium	Sulfate	Nitrate	Chloride	Nitric Acid	Hydrogen
$PM_{2.5}$	1.00						
Ammonium	0.49	1.00					
Sulfate	0.48	0.86	1.00				
Nitrate	0.56	0.77	0.47	1.00			
Chloride	0.25	-0.19	-0.02	0.08	1.00		
Nitric Acid	0.39	0.75	0.51	0.52	-0.28	1.00	
Hydrogen	-0.39	0.52	0.54	0.14	-0.33	0.25	1.00
Tot. Nitrate	0.56	0.87	0.55	0.93	-0.06	0.79	0.21

Particulate ammonium, nitrate, and sulfate have correlation coefficients near 0.5 with $PM_{2.5}$, indicating that they are not always high during periods of high mass concentrations. This probably reflects the lower concentrations of all species during the summer compared to those which are found during the fall.

3.3 Comparison of Medvol and HEADS Measurements

Figure 3-6 compares collocated measurements from the Medvol and HEADS sampling systems for the twelve collocated samples taken between October 9 through October 20, 1993. Total nitrate (the sum of particulate nitrate and nitric acid), particulate nitrate, nitric acid, and sulfate concentrations are compared in these scatter plots. The total nitrate comparison shows reasonable agreement for the five points with concentrations below 10

$\mu g/m^3$. There is a definite tailing in total nitrate above this concentration, with the Medvol achieving a maximum concentration of ~20 $\mu g/m^3$ while the HEADS yields total nitrate concentrations exceeding 45 $\mu g/m^3$.

The upper right-hand panel of Figure 3-6 compares particulate nitrate between the two samplers. The Medvol results are, on average, slightly higher than the HEADS results for concentrations lower than 10 $\mu g/m^3$. Nitric acid concentrations are the difference between total and particulate nitrate. Though some correlation exists, nitric acid values do not show a good agreement between the Medvol and HEADS samplers. The sulfate comparison in the bottom right panel of Figure 3-6 shows Medvol values to be lower (~20%) than corresponding HEADS values, though they are highly correlated. No tailing at the upper end of the concentration range is observed in this plot.

No standardized concentrations were submitted to the two systems during this comparison, and the comparison was not designed to determine the causes of differences between the two sampling systems. Particulate nitrate and sulfate are in agreement within ±20%, with particulate nitrate being slightly higher and particulate sulfate being slightly lower on the Medvol with respect to the HEADS. Total nitrate (sum of particulate nitrate and nitric acid) was equivalent between the two samplers up to concentrations of 10 $\mu g/m^3$. Further tests with known standards at different concentration levels are needed to determine the causes of these differences.

4.0 SUMMARY AND CONCLUSIONS

Particulate and gaseous constituents of air pollution were measured in downtown Los Angeles during daylight hours (0730 to 1930 PDT) from August 1 through October 30, 1993. Atmospheric acids were quantified as strong acidity in $PM_{2.5}$ (particles with aerodynamic diameters <2.5 μm) and as gaseous nitric acid. $PM_{2.5}$ mass, nitrate, chloride, sulfate and ammonium were also measured. Collocated measurements with a Harvard HEADS sampling system were acquired from October 9 through October 20, 1993. The following conclusions are drawn from these measurements:

- Strong acid concentrations in the particulate phase were generally low. For nearly all of the samples, hydrogen ion concentrations were lower than 10 nmole/m^3, and the highest value of ~ 60 nmole/m^3 was accompanied by a high sulfate concentration (>40 $\mu g/m^3$) which was more than 90% neutralized. Significant levels of aerosol strong acidity were not found during the study period.

- Nitric acid concentrations ranged from <1 to 18 $\mu g/m^3$. Nitric acid concentrations were moderately correlated with particulate nitrate levels, but they were often lower than particulate nitrate concentrations when the latter were at their highest levels.

- More than 50% of the average $PM_{2.5}$ was composed of secondary aerosol, specifically sulfate, nitrate, and ammonium, during the study period. The highest $PM_{2.5}$ concentrations were measured during the fall, and the highest sulfate, nitrate, and ammonium concentrations were also found during this period.

- Medvol and HEADS measurements were comparable, within ±20%, for particulate nitrate and sulfate. Total nitrate (sum of particulate nitrate and nitric acid) were comparable below concentrations of 10 $\mu g/m^3$, but Medvol total nitrate was less than half of HEADS total nitrate for several of the concentrations measured above this level. Since nitric acid concentrations for the Medvol are calculated from the difference between total nitrate and particulate nitrate, the Medvol showed nitric acid concentrations to be less than half of the corresponding HEADS nitric acid levels for several of the twelve collocated samples.

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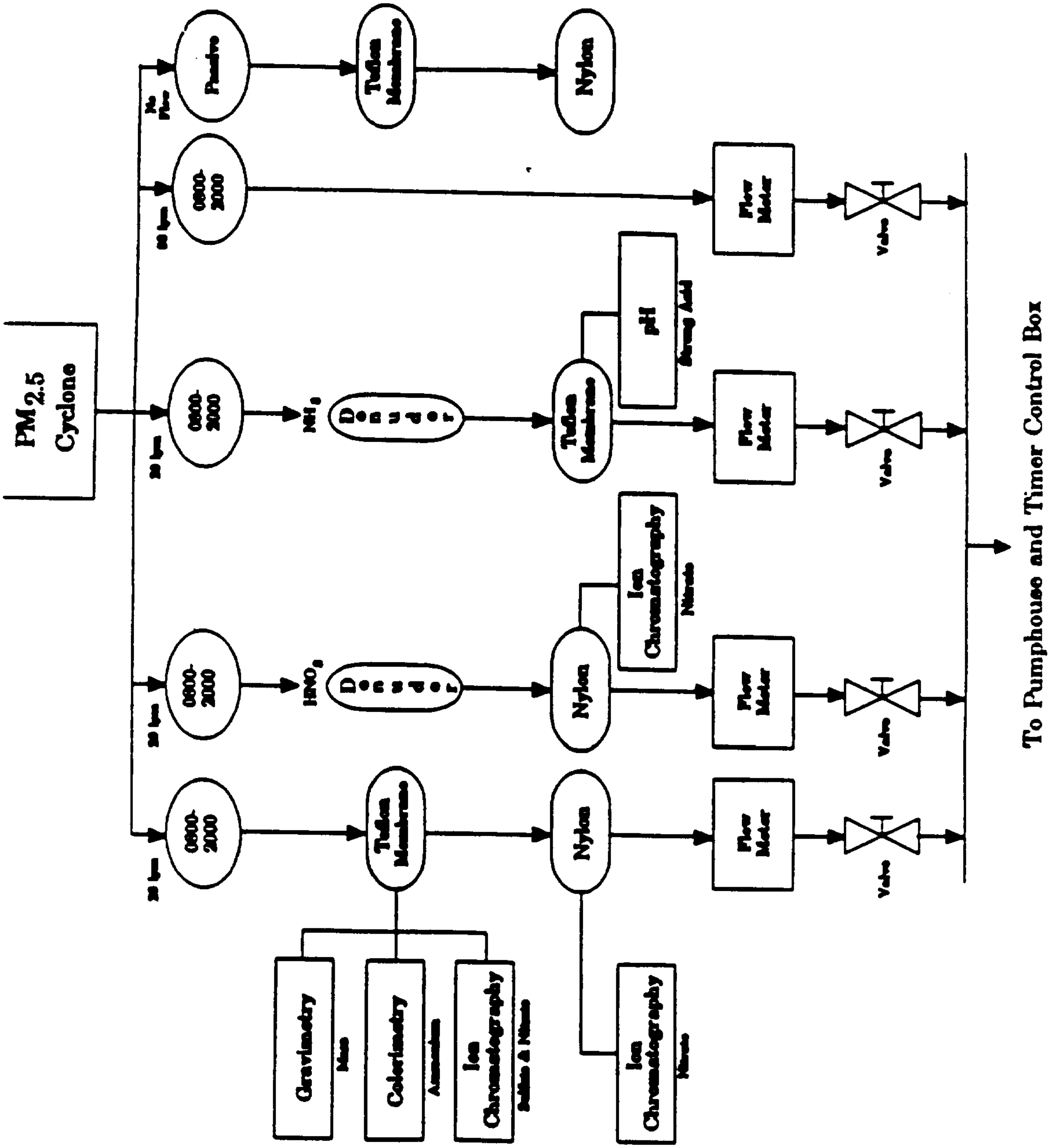
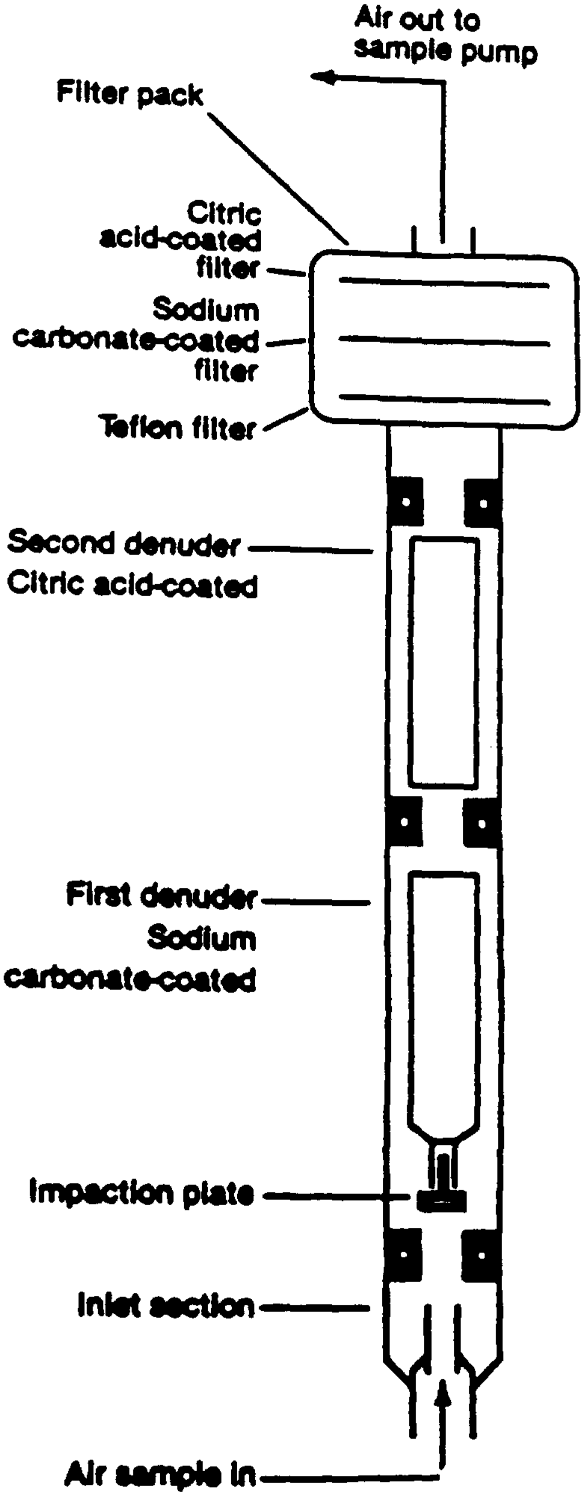


Figure 2-1 Sampling and Measurement Flow Diagram of the $PM_{2.5}$ Unit.

Figure 2-2 Harvard-EPA annular denuder system



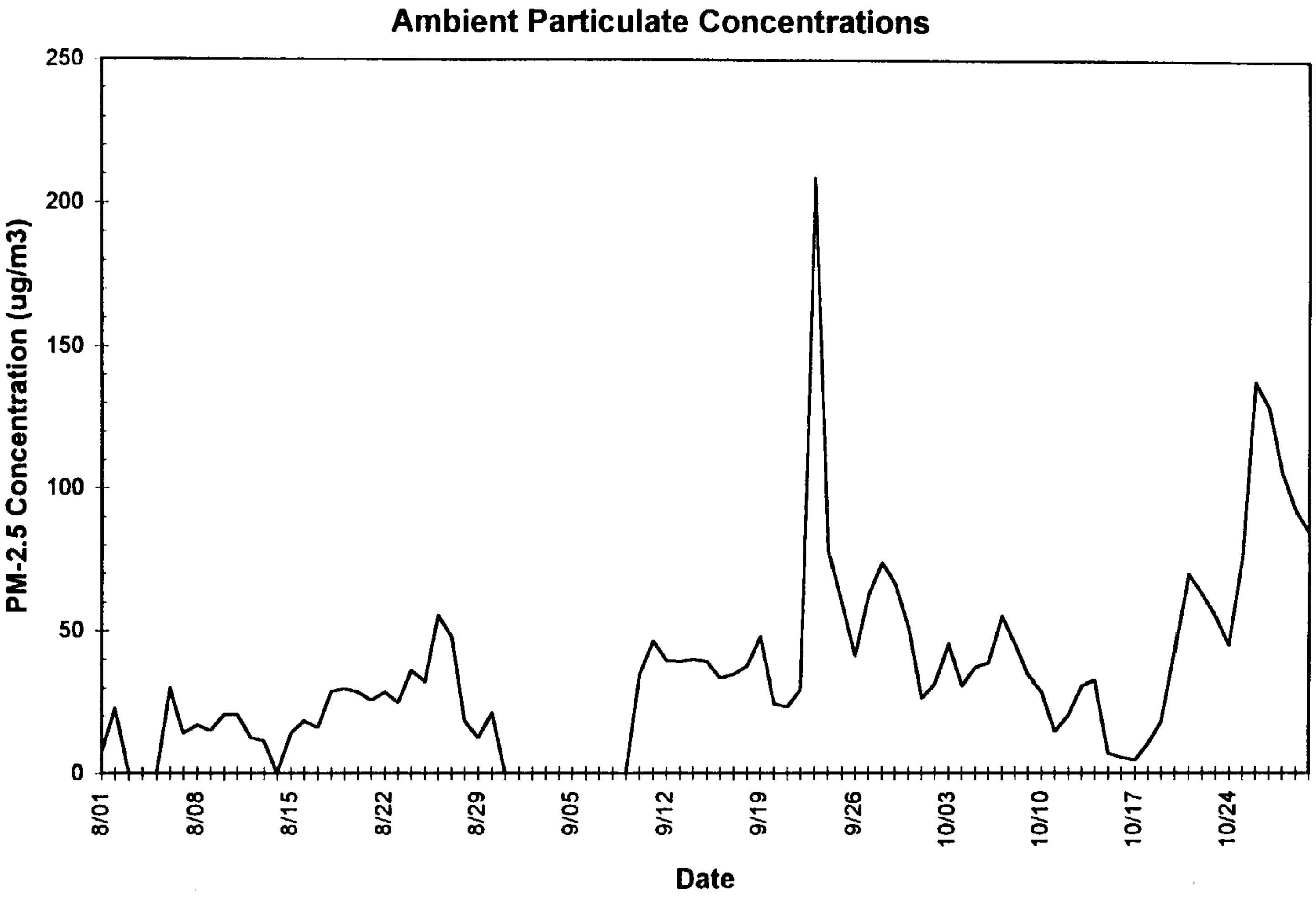


Figure 3-1. Temporal variation in $PM_{2.5}$ mass concentrations.

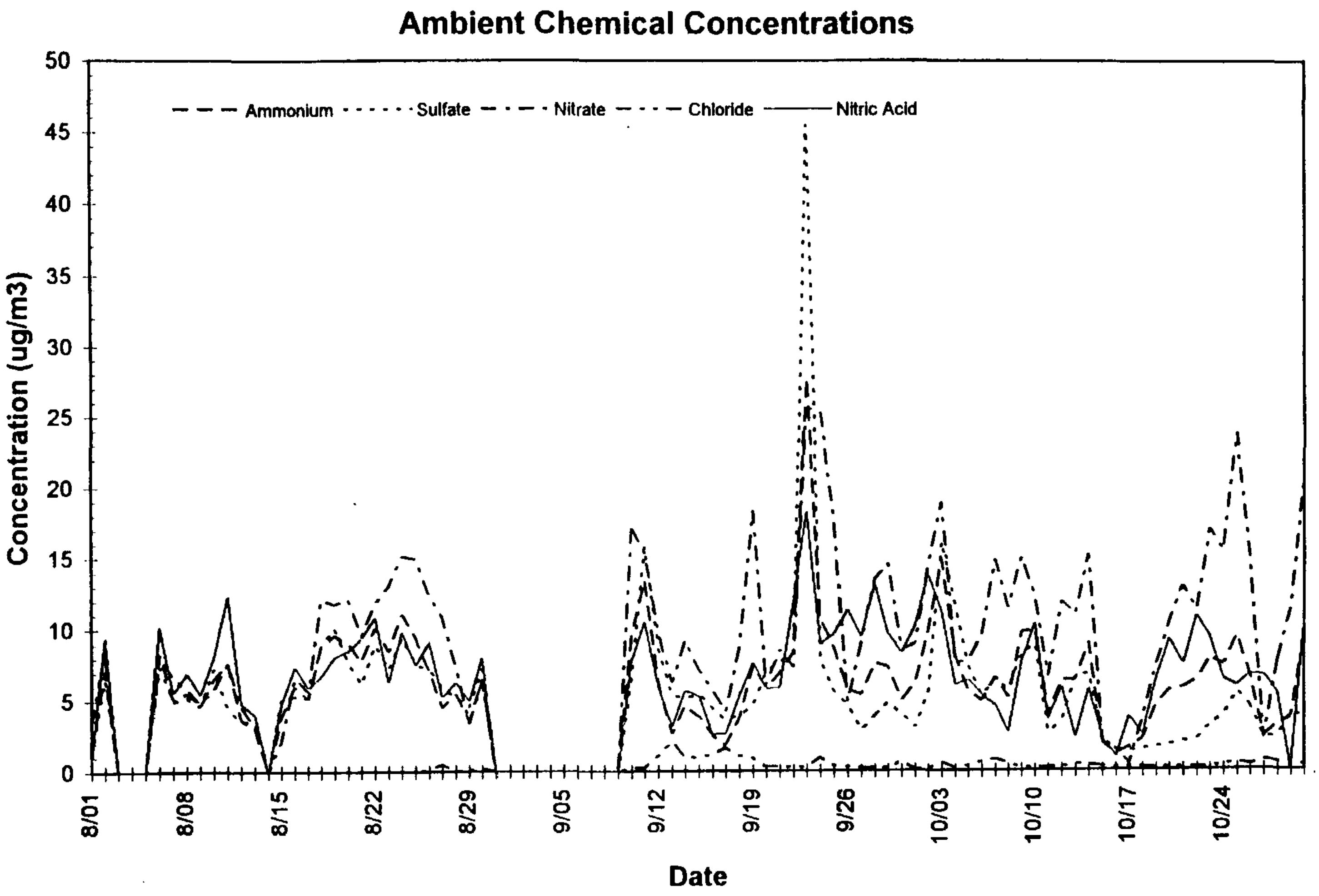


Figure 3-2. Temporal variation in chemical concentrations.

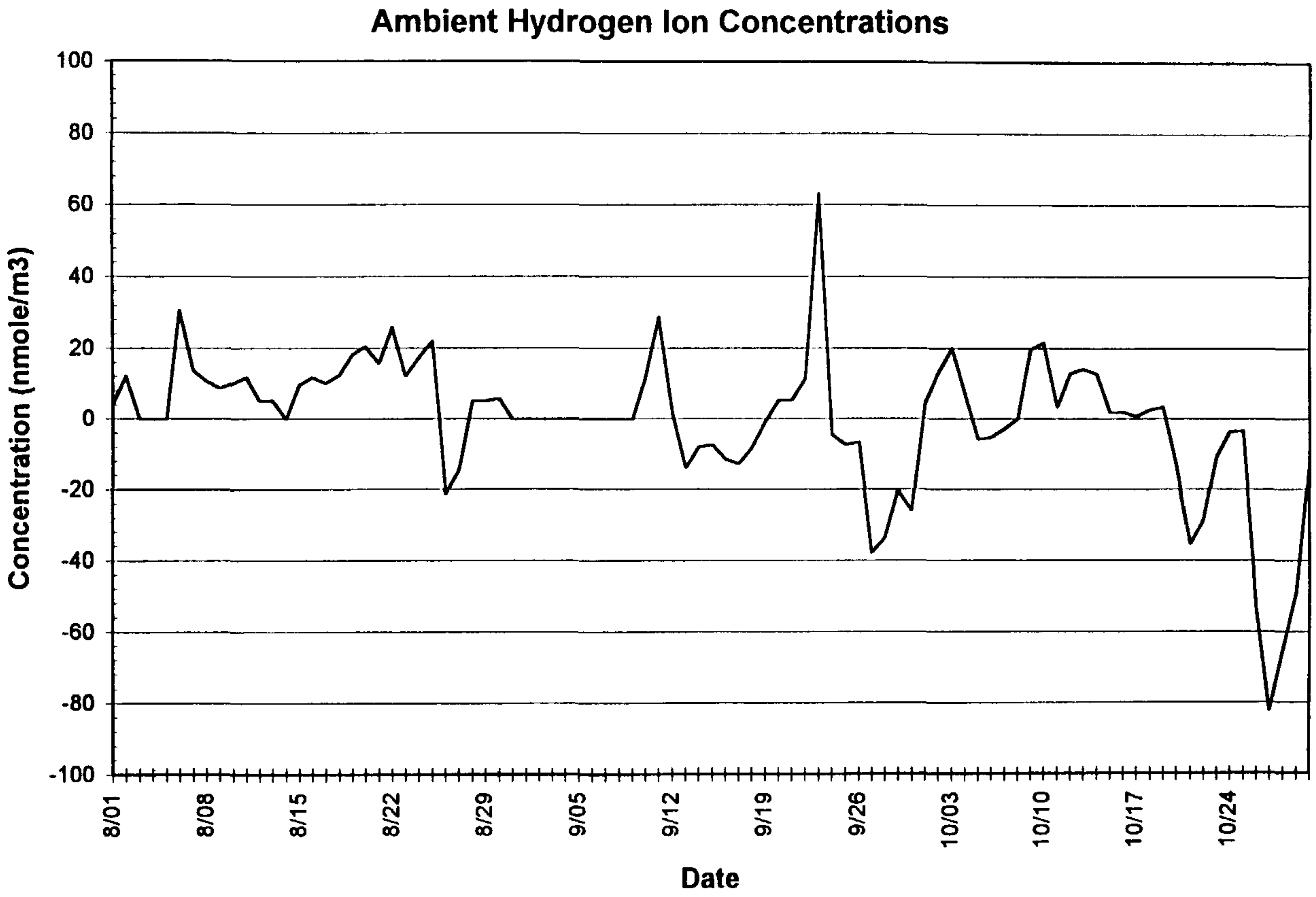


Figure 3-3. Temporal variation in hydrogen ion concentrations.

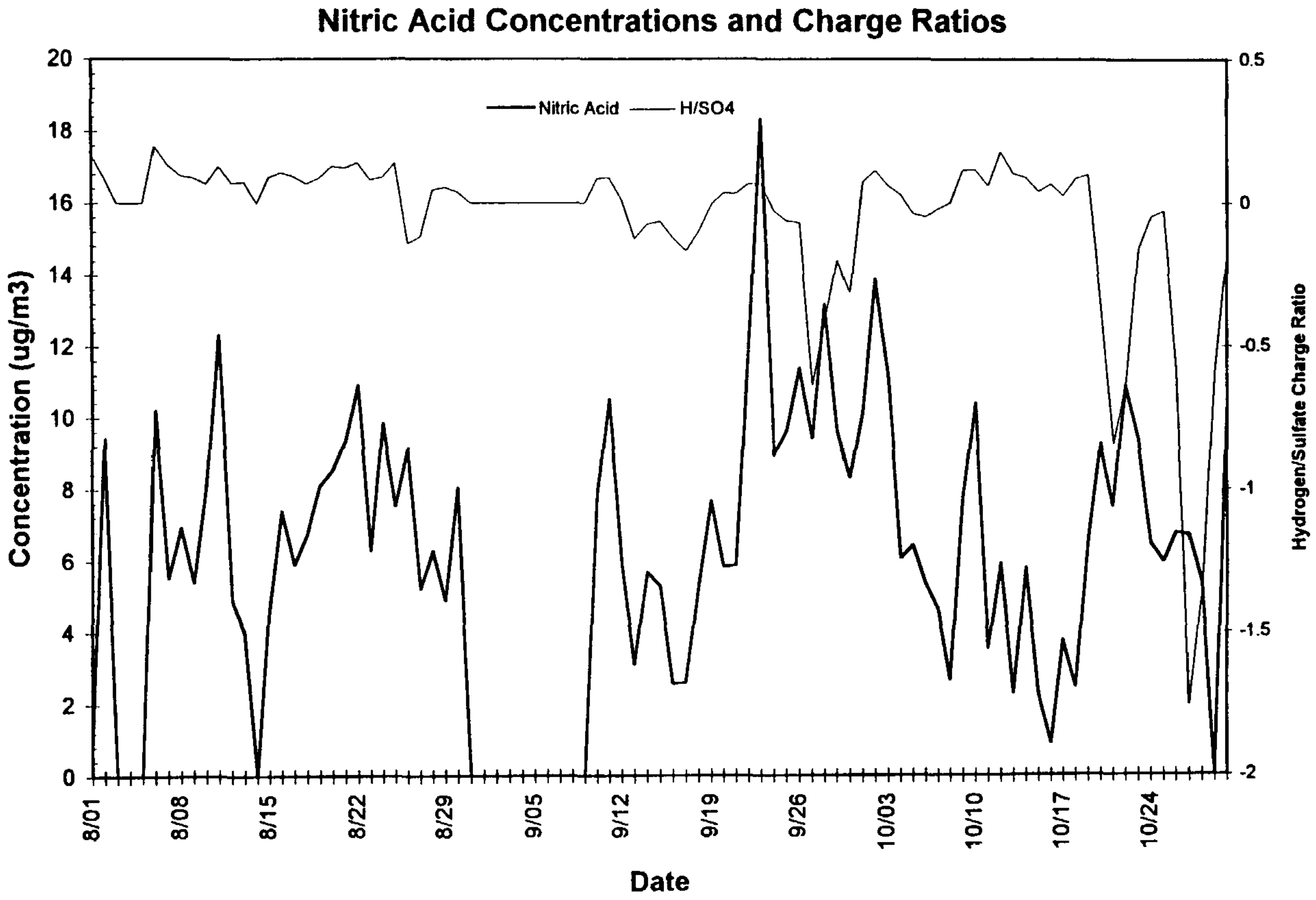


Figure 3-4. Temporal variation in hydrogen ion concentrations.

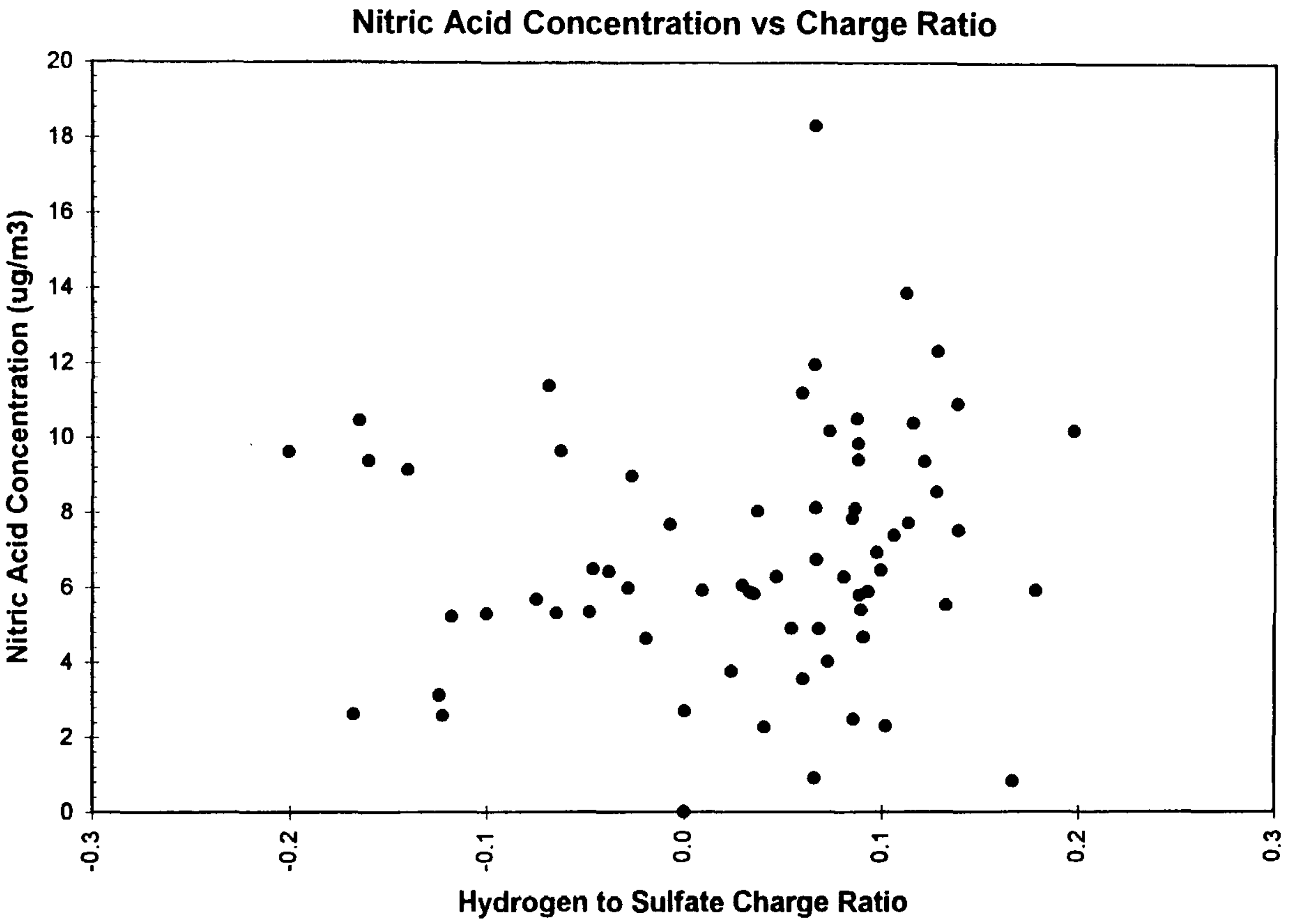


Figure 3-5. Relationship of nitric acid concentrations to strong particle acidity.

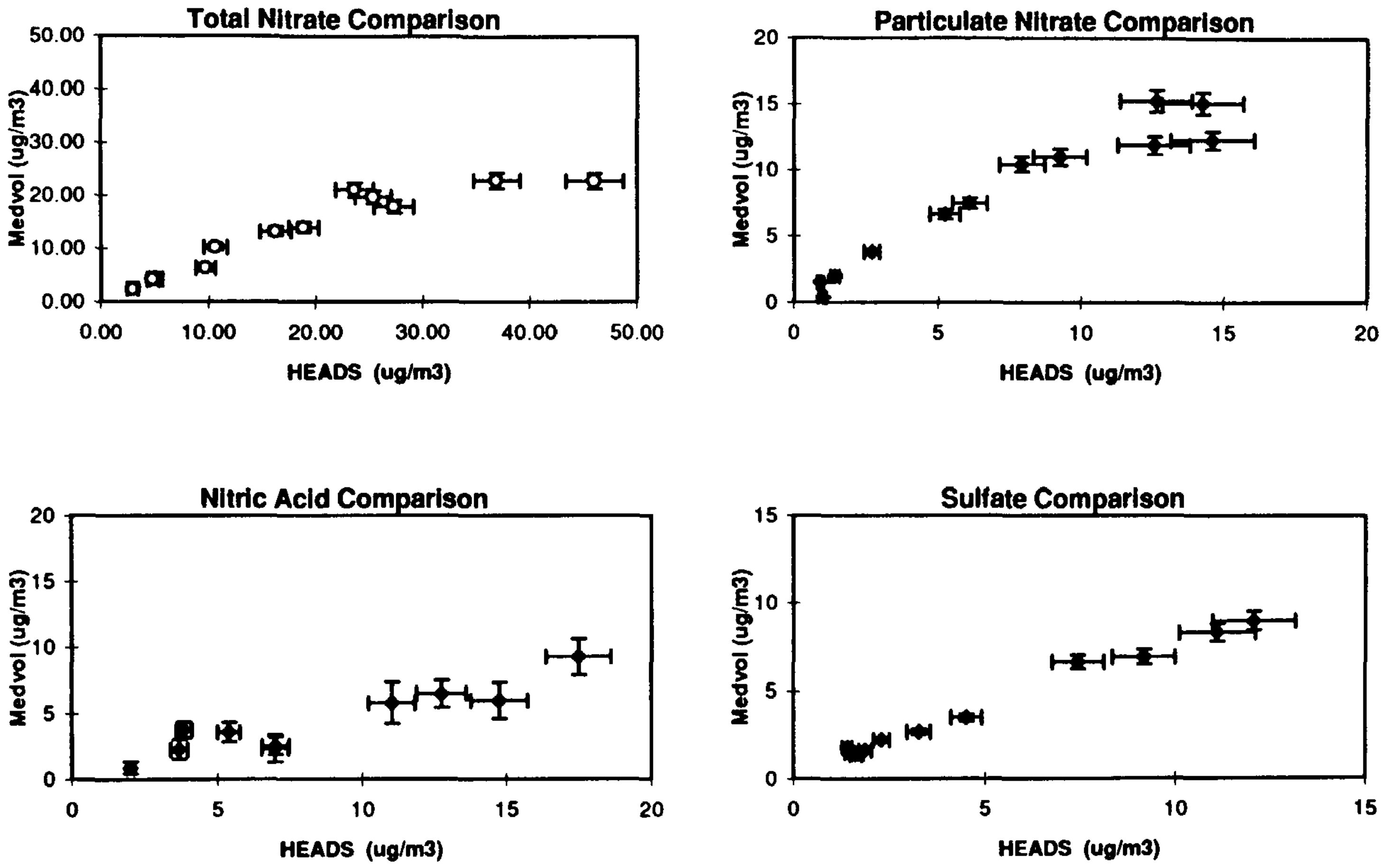


Figure 3-6. Comparisons of Medvol and HEADS measurements for total nitrate, particulate nitrate, nitric acid, and sulfate.

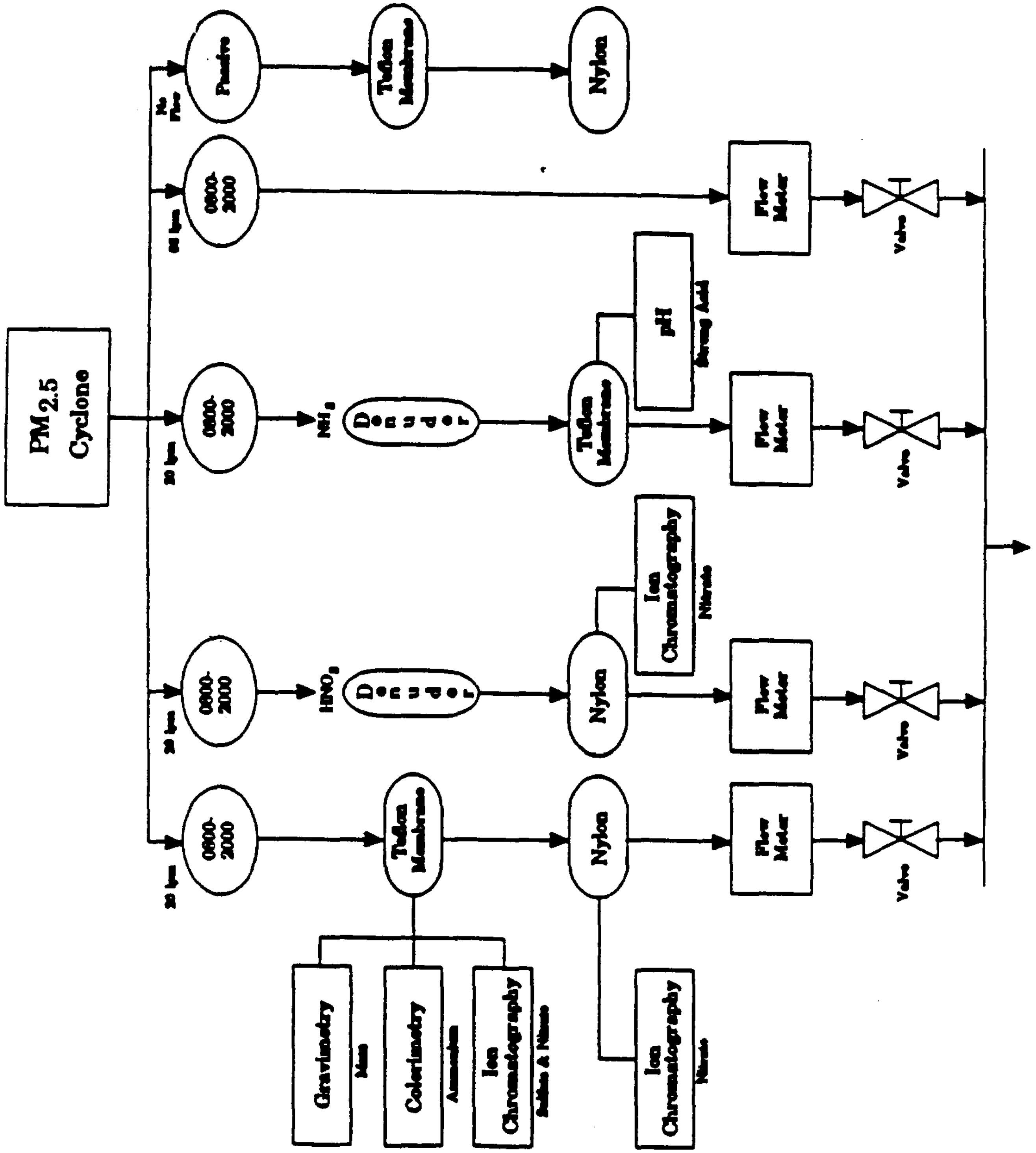
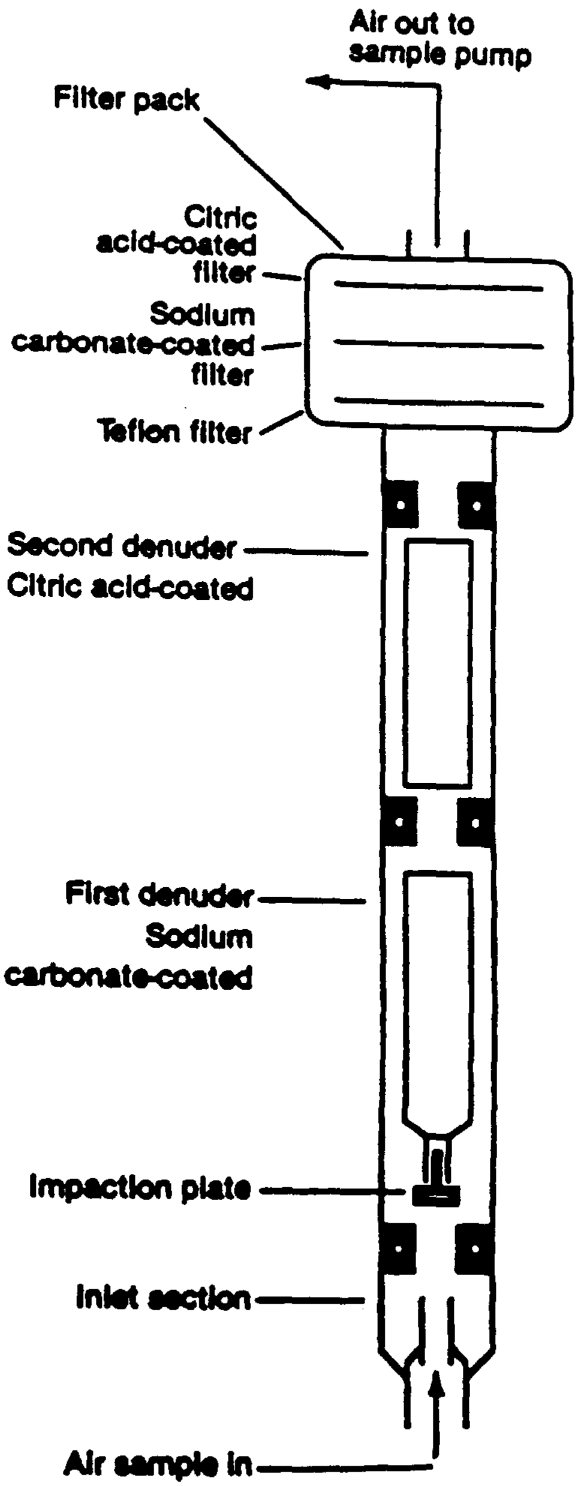


Figure 2-1 Sampling and Measurement Flow Diagram of the PM$_{2.5}$ Unit.

Figure 2-2 Harvard-EPA annular denuder system



APPENDIX A

DRI STANDARD OPERATING PROCEDURE

Title: DRI MEDVOL Particle Sampler for $PM_{2.5}$ and Acidic Species: Operation, Maintenance and Field Calibration

Page: 1 of 26
Date: 3rd Qtr. 1993
Number: 1-227.2
Revision: 5

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

This procedure describes the sampler configuration and instructions for operating the DRI MEDVOL particle sampler that has been modified to collect acidic species. Suspended particulate matter in the 0 to 2.5 micrometer size range ($PM_{2.5}$) and acidic gases are collected on filter substrates which are submitted to different chemical analysis. Air is drawn into the sampler through a size-selective $PM_{2.5}$ inlet and through three different sets of filter media. These filter media are chosen so that mass and acidic species can be quantified by laboratory analyses.

1.2 Measurement Principle

Particles less than 2.5 micrometers in aerodynamic diameter ($PM_{2.5}$) are separated from larger particles with a Bendix 240 cyclone separator. The size separation requires a flow rate of 113 l/min through the inlet. After passing through the inlet, the air enters a conical plenum where it is directed through several paths and filter holders. The conical shape of each plenum diffuses the airflow and minimizes particle deposition. The plenum and inlet have been coated with PFA Teflon to reduce removal of nitric acid from the air stream. The Teflon surfaces are treated the a dilute solution of nitric acid to expose those sites on the Teflon that might absorb nitric acid vapor during sampling. Open faced filter packs are inserted into either the base of the plenum or several denuders installed on the base of the plenum. Two denuders have been added to the base of the plenum to remove nitric acid and ammonia, respectively. The denuders remove specific species from the air stream before the air passes through the particular filter pack. Each filter holder is connected to a vacuum manifold through differential pressure regulators. A vacuum pump draws air through these filters when the pump is activated by a timer. The flow rates are controlled by maintaining constant pressure across valves with the differential pressure regulators. Twenty liters per minute are drawn through three filter packs simultaneously. The additional flow required to maintain the total flow rate of 113 lpm for 2.5 μm cut-points of the inlets is drawn through a makeup air ports. An fifth port is provided in each plenum for a field blank which is used to evaluate filter loading during passive sampling periods and during filter handling.

The three filter packs contain 1 or 2 separate 47 mm diameter filter substrates which collect particles and gases for later analyses. The filter holders are made by Savillex of PFA Teflon to minimize their reaction with the sample and contain redesigned filter backing trays that have reduced flow restriction. Filters that are used include PTFE Teflon membranes (e. g., Gelman (Ann Arbor, MI) polyolefin ringed, 2.0 µm pore size, (#R2PJ047)) for gravimetric and x-ray fluorescence analysis) and nylon filters for the collection of acidic vapor.

The sampler has a timer that controls the sampler operation. Samples will be collected every day from 0800 to 2000 PDT. Elapsed time indicators measure the duration of each sample.

1.3 Measurement Interferences

1.3.1 Passive Deposition

Passive deposition occurs when particles and gases deposit on filters prior to and after sampling. Field blanks are used to quantify this bias, which is usually less than 30 µg of mass per filter.

1.3.2 Inlet Loading and Re-entrainment

Material collected in the size-selective inlet can become re-entrained in the sample flow. The $PM_{2.5}$ inlets are cleaned annually to minimize overloading and re-entrainment.

1.3.3 Pump Exhaust Recirculation

Recirculation occurs when the pump exhaust, which contains carbon and copper particles from the motor armature and pump vanes, is entrained in the sampled air. Recirculation is minimized by re-conditioning the pumps annually, filtering exhausted air with a total filter, and locating pump exhaust inside an enclosure over 1 meter below the sampling inlet. Exhaust filters are replaced semi-annually.

1.3.4 Particle Volatilization

Ammonium nitrate can dissociate and the particulate nitrate can escape as nitric acid gas. This effect can be quantified by placing a nylon backup filter behind a quartz filter to absorb volatilized nitric acid. The PFA Teflon Savillex filter holder has been shown to be inert to nitric acid absorption and can accommodate stacks of filters. Filters are unloaded and kept under refrigeration after sampling to minimize long-term volatilization.

1.3.5 Filter Gas Absorption

Nitric acid absorbed by nylon or NaCl-impregnated filters will appear as nitrate in the analysis. A set of tubular denuder coated with sodium hydroxide can be placed in front of the filters to remove gaseous nitric acid.

1.3.6 Filter Integrity and Contamination

Filter integrity is compromised by handling which causes pieces of the filter to be lost after the pre-exposure weighing. Filter contamination results from material other than sampled aerosol being deposited on the filter (e.g. fingerprints, dirt). The effects of filter material losses are minimized by performing gravimetric analysis on Teflon membrane filters which are less friable than the quartz fiber filters. Filter material losses and contamination are minimized by the placement and removal of filters to and from filter holders in controlled laboratory conditions. Gloved hands and forceps are used in this filter processing. Spare, loaded filter holders are provided in the field to remove the need for field loading and unloading. Each filter holder is separately sealed prior to and after sampling. Batches of filters are inspected and submitted to chemical analysis prior to use to assure that they meet minimal standards when received from the manufacturer.

1.3.7 Particle Loss During Transport

Particles have been found to be shaken from filters during transport of coarse (greater than 2.5 µm) particles which are heavily loaded on the filter. Flow rates have been adjusted to minimize overloading of filters for the specified sample duration.

1.3.8 Transmission Losses

The necessity of particles to pass through a size-selective inlet could result in particle losses. Distances between the inlet and the filter surfaces have been minimized to minimize these potential losses.

1.4 Ranges and Typical Values

The range of concentrations measured by this method is limited by the sensitivity of the analysis instrument and the standard deviation of the values obtained by the dynamic blank. For mass concentrations, the range is approximately 5 to 300 $\mu g/m^3$.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

For mass concentrations, the typical lower quantifiable limit is 1 $\mu g/m^3$ and the precision is approximately ±10% for mass concentrations which exceed ten times the lower quantifiable limit. Accuracy is generally within ±10% for mass concentrations.

1.6 Responsibilities

The field technician is responsible for carrying out this standard operating procedure and for the completion and submission of all documents.

The field operations supervisor is responsible for scheduling the field technician's visits, reviewing documentation, identifying and reviewing deficiencies, and receiving samples from and transmitting samples to the laboratory.

The laboratory supervisor is responsible for preparing samples, transmitting them to the field, and receiving them from the field.

1.7 Definitions

The DRI MEDVOL is the entire sampling unit.

The inlet for $PM_{2.5}$ particles is the Bendix 240 cyclone separator inlet which provides the 2.5 μm cut-point for particles entering the sampler.

The plenum is the conical chamber into which filter holders are inserted.

1.8 Related Procedures

This standard operating procedure covers all aspects of sampler operation.

2.0 APPARATUS, INSTRUMENTATION, SUPPLIES, AND FORMS

2.1 Instrumentation

DRI MEDVOL Particle Sampler. The sampler is pictured in Figure 1. Air enters the inlet and flows into the conical plenum where filter holders are arranged in a circular pattern at the base. The flow goes through filters, then through differential pressure valves and ball valves to a GAST 1022/1023 carbon vane pump. The pump provides enough flow for several filter packs of 30 l/min and enough additional flow to obtain 113 l/min. The differential pressure valves maintain constant pressure, and therefore a constant flow rate, across ball valves for the sampling ports containing filters, as filters load up during sampling. The makeup flow rate is controlled by the position of the ball valves. Table 1 lists each component of the sampler and its function. Literature describing the timer, differential pressure regulator, magnehelics, and pumps are attached to this procedure.

Five Savillex Filter Holders for Each Sampler. The filter holders are open faced and accommodate 47 mm diameter filters. Figure 2 shows an example of the filter holder and the placement of filters in them. Labels with ID numbers for the filters are attached to the filter holders when the filters are loaded. The filter holders are designated as follows:

TN for Teflon followed by nylon filters.
DN for aluminum denuder followed by nylon filter.
DT for ammonia denuder followed by nylon filter.

Dwyer 0 to 100 SCFH Rotameter with number 9.5 rubber stopper adapter. This rotameter is used to set and verify flow rates through filter packs and makeup ports.

Dwyer 0 to 400 SCFH Rotameter with number 9.5 rubber stopper adapter. This rotameter is used to verify the total flow rate into the inlet.

2.2 Supplies

Spare Carbon Vanes and Starting Capacitor. The GAST 1022 pump requires replacements after approximately 5000 hours of operation. The pump literature contains details on these pump components.

Pump Exhaust Filters. GAST #A393 cylindrical exhaust filters are replaced on a quarterly basis or when they show signs of carbon breakthrough. Gelman capsule filter #12116 are placed on the exhaust of the pump and replaced semiannually.

2.3 Data Sheets

The data sheet for recording field data is shown in Figure 3.

3.0 CALIBRATION STANDARDS

The transfer standards for flow rates are the rotameters specified in Section 2.2 and have been calibrated against a positive displacement Roots meter, model 1.5M125, serial number 8623119. Elapsed time indicators are checked against a stopwatch that is compared to WWV time.

4.0 SAMPLER OPERATION

4.1 Flow Diagram

Figure 4 summarizes the routine operating procedure for the DRI MEDVOL. Samples are normally changed every day before 0800 PDT, if possible. Sample changing requires approximately 20 minutes per sampler. Flow rate performance tests are performed once a month requiring about an additional 15 minutes per sampler. Exhaust filter replacement and leak testing are carried out every quarter and require an additional 30 minutes per sampler. The inlet and plenum are dis-assembled and cleaned every six month and requires approximately 45 minutes per sampler.

4.2 Sampler Installation and Start Up

4.2.1 Installation

Prior to deployment, all Teflon surfaces are treated with a dilute solution of nitric acid (0.5 molar) to remove active sites that might absorb nitric acid vapor during sampling.

The sampler should be installed on a wooden platform, if possible. It requires one square meter of space for itself and an additional square meter of work area in front and to at least one side. The inlet should be separated from the inlets of other samplers by at least two meters.

Make sure inside of plenum and base plate are clean. Place large "O"-ring in groove in base plate and attach plenum to plate. Install small "O"-rings in grooves that are in the holes in the base plate. Attach four legs loosely to plenum with metal conduit straps. Secure the four legs of the sampler to the platform with similar metal straps. Even legs on plenum so that base is horizontal and tighten straps.

Attach control box to two of the legs. Attach Tygon tubing to the external metal tubes on the left-hand side of the control box in the following order, top to bottom: Filter Pack 1, Filter Pack

2, Skip tube for pump, Filter Pack 3, and Makeup. Secure Tygon tubing with hose clamps. Insert 3 inch-long, 3/8 inch-diameter plastic tubes in ends of Tygon tubing and secure with hose clamps. Score exposed ends of plastic tubes with 3/8 inch scoring tool and insert into filter holder nuts. The nuts will stay with the sampler not the filter holders.

For $PM_{2.5}$ sampler, remove clamp, collar, and protective covering from top of plenum. Place collar over top of 3 1/2 inch inlet tube. Install "O"-rings in the grooves that are in the throat of the plenum inlet. After removing packing material, replace cap but do not attach screws. Attach to the top of the cap with the screws, the plate that holds cyclone inlet chamber. Place 1/2 inch Swagelock bulkhead fitting on end of cyclone. A nylon ferrule is used on the cyclone. Install bulkhead fitting through bottom of stainless steel container with cyclone inside. This chamber acts to still the air entering the cyclone. Place red end cap on cyclone. Center chamber and screen over opening on top side of plate and attach with small screws and clamps. The screen to will prevent large bugs from entering the sampler. Attach one end of 1/2 inch Teflon or stainless steel tube to Swagelock fitting on cap and the other end to the bulkhead fitting on the stilling chamber. Insert inlet tube into top of plenum and secure collar to flange with clamp. The sampler should be leak checked at the connection of the 1/2 inch tube to the cyclone following Section 4.2.4.

Attach one open filter holder to the Makeup flow tube and insert filter holder receptacle tubes into one of two outside holes in the base plate. This holder will stay in place except for flow rate checks. Place a Teflon plug on a second filter holder and install in the middle hole in the base plate or place a 9½ stopper in middle hole. This position is used for blank samples and needs to be blocked during sampling. Attach TN filter pack holder to tube for Filter Pack 1. Insert into remaining outside hole in base plate. Attach DN filter pack holder to tube for Filter

Pack 2. Insert into aluminum denuder. Attach DT filter pack holder to tube for Filter Pack 3. Insert into ammonia denuder.

In regions of high winds, the inlet should be guyed to the platform to prevent its being blown over.

Place the pump below and as far away from the sampling inlet as possible. Even though the pump exhaust is filtered and contained, it is good practice to have it removed from the sample inlet. If possible, place the pump underneath the platform. This may require increased length of tubing and electrical cord. Attach Tygon sample tubing to middle of the external tubes on the left-hand side of the control box and secure with a hose clamp. Attach the other end to the inlet side of the pump enclosure and secure with a hose clamp. Plug electrical cord from pump box into receptacle on right-hand side of control box.

4.2.2 Set Time on Timer

Push "Set Time" button while:

1) pushing the day of the week button so that the LCD bar is above the proper day;
2) pushing the h+ (or h-) button until the proper hour is shown (including am or pm); and
3) pushing the m+ (or m-) button until the proper minutes are shown.

The clock will start running when "Set Time" button is released. The current time should be verified on each site visit and re-set if it is not within 5 minutes of watch time. A built-in rechargeable NiCd battery will maintain the correct time for up to 100 hours in the event of a power outage.

4.2.3 Set Flow Rates.

Follow the calibration procedure described in Section 5 to set flow rates to 20 l/min through each filter holder and 53 l/min through the makeup port.

4.2.4 Check for Leaks.

Disconnect Teflon tube from cyclone. Close all ball valves except makeup flow valve. Attach the 0 to 400 SCFH rotameter to that filter holder and turn pump on. Set flow rate to be about 250 SCFH on rotameter. Insert makeup flow filter holder in plenum. With other filters in place, attach rotameter to flow adapter at inlet of plenum and measure total flow rate into plenum. The flow rate through the top and through the filter holder should agree to within 10 SCFH. If they do not, then the sampler has excessive leaks through the plenum which must be identified and eliminated. These can occur: 1) where the filter holders are connected to the plenum, or 2) where the rotameter adapter is connected to the plenum. Record the results of the test in the station log and flow calibration sheet.

4.2.7 Program Timer.

Two programs are required: one to turn the pump (channel 1) on, 8:00 AM for this project, and the second to turn the pump off, 8:00 PM for this project. Sampling will occur every day. Two methods of timing are possible. One method sets the timer to start the sampler at 8 AM every of the week and end at 8 PM. This method requires that the filters are changed every day before 8 AM so that the sampler does not collect sample on the previous day's filter. The second method has only one set of programs that run on Mon on the timer. The day of the week on the timer is changed to Mon on each day. The sampler will not start the next day.

For the starting program, push the timer button corresponding to the day the sample is intended to be taken. Push +H to display correct starting hour (12 am). Push +M to display correct minute (00). Push the I/O button to display a bar below I. Push "WRITE" to save this program.

For the sample ending program, push timer button corresponding to day sample is intended to end (one day past the starting day). Push +H to display correct ending hour (12 am). Push +M to display correct minute (00). Push the I/O button to display a bar below O. Push "WRITE" to save this program.

To review programs, push "SET TIME" to display clock time. Push "READ" once to display the first program, and push "READ" again to display the second program.

If problems occur while programming or during operations, the timer should be reset by pushing the recessed "RESET" button. The time will have to be set again if the "RESET" button is pushed.

4.3 Routine Sampler Operations

The normal operation of the MEDVOL sampler consists of installing and removing filters, checking flow rate indicators before and after sampling, recording the elapsed time readings, and performing periodic flow rate checks. The site visit should be before 8 AM if possible. After removal, the filters should also be kept cool until they are analyzed to reduce loses. Procedures are in the order of normal operations: first removal of exposed filters followed by installation of new filters.

4.3.1 Removal of Filters

a. Inspect MEDVOL Sampler and Record Final Elapsed Time.

Open control panel door and compare time on timer to time on accurate watch. Record date and time on the data sheet for the samples in the sampler. Record ambient temperature and pressure if available. Record elapsed time indicator value in the "Remove" space and calculate the sample elapsed time. It should be within 60 minutes of 1440 minutes for a 24 hour sample. Note any discrepancies on the data sheet.

b. Record Post-Exposure Magnehelic Readings.

Before removing filters, check that Magnehelic pressure gauges are reading zero and adjust if necessary. Turn the sampler on by pushing the timer override button on Channel 1 and record Magnehelic readings on the data sheet in "Remove" spaces. Turn the sampler off.

c. Flow Rate Performance Test.

A flow rate performance test should be done once a every two weeks and can be done while the filters are being removed. Remove each filter holder from the plenum one at a time and place cork of 0 to 100 SCFH rotameter into receptacle of filter holder. Turn on the pump and measure the indicated flow rate through each holder. Record indicated flow rate and Magnehelic reading on log sheet. Notify field supervisor of results by telephone. Field supervisor will calculate flow rates and notify field operator if flow rates should be changed. Ambient flow rates are calculated using the rotameter calibration curves as in Section 5. If the ambient flow rates vary by more than 7% from the calibration flow rates, new flow rate setpoints need to be determined.

d. Remove Exposed Filters.

Remove the exposed filter holders by pulling them from the plenum on at a time. Loosen the ferule nut on each filter holder and remove holder from flow tube. Nut remains on flow tube. Remove top and bottom caps from plastic bag and check that they are clean. Cover each filter holder with the top and bottom caps, and place in cooler. Place the top cap on before the bottom cap to prevent pressure buildup in the filter holder caused by compressing air under the cap. Verify that ID of filter holder is same as indicated on log sheet. If it is not, then note correct filter holder ID on log sheet.

4.3.2 Installation of Filters

a. Inspect Unexposed Filters.

Be sure each unexposed filter holder is clean (no obvious foreign material on the filter). Replace filters which do not pass inspection with one of the holders designated as a field blank, if available. Change the data sheet accordingly. Make sure each filter holder ring is snug.

b. Install Unexposed Filters.

Remove the caps from TN Filter Pack. Remove the large top cap by gently prying the side of the cap up until it is off. Then remove the small bottom cap. This cap removal method prevents air from being pulled through the filter in the wrong direction with possible filter damage. Place top and bottom caps in a plastic bag to keep them clean. Check that locking ring is snug but do not overtighten. Attach tube for Filter Pack 1 sampling to bottom of filter holder and install holder in plenum by pushing the receptacle into the hole in the bottom of the plenum until the knurled portion of the receptacle comes into contact with the plenum base. Similarly install DN and TN Filter Packs in the their respective denuders. If blank sample is to be run, install filter in center hole and enter ID on log sheet.

c. Record Pre-Exposure Magnehelic Readings.

Check that Magnehelic pressure gauges are reading zero. Turn pump on. Check the Magnehelic readings. If the Magnehelic reading differs from the set-point by more than ±0.05 in H_2O from the calibration set point, adjust the ball valve to bring it into specification. Record Magnehelic readings on the data sheet in the "Load" spaces. Turn the pump off.

d. Record Initial Elapsed Time.

Record the elapsed time indicator reading on the data sheet for the unexposed filters in the "Load" space.

e. Reset Clock Day.

If samples are run by only one set of programs the Clock Day will have to be reset from Tu to Mo. Hold Set Time button in and press Mo to move line to Mo.

Check that programs are On at 8:00 AM and Off at 8:00 PM.

f. Manual Start

If filters are changed after 8:00 AM, the sampler will have to be started manually. Press override on Channel 1 to start pump. Timer will turn off automatically.

4.4 Maintenance

4.4.1 Change Pump Exhaust Filters.

Both the fiber filter and total filters on the exhaust of the Gast 1022 pumps should be changed on a regular schedule. Once a quarter and before starting a new sampling program, change the fiber exhaust filter. Unscrew the glass jar enclosing the exhaust filter. Grasp the filter (work gloves may be desirable to avoid fiber slivers in the hands), pull downward slightly and unscrew the bottom filter retainer plate. Insert a new filter and finger-tighten the retaining plate. Wipe any residue from the glass jars before replacing them. Inlet filters should be changed once a year. The total exhaust filter should be changed every 6 months. If a Gast 1023 pump is used, there are no fiber filters.

4.4.2 Clean Inlets and Inside of Plenum.

On the $PM_{2.5}$ sampler, remove the inlet assembly from the top of the plenum by loosening the collar and pulling it off. Clean the inside of the plenum as above. Remove cyclone covering from plate and remove screen. Remove and clean the red, plastic cap on the bottom of the cyclone. Remove the cyclone from its housing and clean in soapy water. Rinse with distilled water and dry. Clean tube from inlet to plenum by soaking in soapy water. Rinse in distilled water and dry. If desired, the cyclone can be greased to ensure that particles are not re-entrained into the air stream.

4.4.3 Change "O"-rings in Sampler Ports.

Annually, the "O"-rings in the sampler ports should be replaced. Remove each "O"-ring with small pointed object and install new "O"-ring making sure it is in groove all the way and not twisted. The "O"-rings may have to be replaced more often if they become hard or cracked and filter holders become loose in their ports. In such cases, those "O"-rings with problems should be replaced.

4.5 Shutdown

At the end of the sampling program, perform one set of leak and performance tests. Record the condition of the sampler in the station logbook.

5.0 QUANTIFICATION

5.1 Flow Rate Calibration Procedures.

Magnehelic differential pressure meters are installed in each flow leg of the sampler to act as flow indicators. The Magnehelics measure pressure drops in the range of 0 to 2 inches of water across orifices in the flow lines. These pressure drops are used to set and track the flow rates through each filter holder. The calibrated rotameters (10 to 100 SCFH and 40 to 400 SCFH) and calibration curves, test filter holders, MEDVOL Logbook, and calculator are needed for flow rate calibration.

5.1.1 Nominal Flow Rates

Nominal flow rates, as referenced to ambient conditions, for the samplers are

Filter	Flow Rate(l/min)
TN Filter Pack	20
DN Filter Pack	20
DT Filter Pack	20
Makeup	53
Total	113

5.1.2 Rotameter Flow Rate.

a. From nominal flow rates Q_N in lpm, obtain indicated flow rate Q_I on rotameter from

$$Q_I = \{Q_N/[0.472 \cdot (\text{Correction Factor})] - B\}/A$$

$$\text{Correction Factor} = [(P_{STD}/P_{AMB}) \cdot (T_{AMB}/T_{STD})]^{1/2}$$

where A and B are coefficients of rotameter calibration,

P_{STD} = pressure at standard conditions (1 atm, 760 mm Hg, 1013.25 mb, 29.92 in Hg),

T_{STD} = temperature at standard conditions (25 °C) in deg K (298 °K),

P_{AMB} = average ambient pressure in same units as P_{STD},

T_{AMB} = average ambient temperature in °K,

b. Method 1: Calculate correction factor for site from estimated average temperature and average pressure for the site:

Estimate average temperature for period of interest, usually a seasonal average in which the actual temperature does not vary by more than 15 °C from the average. Temperature can be from onsite measurements or from nearby National Weather Service station. Enter value in Logbook in both °C and °K (°K = °C + 273).

Estimate average pressure for period of interest from the locally measured seasonal average pressure (in same units as standard pressure). Enter value in Logbook. Compute correction factor to convert rotameter reference flow rate to flow at ambient conditions as above.

c. Method 2: Determine average temperature as above. Determine elevation of sample site from USGS topographic map. Interpolate where necessary.

Determine average pressure for site elevation from Table 2. Compute correction factor as in Section 5.2.2(a).

5.1.3 Magnehelic Settings.

Install Filter Pack 1, Filter Pack 2, Filter Pack 3, and open makeup holder on sampler. Attach flow meter to each filter sequentially and adjust flow rate to required indicated value. After all flow rates are set, check flow rates again and adjust if indicated flow rates on rotameter are more than ±0.5 SCFH from required value. Note Magnehelic readings and mark value near each one.

5.2 Total Flow Rate Measurement.

The flow rate through the size-selective inlet should equal the sum of the individual flow rates. If leaks are present, the total flow rates will be less than the sum of the individual flow rates.

The plenum can be checked for leaks by removing tube connecting inlet to plenum, shutting all flows off but one makeup flow, and comparing the flow rate through the open holder to the flow rate through the top of the plenum when the holder is installed. Procedures for performing flow rate checks through the plenum are described in section 4.2.4.

6.0 QUALITY CONTROL

6.1 Calibration Checks.

Performance flow rate checks as described in Section 4.3.3 are made monthly.

6.2 Leak Checks

A leak check as described in Section 4.2.4 is performed every 6 months.

Table 1

Components of the MEDVOL $PM_{2.5}$ Sampling Systems

Code	Part Name	Specification and Rationale
1	$PM_{2.5}$ Inlet	Bendix 240 cyclone separator. This inlet provides a 50% size cut of 2.5 μm at a flow rate of 113 lpm.
2	Inlet Connection	O-ring seal inside inlet for $PM_{2.5}$ inlet.
3	Plenum and Base	Spun aluminum cone welded to inlet flange attached to removable base of machined aluminum with internal o-ring to allow pressfit of Savillex filter holders into base.
4	Filter Holders	47 mm diameter Savillex three stage PFA Molded Teflon Filter Holders (Catalog #6T-47-6T) with ferrule nut, 3/8" tubing and 3" long open face receptacle (Catalog #4750). The only Teflon/stacked filter holder available within the U.S. Support grids have been modified to provide homogeneous porosity. Open face needed for uniform deposit on filter.
5	Teflon Tubing	1/8" O.D. Teflon connects pressure gauge.
6	Vacuum Manifold	1/2" brass pipe "T"s. Manifold connects the solenoid valves to the flow meters. Valves switch samples every twelve hours, according to timer settings.
7	In-line Orifice	Custom built, stainless steel. This orifice creates a small pressure drop which is measured by Magnehelic to set flow rates.
8	Pressure Gauge	Dwyer Magnehelic Low Pressure 0 to 2" H_2O differential gauge. Used to measure pressure drop across orifice for flow rate adjustment. One magnehelic is attached to every filter and make-up flow channel.

Table 1 (Continued)

Components of the MEDVOL $PM_{2.5}$ Sampling Systems

Code	Part Name	Specification and Rationale
9	Pressure Regulator	Conoflow Regulator & Controls, GH21XTXM fixed differential regulators. Maintains a fixed differential pressure across a valve downstream from the regulator.
10	Ball Valve	TOYO 3/8" stainless steel ball with brass body. This valve is adjusted to set the flow rate at the desired value.
11	Legs	Four legs to obtain necessary inlet height.
12	Control Box	Contains flow distribution, calibration, and timing mechanisms.
13	Elapsed Time Indicator	Cramer Elapsed Time Indicator. Minute resolution (Catalog #35F3803) type 10184K/115 A.C., 6 figures, nonreset, rectangular shape. Determines sample duration.
14	Relay	Square D A.C. Control Relay, DPST-2NO 10 AMP at 277 VAC/ 5 AMP at 600 VAC, Coil 120 V/60 Hz. Turns pump on.
15	Timer	Grasslin model Digi 56-72. A programmable 2 channel microprocessor-based controller with program storage. This timer controls sample start and stop times and channel switching.
16	Pump House	Mail box protects pumps from exposure.
17	Pump	GAST 1022 carbon vane pump, 3/4 HP. Pumps pull 25" vacuum, applicable for 113 lpm sampling flow rate.
18	Absolute Filter	Gelman #12116 Capsule Filter. Addition to the exhaust of carbon vane pump. Prevents exhaust recirculation.

Table 1 (Continued)

Components of the MEDVOL $PM_{2.5}$ Sampling Systems

Code	Part Name	Specification and Rationale
19	Fan	Installed in pump enclosure to facilitate cooling.
20	Aluminum Denuder	Removes nitric acid from air stream
21	Ammonia Denuder	Removes ammonia from air stream.

TABLE 2
Pressure as a Function of Elevation in Feet

Elevation	Pressure			
Ft	Atm	mb	mm Hg	in Hg
0	1.000	1013.3	760.0	29.921
250	0.991	1004.1	753.2	29.651
500	0.982	995.1	746.4	29.383
750	0.973	986.1	739.6	29.118
1000	0.964	977.2	732.9	28.854
1250	0.956	968.3	726.3	28.593
1500	0.947	959.5	719.7	28.333
1750	0.938	950.8	713.2	28.076
2000	0.930	942.1	706.7	27.820
2250	0.921	933.5	700.2	27.566
2500	0.913	925.0	693.8	27.314
2750	0.905	916.5	687.4	27.064
3000	0.896	908.1	681.1	26.815
3250	0.888	899.8	674.9	26.569
3500	0.880	891.5	668.7	26.324
3750	0.872	883.3	662.5	26.082
4000	0.864	875.1	656.4	25.841
4250	0.856	867.0	650.3	25.602
4500	0.848	859.0	644.3	25.364
4750	0.840	851.0	638.3	25.129
5000	0.832	843.1	632.4	24.895
5250	0.824	835.2	626.5	24.663
5500	0.817	827.4	620.6	24.432
5750	0.809	819.7	614.8	24.204
6000	0.801	812.0	609.0	23.977
6250	0.794	804.4	603.3	23.752
6500	0.786	796.8	597.7	23.529
6750	0.779	789.3	592.0	23.307
7000	0.772	781.8	586.4	23.087
7250	0.764	774.5	580.9	22.869
7500	0.757	767.1	575.4	22.652
7750	0.750	759.8	569.9	22.437
8000	0.743	752.6	564.5	22.224
8250	0.736	745.5	559.1	22.012
8500	0.729	738.3	553.8	21.802
8750	0.722	731.3	548.5	21.594
9000	0.715	724.3	543.3	21.387
9250	0.708	717.3	538.0	21.182
9500	0.701	710.4	532.9	20.978
9750	0.694	703.6	527.7	20.776
10000	0.688	696.8	522.7	20.576

TABLE 2 (Continued)
Pressure as a Function of Elevation in Meters

Elevation	Pressure			
M	Atm	mb	mm Hg	in Hg
0	1.000	1013.3	760.0	29.921
100	0.988	1001.3	751.0	29.567
200	0.977	989.5	742.2	29.217
300	0.965	977.7	733.4	28.871
400	0.953	966.1	724.6	28.528
500	0.942	954.6	716.0	28.188
600	0.931	943.2	707.5	27.852
700	0.920	931.9	699.0	27.519
800	0.909	920.8	690.6	27.189
900	0.898	909.7	682.3	26.862
1000	0.887	898.7	674.1	26.539
1100	0.876	887.9	666.0	26.218
1200	0.866	877.2	657.9	25.901
1300	0.855	866.5	649.9	25.587
1400	0.845	856.0	642.0	25.276
1500	0.835	845.6	634.2	24.968
1600	0.824	835.2	626.5	24.663
1700	0.814	825.0	618.8	24.362
1800	0.804	814.9	611.2	24.063
1900	0.794	804.9	603.7	23.767
2000	0.785	794.9	596.3	23.474
2100	0.775	785.1	588.9	23.184
2200	0.765	775.4	581.6	22.897
2300	0.756	765.8	574.4	22.613
2400	0.746	756.3	567.2	22.331
2500	0.737	746.8	560.2	22.053
2600	0.728	737.5	553.2	21.777
2700	0.719	728.2	546.2	21.504
2800	0.710	719.1	539.4	21.234
2900	0.701	710.0	532.6	20.967
3000	0.692	701.1	525.9	20.702

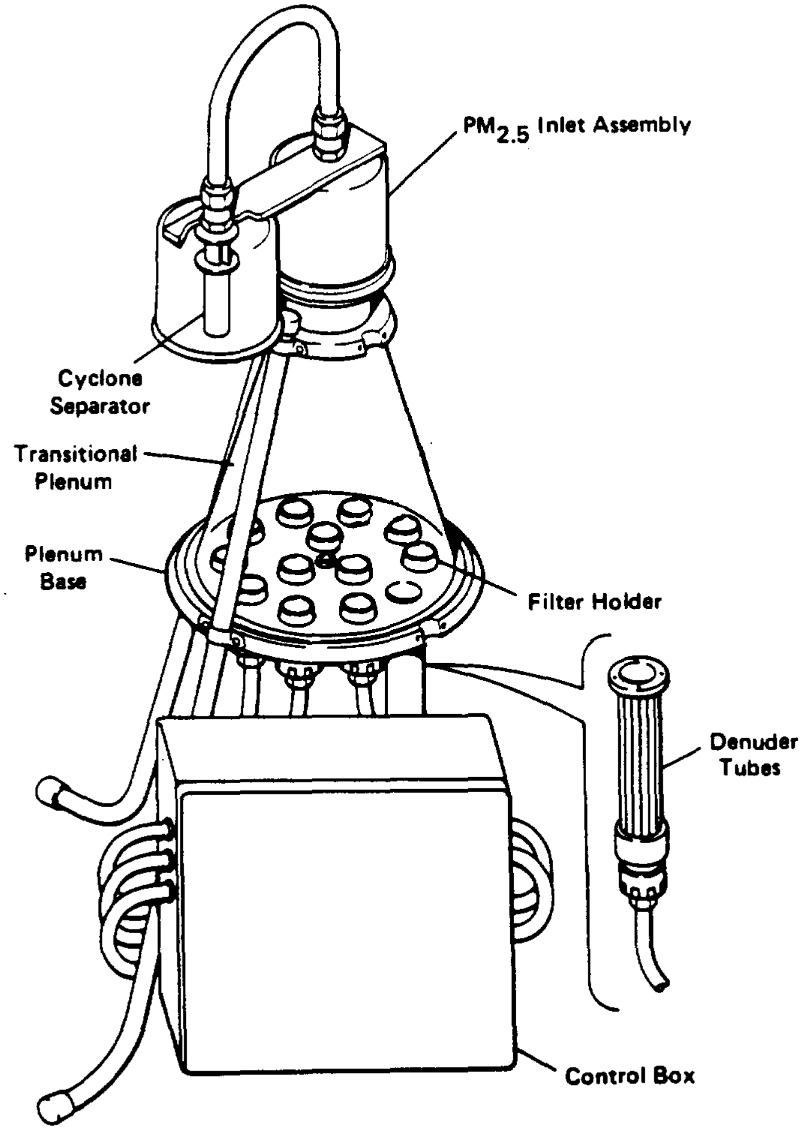


Figure 1: DRI MEDVOL Sampler

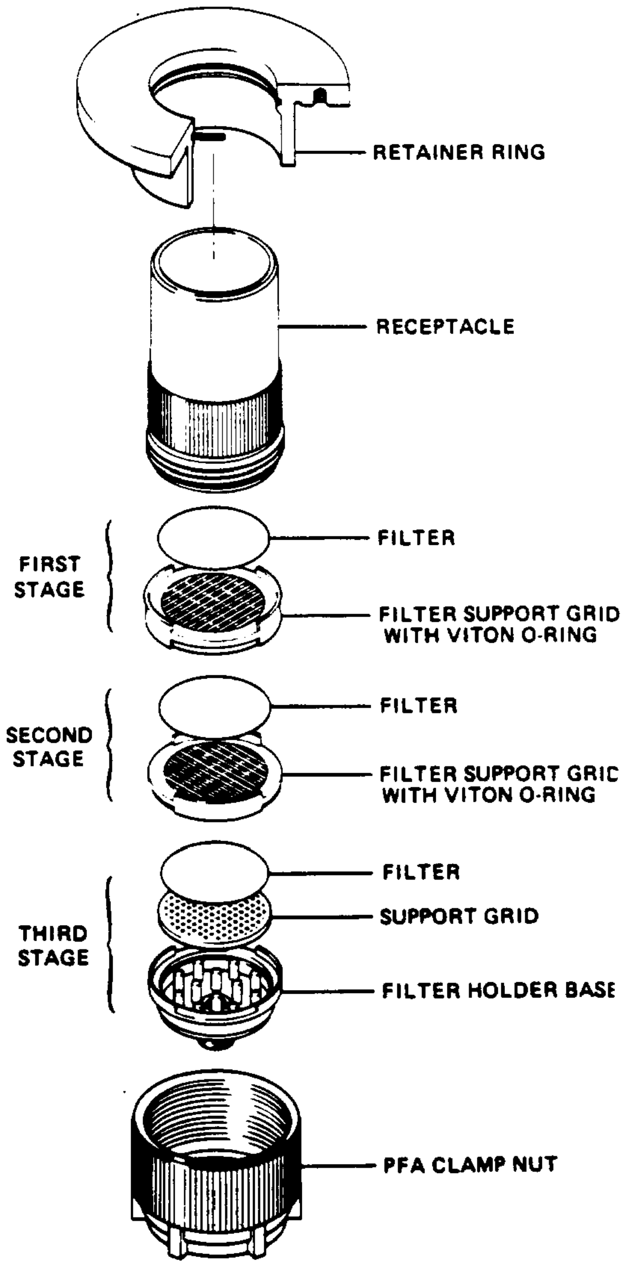
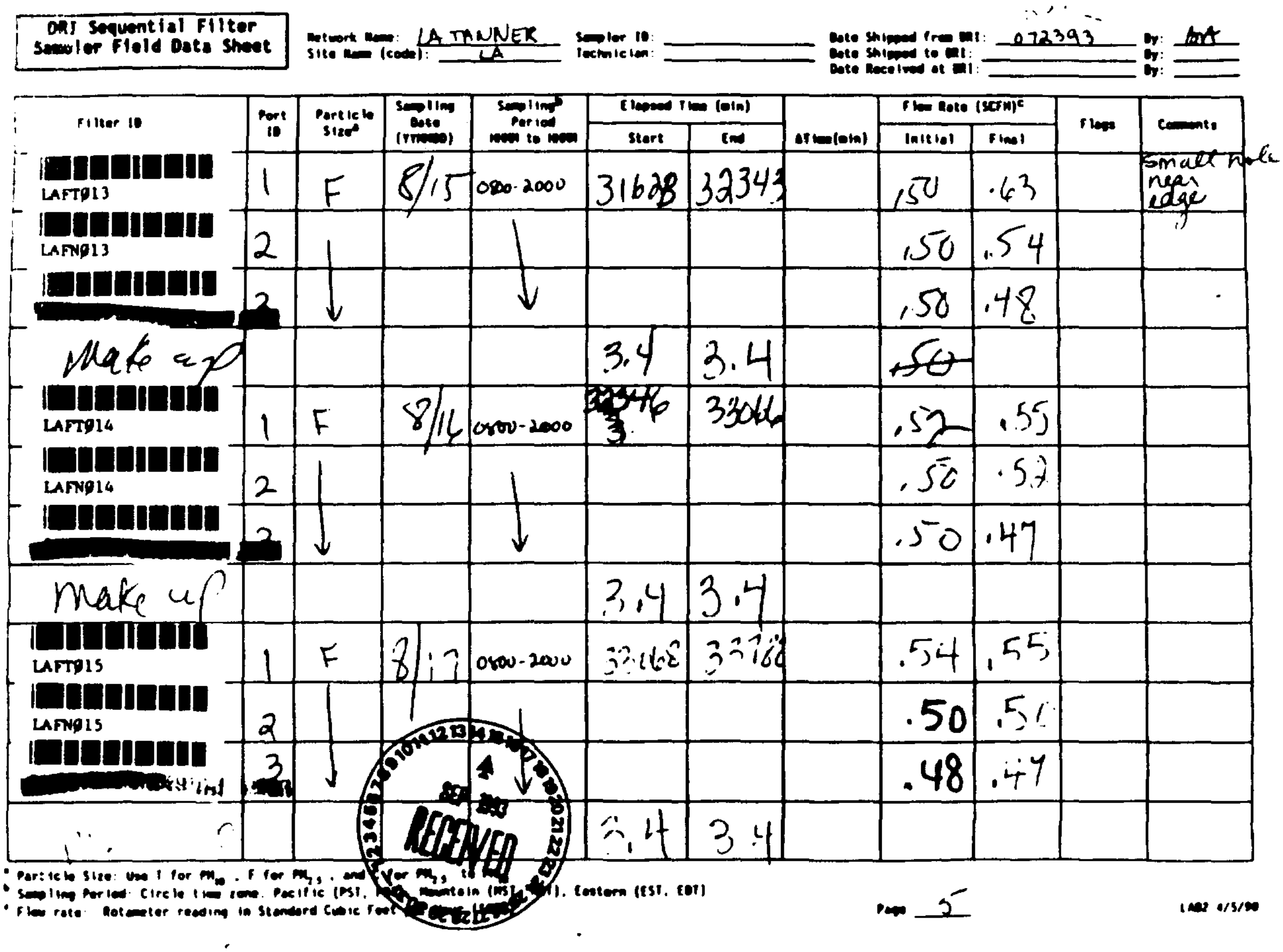


Figure 2: Savillex Filter Holder



DRI Sequential Filter Sampler Field Data Sheet

Network Name: LA TAUNER
Site Name (code): LA
Sampler ID:
Technician:
Date Shipped from DRI: 072393 By: bnk
Date Shipped to DRI: By:
Date Received at DRI: By:

Filter ID	Port ID	Particle Size[a]	Sampling Date (YYMMDD)	Sampling[b] Period HHMM to HHMM	Elapsed Time (min) Start	Elapsed Time (min) End	ΔTime(min)	Flow Rate (SCFM)[c] Initial	Flow Rate (SCFM)[c] Final	Flags	Comments
LAFT013	1	F	8/15	0800-2000	31628	32343		.50	.63		small hole near edge
LAFN013	2	↓		↓				.50	.54		
[redacted]	3							.50	.48		
Make up					3.4	3.4		~~.50~~			
LAFT014	1	F	8/16	0800-2000	33346	33066		.52	.55		
LAFN014	2	↓		↓				.50	.52		
[redacted]	3							.50	.47		
Make up					3.4	3.4					
LAFT015	1	F	8/17	0800-2000	33168	33766		.54	.55		
LAFN015	2	↓		↓				.50	.50		
[redacted]	3	↓		↓				.48	.47		
					3.4	3.4					

[a] Particle Size: Use T for PM_{10}, F for $PM_{2.5}$, and [illegible] for $PM_{2.5}$ to [illegible]
[b] Sampling Period: Circle time zone. Pacific (PST, [illegible]), Mountain (MST, [illegible]), Eastern (EST, EDT)
[c] Flow rate: Rotameter reading in Standard Cubic Feet [illegible]

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Figure 3: Example of Data Sheet for Recording Field Data

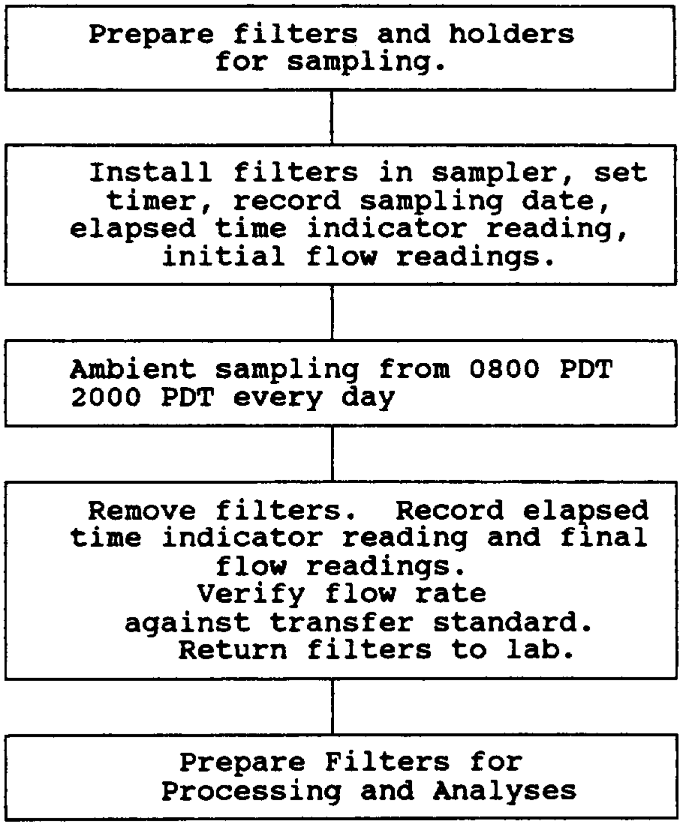

Figure 4: Flow Diagram for Routine Operations

APPENDIX B

Proposed Protocol for Use of the Harvard Annular Denuder Sampler (HEADS) in a Side-by-Side Comparison with the DRI Medium Volume Sampler

1. Assemble the denuder/filter pack portion of the Harvard Annular Denuder Sampler (HEADS) as per the attached instructions (Section 4.1 of the Harvard protocol), preferably at the sampling site, e.g., on the table in the 2nd floor facilities of SCAQMD. The sampling code is the same type as for the DRI sampler, a 4-letter code followed by a number code for tracking. Make sure that the number codes match for both denuders and the filter pack. Any of the inlets may be used with any of the samplers. Put the assembled package in the PVC "carrying case" and take it to the roof.

2. Check the final flow of the previous day's HEADS sample set, then replace it with the new denuder/filter pack. Disconnect the line to the pump at the Quick-Connect, exit of filter pack; put the cap on the filter pack exit and the orange plug in the inlet; remove the old denuder from the mounted holder to the (identical) carrying case. Insert the new denuder/filter pack assembly; reconnect the Quick-Connect to the pump line and remove the orange plug from the inlet. Check the initial flow to the new assembly and adjust with the needle valve if flow is outside the limits, 10 ± 0.5 Lpm. Always make sure the filter pack is at the top and the arrows on the denuders are pointing in the direction of the filter pack.

3. Record flow information and start and stop times on the data sheet with the number code matching that on the denuders and filter pack. Only one set of flow and time information is needed for each assembly.

4. Return with the previous day's denuder/filter pack assembly to the 2nd floor table. Dissemble the assembly from the filter pack end, replacing each cap and minimizing the time the denuders and filter pack are exposed to ambient air. Detailed instructions are included (Section 7.1 of the Harvard protocol, no. 1) through 7)). Note that the matching labels have been pre-placed on the data sheet and the assembly components.

5. There are 2 extra sets of denuders and filter packs which are to be used as field blanks. These are deployed by assembling them as for regular samples, placing the assembly in the spare carrying case, removing the plug on the inlet end and leaving them exposed to ambient air on the roof for 24 hr. The remaining set, used for tests and training, may also be used as a field blank, but be sure to label it Field Blank-"Test" in the Comment column of the Field Data Sheet.

6. Store the used denuders and filters in the shipping case, and return them by the usual shipping procedure at the end of the 10-day side-by-side sampling period. They do not need to be refrigerated, but if the shipping case experiences large temperature changes (>30°F), recheck the denuders to see if the caps are still tight.

Prepared by
Roger L. Tanner
October 7, 1993

4. <u>PREPARATION OF SAMPLERS</u>

4.1 Assembly of HEADS

1) all components must remain capped until they are connected with couplers, to minimize contamination from diffusion of ambient gases. This is especially true for the citric acid-coated denuder (D3, yellow), since human breath contains high concentrations of ammonia, the gas collected on this denuder. The small orange cap on the entrance of the inlet tube must remain connected until the sampler has been installed at the sampling site. <u>it must be removed before connecting the filter pack to the ~~to the~~ pump tubing</u>. The cap on the exit port of the filter pack must also remain connected until just before connecting the filter pack to the pump tube.

2) Refer to the HEADS field data log to choose the correct sample i.d. number for the components.

3) diagram (1) shows the order of the components. <u>NOTE THAT EACH OF THE TWO DENUDERS HAS AN ARROW MARKED ON THE EXIT END. IT IS VERY, VERY IMPORTANT THAT EACH DENUDER IS POINTED IN THE CORRECT DIRECTION. THE ARROWS POINT IN THE DIRECTION OF THE FILTER PACK.</u> It is also important to use a long flat surface for assembly, to avoid strain on the components. also, to prevent cracking of the glass components, <u>do not overtighten the couplers</u>. please make sure that hands are clean to minimize contamination of components with dirt. <u>wipe each o-ring with a kimwipe moistened with distilled water before assembly</u>.

4) assemble the system in the following order:

4a) first, remove the cap from the impactor end of the green denuder (D1), use the impactor plate forceps to make sure that the teflon pin is pushed all the way into the hole, if it has loosen, without use of "excessive force".

4b) <u>be especially careful</u> to use the thick O-ring with a coupler to connect the inlet to the impactor plate end of the green (impactor) denuder. [If the thin O-ring is used, the distance between the inlet jet and the plate will be too short, causing an error in the size cut-off of the impactor]. make sure that the arrow on the denuder points toward the filter pack.

4c) when attaching the couplers, in addition to being absolutely sure to put an O-ring between the glass ends, make sure that the two glass ends are approximately equally spaced within the coupler. Again do not overtighten the couplers, to avoid breaking the glass.

4d) after connecting the inlet to the impactor denuder (green, D1), connect the "third" denuder (yellow, D3) to the impactor denuder. use couplers with the ~~thick~~ thin O-rings. check to make sure the arrows point toward the filter pack.

4e) finally, connect the filter pack with the "third" denuder, using a thick or thin O-ring. after making this last connection, there can be a substantial strain on the glass tubes. handle the assembled system with special care.

4f) once the components have been assembled, carefully insert the inlet end into the long plastic protector pipe. then connect the filter pack to the pipe using wide plastic tape, stretching the tape to make a tight connection.

4g) keep the HEADS assembly in the pipe until it has been transported to the sampling site, to help prevent breakage. also, make sure the assembled HEADS is securely protected from rolling off the table!!

4h) FOR COLD WEATHER: the filter pack loosens when it is chilled. therefore, when the outside temperature is below 45 degrees F (or 7 degrees C), use the following method: chill the capped filter pack outdoors for at least 30 minutes. while it is chilling, assemble the two denuders and inlet. after filter pack has chilled, bring it inside, quickly tighten it with the strap wrenches and attach it to the denuders. without further delay, place the assembly inside the protective pipe and take outdoors to install in the temperature-controlled box.

[not necessary in LA]

6.2 Sampler protection

1) connect caps to inlets and exit ports of all samplers.
2) remove samplers from their holders and take them to the field lab.

7. FIELD SAMPLE PROCESSING

7.1 HEADS sampler

1) This system must be processed immediately following the end of sample collection to prevent cross contamination inside the filter pack due to vaporization of some particle species. each piece must also be capped quickly after it has been separated from the other pieces, to prevent contamination by room air.
2) carefully place the system on the long, clean flat space.
3) first, disconnect the filter pack from the denuder system, because this minimizes strain on the glass pieces. immediately cap the entrance to the filter pack and the end of the yellow (third) denuder.
4) second, disconnect the green and yellow denuders, immediately capping the open ends.
5) third, leaving the cap on the entrance to the inlet section, disconnect the inlet from the green denuder. immediately remove the impactor plate from the green denuder with the impactor plate forceps. this plate must be removed before attaching a cap to the denuder or else the glass will be cracked when attaching the cap attach caps to seal both the denuder and the inlet.
6) repack the glass components in the shipping box, rechecking to make sure all caps are securely attached.
7) DO NOT OPEN THE FILTER PACK IN THE ROOM AIR. transfer one of the duplicate sample i.d. labels from the filter pack to the HEADS data log. ← This is already done – one label on sampler components, matching ~~one~~ set on data sheet.