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Measurement of Atmospheric Nitric Acid at Azusa by Tunable Diode Laser Absorption Spectrometry

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

Measurement of Atmospheric Nitric Acid at Azusa by Tunable Diode Laser Absorption Spectrometry

Final Report

Contract No. 93-300

Prepared for:

California Air Resources Board
Research Division
2020 L Street
Sacramento, California 95814

Prepared by:

Gervase I. Mackay, Ph.D.

UNISEARCH ASSOCIATES INC.
222 Snidercroft Rd
Concord, Ontario L4K 1B5
CANADA

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Final Report to the

STATE OF CALIFORNIA
AIR RESOURCES BOARD

in

completion of research under
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We also gratefully acknowledge the SCAQMD for providing the site and thank the station Technologist, Mr. Sumner Wilson, for his assistance during the study.

EXECUTIVE SUMMARY

HNO_3 plays an important role in the photochemistry of urban and rural air and its accurate measurement provides a sensitive test for current acid deposition models. Measurements of nitric acid (HNO_3) by denuder tube technology are made on a routine basis in the Southern California acid deposition network. Recently, the HNO_3 results from a number of these stations have shown variability inconsistent with the expected behavior. It was thought to be prudent, therefore, to compare the measurements with a reference standard air monitoring technique at one of these sites which might help to identify the source of the variability.

Tunable diode laser absorption spectroscopy (TDLAS) offers a number of advantages for making this measurement. Its high spectral resolution provides an unequivocal identification of the measured gaseous species free from interferences of other atmospheric constituents. This specificity makes it an ideal instrument to use as a standard against which other, less definitive methods, can be compared. In addition the TDLAS has high sensitivity and rapid response time so that it can provide real time measurements with detection limits much better than those required for ambient concentrations of the majority of trace constituents under most atmospheric conditions.

The Unisearch model TAMS-150 TDLAS was employed for the measurement of HNO_3 and had detection limits of better than 0.2 ppbv.

Measurements of HNO_3 by the TDLAS were made during the period 12:00, September 30, 1993 through 24:00, October 30, 1993 inclusive. Data was obtained over 1 minute averaging periods. The results have also been reduced to 1 hour average values and Daytime average value (10:00 -- 18:00) for comparison with measurements made by the ARB denuder samplers. Data coverage was better than 98%.

The diurnal behavior of HNO_3 was quite regular. The maximum concentrations generally occurred between 14:00 and 16:00 each day. The HNO_3 daily maximum varied between 3 ppbv (during wet weather) and 30 ppbv (hot dry weather) with the median value of about 15 ppbv for the entire period. The averages calculated for the period 10:00 -- 18:00 (the denuder sampling period) were on average twice the nighttime (18:00 -- 10:00) average and represented ~75% of the total daily HNO_3 burden. This indicates that, on most occasions, the denuders should capture a major fraction of the HNO_3 produced during a 24 hour period.

There was no evidence for any large particle nitrate (>2 μm) dissociation from the particulate matter collected on the inlet filter contributing to the HNO_3 signal measured by the TDLAS. While it could not be completely ruled out, dissociation of small nitrate particles (<2 μm) (which passed through the filter) in the White cell was not obvious and the results indicate that it could contribute at most 10% of the measured signal at any time.

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1. INTRODUCTION

Nitric acid is a major final product for "odd nitrogen" in the atmosphere and its measurement is important in evaluating nitrogen photochemistry. It is also a major component in acid deposition. It is particularly important in the South Coast Air Basin [1] where the ratios of NO_X to SO_X emissions are higher than those in central and eastern USA In addition, the relatively dry climate in the Basin, favors the formation of HNO_3 which occurs readily in the gas phase whereas much of the SO_2 oxidation in other regions is believed to occur in cloud droplets.

Measurements of nitric acid (HNO_3) by denuder tube technology are made on a routine basis in the Southern California acid deposition network. Recently, the HNO_3 results from a number of these stations have shown variability inconsistent with the expected behavior. It was, therefore, thought to be prudent to compare the measurements with a reference standard air monitoring technique at one of these sites in an attempt to identify the source of the variability.

In October 1993 the Research Division of the State of California Air Resources Board sponsored a four week comparison between the Tunable diode laser absorption spectrometer (TDLAS) and the denuder technique at the Southern California Air Quality Management monitoring site in Azusa, CA. Two denuder systems were employed in the study and they were situated within 10 ft of each other.

Tunable diode laser absorption spectroscopy (TDLAS) is a good choice for a reference standard for the following reasons [2]. Its high spectral resolution provides an unequivocal identification of the measured gaseous species free from interferences of other atmospheric constituents. In addition, the high sensitivity and rapid response of the TDLAS provides real time measurements with detection limits much better than those required for the ambient concentrations of most trace constituents under most atmospheric conditions.

Unisearch Associates Inc. used the TAMS-150 TDLAS designed for tropospheric air monitoring, to make real time measurements of HNO_3. The detection limits of the TAMS-150 system were more than adequate for following the diurnal behavior of HNO_3 during the study period.

2. EXPERIMENTAL

2.1 Principle of the TDLAS System

The TDLAS method takes advantage of the high monochromaticity and rapid tunability of Pb salt diode lasers to measure absorptions arising from single rotational-vibrational lines in the mid-infrared spectrum of a molecule. In order to facilitate the measurement of very low optical densities ($<10^{-5}$) at line center and to reduce the chances of overlap between adjacent absorption lines, reduced pressures (~25 Torr) are used to minimize pressure broadening of the rotational lines. The atmospheric sample is pumped rapidly at the reduced pressure through a White cell which also provides the long optical path lengths (153 m) required to achieve the desired detection limits. The White cell is Teflon lined to minimize sticking of HNO_3 on the walls.

The technique of measuring HNO_3 by TDLAS has been described in detail by Hastie et al. [3] and a full description of the TAMS-150 field instrument may be found in the Unisearch Final Report to the State of California Air Resources Board, November 1987 [4] and in a paper by Mackay et al. [5].

2.2 Sampling and Calibration Procedures

Sample air was drawn through a 6 mm OD. 0.75 mm wall, PFA type Teflon tube approximately 4 m long. Particles were removed from the air by a 2 micron pore size Teflon filter located at the tubing entrance. A Teflon needle valve located 1 m upstream of the entrance to the White cell maintained the flow into the White cell at 10 standard liters per minute (SLM). The air traversed the inlet line in a few tenths of a second while the residence time in the White cell was about 4 seconds. The flow of air entering the White cell was monitored with a calibrated mass flowmeter just prior to each calibration and was adjusted by the needle valve as necessary. A motorized valve referenced to a MKS Baratron pressure gauge controlled the pressure in the White cell at 25 Torr.

The sensitivity of the TAMS-150 toward HNO_3 was determined by introducing a 'spike' of known concentration of the target gas to the air stream about 1 m upstream of the White cell entrance at a point immediately in front of (high pressure side) the Teflon needle valve. The concentration of the spike was chosen to provide mixing ratios similar to that of HNO_3 in the sampled air. In this way, any surface effects that may occur will be the same for the sampled and spiked air and should, therefore, cancel. A complete description of sampling integrity testing performed in the laboratory is described in Hastie et. al. [3]. Periodically, the sampling integrity of the rest (~3 m) of the sampling line was tested by introducing the spike at the sampling inlet in front of the particle filter. No differences were observed in the measured mixing ratio when the HNO_3 spike was added at the inlet or just up-stream of the White cell. The only difference noted was the time response (>80% change) to the added spike which was about 5 minutes when added at the inlet and less than 3 minutes when added at the needle valve.

Figure 1 demonstrates the response of the system to spike of nitric acid added to ambient air with and without the scrubber in place. The HNO_3 was added to the high pressure region of the sampling line ~1 meter upstream of the normal calibration injection point. With reference to Figure 1, after the system had been sampling ambient air which was at a level of about 3.5 ppbv, the Nylon scrubber used to obtain background spectra was interposed in the sampling line to scrub the sampled air of ambient nitric acid (BKGD). The measured signal was observed to drop to a value of about 1 ppbv after 5 minutes (background structure noise). A spike equivalent to 6.9 ppbv was then introduced and the signal rose to the expected level within 5 minutes. A second Nylon filter was then interposed into the sampling line immediately down stream of the HNO_3 spike injection point. The measured signal dropped to the previously measured background level within 5 minutes. Removal of the HNO_3 spike (at 09:42) showed no change in the measured background signal indicating that the Nylon filters effectively remove HNO_3 from the air stream. The response time is also shown to be of the order of 2-3 minutes and complete recovery of the HNO_3 spike is obtained

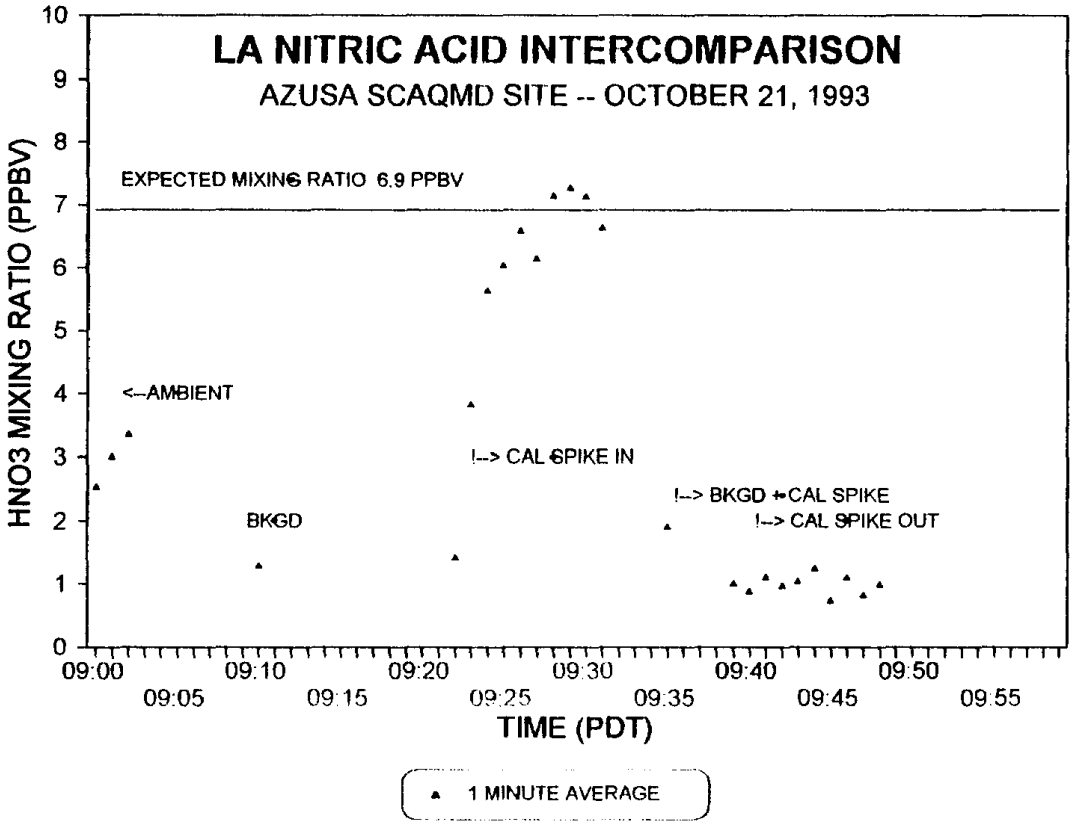

Figure 1: Response time of the TDLAS to a 6.9 ppbv spike of HNO_3 added into the ambient pressure side of the sampling line ~1 m upstream of the White Cell. Efficiency of the background scrubber is also demonstrated.

During the measurement periods the calibration gases flowed continuously through the addition lines. When not required for calibration, the gas mixture was exhausted far away from the inlet. During a calibration the addition line was inserted into the inlet line to introduce the calibration gas mixture to the sampled air stream. The addition point of the calibration spike was chosen for ease of calibration and as discussed above, to minimize the time required to stabilize before and after a calibration (~3 minutes).

The minimum detectable concentration, MDC, defined as a signal-to-noise ratio of 1, was determined experimentally at the selected laser operating condition. A 1 micron pore size Nylon filter was inserted into the sampling line at a point immediately upstream of the calibration gas inlet and the laser current scanned over the range of the absorption feature to obtain a background noise level, S_n. A known mixing ratio, MR, in ppbv of trace constituent is then added and the signal, S_s measured. The ratio of S_n/S_s X MR provides the MDC in ppbv, which for most of the time was about 0.5 ppbv for a 1 minute average and ~ 50 -- 100 pptv for 1 hour averages.

The following description of the sequence of events during an automatic ambient air monitoring experiment illustrates how laser control, as well as data analysis, is achieved.

Information for the operating parameters selected for the HNO_3 measurements were input to the computer. The software then operated the system automatically. Under conditions when the ambient levels of HNO_3 were below 4 ppbv, a background spectrum was obtained by passing the air through the nylon filter every 30 minutes. Since the collection efficiency of the nylon filter was observed to be >80%, the mixing ratio of HNO_3 in the White cell was below the detection limit for levels below ~4 ppbv. The background spectrum was obtained and archived. Next, calibration gas was added to the scrubbed ambient air flow and, after a suitable stabilization period, a calibration-reference spectrum was obtained. The reference spectrum was also archived in its untreated form as were all subsequent spectra of ambient air. The background spectrum was subtracted (channel by channel) from the reference spectrum and the result normalized to the mean value of the untreated reference spectrum. This procedure essentially removes the frequency dependent structure present in the background from the reference spectra.

Under conditions where the HNO_3 mixing ratio was greater than 4 ppbv, no background subtraction was performed. The HNO_3 laser power was low enough that there was little frequency dependent laser noise. Eliminating the background subtraction procedure for concentrations above 4 ppbv did not introduce significant error in the analysis.

Figure 2 shows the data obtained on October 22, 1993 along with the measured background. The results show that the measured background is essentially at the detection limit during the night when the ambient HNO_3 levels are below 2 ppbv. The background increased during the day to about 1 ppbv when the HNO_3 reached a maximum of 13 ppbv for the 1 hour period 17:00 -- 18:00. This is consistent with some point measurements made on October 30 with a nylon filter at the inlet. The nylon filter appears to trap >85% of the ambient nitric acid.

Some of the measured background signal shown in Figure 2 may be due to outgassing of HNO_3 from the walls of the White cell where it has accumulated during the ambient sampling period.

The measured signal was generally observed to decrease below the detection limit when the scrubber was left in the sampling line for longer periods (~15 minutes) although on occasion, a small residual signal (≤10%) was observed to persist even after 30 minutes. A second possible source of the measured background signal is that it may be due to dissociation of fine particle nitrate (< 2 μm) at the reduced pressures in the White cell. This size fraction will not be collected by the Teflon inlet filter and most would also pass through the Nylon filter. Nevertheless, whichever is the case, it represents a very small (<10%) error in the measurements.

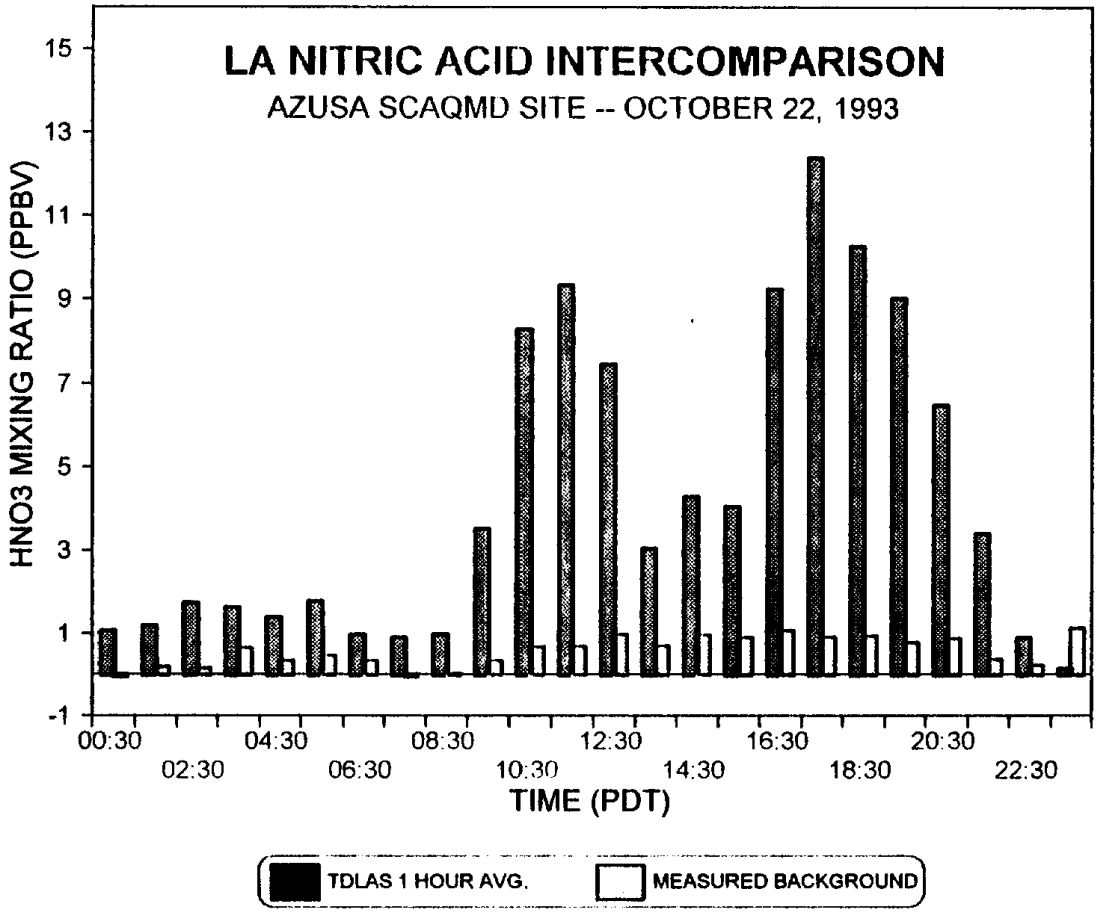

Figure 2: .Diurnal variation in ambient HNO_3 and the measured background signal obtained by passing ambient air through a 1 μm pore size Nylon filter on October 22, 1993. Background measurements made every 15 minutes were combined to provide hourly average values.

Course particulate Nitrate (>2μm) did not appear to present a problem. The Teflon filter used to collect coarse particle matter at the inlet was changed each day and there was no evidence for a variation in the measured HNO_3 mixing ratio when the filter was changed. Also, HNO_3 was often observed to drop rapidly at sunset to near the detection limits. This would not be the case if particle nitrate were dissociating on the filter and bleeding HNO_3 into the sampled air. Furthermore, nighttime HNO_3 values would have been expected to be much higher if significant

dissociation was occurring as the decomposition would be favored during this period when the ambient gas phase HNO_3 was the lowest. Dissociation during the day should not be important as high HNO_3 would tend to force the equilibrium towards nitrate formation and not decomposition.

Once the calibration-background procedure was complete the software reset the solenoid valves to admit ambient air and, after an appropriate delay to achieve steady conditions (3 minutes), an ambient air spectrum was acquired. The background structure was subtracted (for mixing ratios below 4 ppbv).

The ambient air spectrum was then compared to the calibration spectrum using a least squares fitting procedure. Since the mean values of the calibration spectrum and the ambient air spectrum may differ due to potentially varying broad band transmittance of ambient air outside the White cell and since the mean value of the ambient spectrum contains no useful information, the calibration spectrum was adjusted to have a zero mean value before fitting. Thus, the intensity of the absorption line in the ambient air spectrum was obtained as a fraction of the calibration line intensity. Since shifting of the background spectra eventually reduces the integrity of the background spectrum, new background spectra are obtained at intervals determined by the operator (every 30 minutes on average).

During ambient air monitoring, spectra were obtained in one second blocks. These blocks of data were co-added and an average value of the ambient spectrum was obtained for the 1 minute integration time chosen. For each 1 second block the computer identified the spectral line center using the gas in the reference cell and shifted the ambient spectra as necessary to ensure accurate co-addition of spectra. When the reference spectrum was observe to have shifted by a significant number of channels (the spectrum is made up of 128 channels), which in this case was 3 channels, the computer commanded the temperature feedback circuit to adjust the laser temperature to restore the HNO_3 line center to coincide with the channel value employed during the calibration. This procedure results in greatly improved precision in the determination of the ambient mixing ratio.

2.3 HNO_3 Reference standard Calibration Procedures

The calibration spike was generated from a permeation device of our own design [3]. The HNO_3 permeation tube was constructed just prior to the field study and a permeation rate of ~280 ng/min. was measured in the laboratory with the NaOH standard to be employed in the field. The device was calibrated by titration against this standard NaOH solutions during the field study. In the field, two measurements were made with de ionized water brought from Unisearch and these gave results similar to that determined in the laboratory. Six measurements were made with de ionized water obtained from the local supermarket. Considerable difference was observed between the two sets of measurements. It appeared that the use of the de ionized water from the local store introduced an error in the on-site determination of the permeation rate. The measured titration end-point was found to be dependent on the volume of water employed. This suggested that something in the "de ionized" water was acting as a buffer. All of the determinations using local de ionized water provided permeation rates that were lower than the final, accepted rate, by 20% -- 40%. This error was not noted until the last week of the study.

One final determination was made with distilled water supplied by Cal Tech. The results were similar to those obtained with Unisearch distilled water. Table 1 summarizes the permeation rate measurements made prior to and during the field study.

In order to obtain an accurate determination of the permeation rate before the permeation system was turned off for the return trip, 6 samples were obtained in which the output of the permeation system was bubbled into various volumes of a basic aqueous solution for different bubbling times. This provided a wide range in the concentrations of the samples which were subsequently analyzed for NO_3^- by Ion Chromatography at the ARB laboratories in Sacramento. Table 2 summarizes the results of these determinations. They provided an average value for the permeation rate of 202 ± 3 ng.min.$^{-1}$.

The permeation rate was also measured back at Unisearch after the study with a new NaOH standard. The results are provided in Table 3. Inspection of the three tables shows that the in-field titrations with "good" distilled water (Table 1 # 1, 2 and 10) were about 20% higher than the values determined by the IC and the titrations after the study at Unisearch. It was subsequently discovered that the technician who produced the standard NaOH used in the field determinations had prepared the 0.1 M solution by weighing and not from a Reference Standard solution. As NaOH is very hydroscopic, the amount of NaOH weighed out would have been too low by the weight of water absorbed by the NaOH crystals, an error that could easily amount to 20%. These results (1, 2 and 10 in Table 1) are not, therefore included in the calculation of the average value. Results 1, 2 and 10 are very consistent, however, and provide strong evidence that the permeation rate did not change throughout the 1 month field study. The average permeation rate from all titrations was 198 ± 10 ng.min.$^{-1}$ in good agreement with the value obtained from the Ion Chromatograph. The value employed for the analysis of the data, 200 ng.min.$^{-1}$, was calculated from the average of the results in Tables 2 and 3.

Table 1: Permeation rates for the Unisearch HNO_3 permeation device determined by titration against standard NaOH prepared prior to the field study using lab distilled water (1, 2, 3 and 10) and local store de ionized water (3 -- 9).

#	DATE	MOLES OF NaOH	VOLUME OF H_2O (ml)	TRAP TIME (min.)	PERM. RATE (ng.min.$^{-1}$)
1	August 19	5×10^{-6}	20	1125	280
2	September 21	$3 \times 10^{-}$	20	720	263
3	September 25	5×10^{-6}	15	1220	258
4	October 13	2×10^{-6}	10	1860	169
5	October 15	2×10^{-6}	20	970	130
6	October 16	2×10^{-6}	20	960	131
7	October 17	2×10^{-6}	15	885	142
8	October 18	2×10^{-6}	15	890	142
9	October 19	2×10^{-6}	20	960	131
10	October 25	2×10^{-6}	20	495	255

Table 2. Permeation rates for the Unisearch HNO_3 permeation device determined by Ion Chromatography from samples obtained during the field study.

SAMPLE	VOLUME OF ELUENT (ml)	TRAP TIME (min.)	CONCENTRATION ($\mu g.ml^{-1}$)	PERM. RATE ($ng.min.^{-1}$)
A	10	143	2.98	209
B	25	584	4.68	201
C	10	240	4.84	202
D	25	300	2.40	200
E	10	200	4.09	204
F	25	690	5.58	202
			AVERAGE	**202±3**

Table 3 Permeation rates for the Unisearch HNO_3 permeation device determined at the Unisearch laboratory subsequent to the field study.

DATE	MOLES OF NaOH	VOLUME OF H_2O (ml)	TRAP TIME (min.)	PERM. RATE ($ng.min.^{-1}$)	WATER TYPE
November 12	2×10^{-6}	20	636	198	de ionized
November 16	2×10^{-6}	20	654	193	de ionized
November 17	2×10^{-6}	20	637	198	distilled
November 23	2×10^{-6}	10	660	191	de ionized
November 24	2×10^{-6}	10	677	186	distilled
November 25	2×10^{-6}	20	662	190	distilled
November 27	2×10^{-6}	40	610	207	distilled
November 29	2×10^{-6}	60	570	221	distilled
November 30	4×10^{-6}	60	1260	200	distilled
			AVERAGE	**198±10**	

3. AMBIENT AIR MEASUREMENTS HNO_3

3.1 Experimental Configuration

On September 29, 1993, the Unisearch mobile laboratory containing the TAMS-150 arrived at the Azusa SCAQMD monitoring station where the nitric acid measurements were to be made. The site is on the edge of a mixed residential/industrial area at the base of the San Gabriel mountains which are to the north. The Glendora Canyon empties into this area several miles to the east. Dr. Gervase I. Mackay and Dr. David R. Karecki from Unisearch shared the operation of the TAMS-150 during the study. The TAMS-150 was configured for single measurements of HNO_3 with a 1 minute integration time. The mobile laboratory was positioned at the north end of the SCAQMD building which housed the nitric acid denuders on its roof.

The inlet systems used in this study was constructed entirely of PFA Teflon fittings and tubing. The sampling port was positioned on the roof of the building at approximately the same height as the denuder sampler inlets some 1 m above the roof (~3 m above the ground) and about 5 m away from the nearest denuder system. The second denuder was located about 2 m from the first. The TDLAS inlet tube consisted of 4 m of 6 mm OD, 0.75 mm wall PFA Teflon tubing. A filter holder containing a 2μm pore size Teflon filter was installed at the sampling end of the line. This filter was replaced daily between 07:00 and 09:00.

3.2 Measurement Procedure

The TAMS-150 obtained data points every minute. The raw data were stored on floppy diskettes for future analysis in the laboratory and the real time measurements were printed out at 1 minute intervals. Calibrations were performed at least 4 times a day at operator chosen intervals. The sensitivity of the instrument toward HNO_3 never varied by more than 10% and the changes were random in nature. Backgrounds were usually obtained every 30 minutes and on occasion at more frequent intervals.

The accuracy of the measurements is estimated to be $\pm$ 15%. Three sources of error contribute to the overall accuracy; Calibration errors, Precision and Optical alignment variations which contribute to changes in the sensitivity of the instrument between calibrations. The major source of calibration error was the standardization of the permeation device (pH or IC) which has an uncertainty assessed at 5%. Additional uncertainties of $\pm$ 2% are caused by temperature variations of the permeation device, and $\pm$ 1% from the measurement of the total gas flow into which the HNO_3 spike was added. The flowmeter (Tylan, model FM360-20SLM) was calibrated against a dry test meter prior to the study with agreement within 1%. The precision of the instrument has been determined empirically to be better than 1% and the long term variability of the sensitivity between calibrations was observed to be within 7%.

Data coverage was excellent. A total of 30 ½ days of measurements were obtained. Only 15 hours out of a total of 732 hours were lost due to instrument malfunction. Less than 10 minutes of any hour was lost due to calibration periods and this occurred on average only 4 times per day. Usually only one calibration was made during the hours of comparison with the denuders.

4. RESULTS AND DISCUSSION

The measurement period was 12:00, September 30, through 24:00, October 30, 1993 inclusive. Data points were obtained over 1 minute averaging periods. The one minute HNO_3 data were re-analyzed into hourly average values at Unisearch. During the first 12 days of the study the system was not performing optimally and the detection limit for 1 hour averages was in the range 0.3 -- 0.5 ppbv. After October 12, a better absorption feature was identified and the detection limit was much better, in the range 50 -- 100 pptv. Nevertheless, the mixing ratios were well above the detection limit during the daytime comparison period of 10:00 -- 18:00 throughout the study. The results are presented in tabular form in Appendix A which contains the 1 hour average values (determined on the half hour) for HNO_3 over the entire study.

Figure 3 shows the results obtained on October 25 which were typical of the observations for most days of the study. On a few occasions HNO_3 exhibited two peaks (see Figure 2).

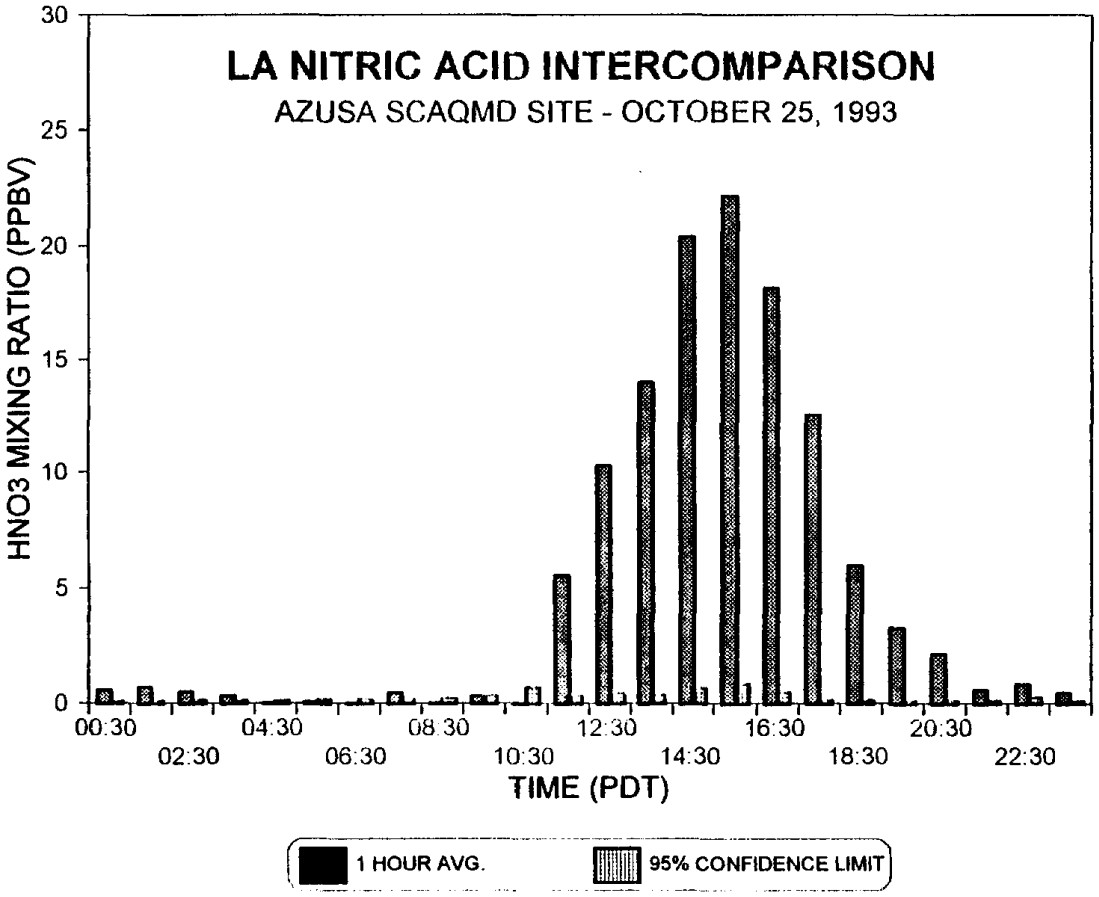

Figure 3: .Diurnal variation in the one hour average ambient HNO_3 measured by the TDLAS on October 25, 1993. The lower trace is the calculated hourly average confidence limit which is comparable to the minimum detection limit for that period.

Figure 4 shows the variation in the ambient HNO_3 mixing ratio measured by the TAMS-150 during the entire study period. The diurnal behavior was quite regular. The maximum concentrations occurred between 12:00 and 18:00 each day with most peaking in the 15:00 -- 16:00 hourly period. Nighttime levels were generally in the 0.2 -- 1 ppbv range. On occasion HNO_3 reached the instrument detection limit at nighttime (even after improved detection limits of <100 pptv were obtained -- see Figure 3) while at other times the nighttime levels remained high, in the 2 -- 4 ppbv range.

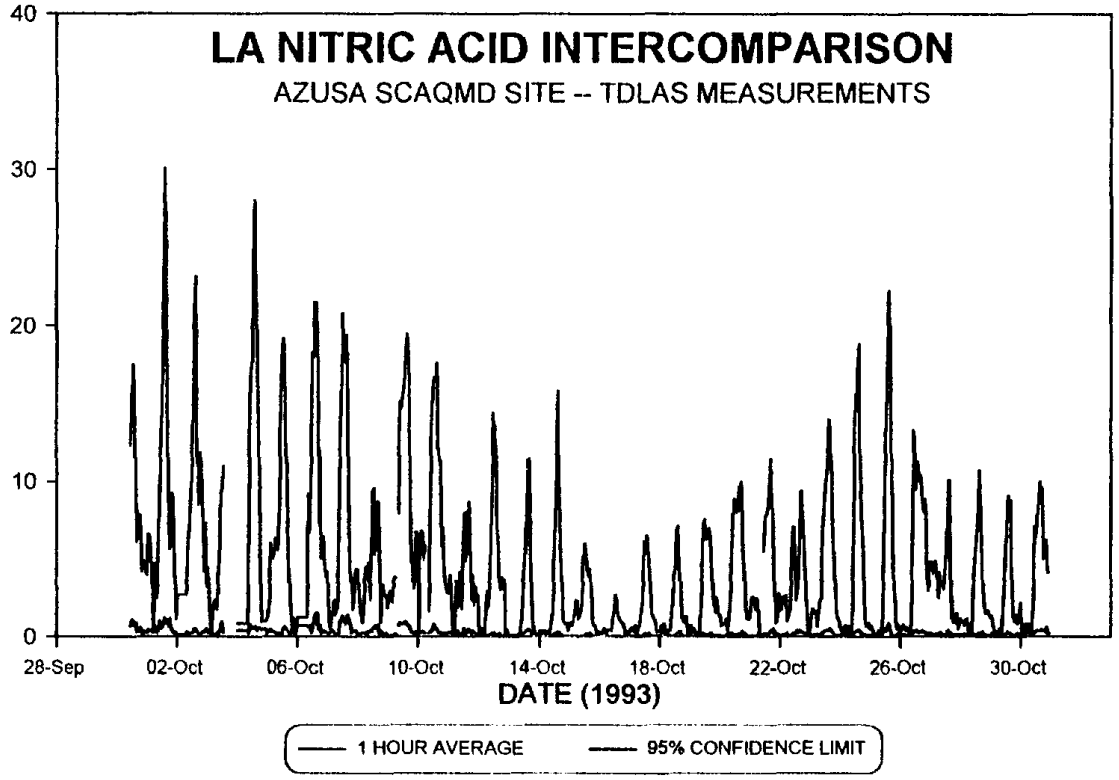

Figure 4: Diurnal variation in the one hour average ambient HNO_3 measured by the TDLAS during the period 12:00, September 30, 1993, through 24:00, October 30, 1993. The lower trace is the calculated hourly average confidence limit which is comparable to the minimum detection limit for that period.

The HNO_3 daily maximum was observed to decrease from ~30 ppbv on September 30 to only 3 ppbv on October 16. The decrease was gradual until October 15 when the levels abruptly dropped from 15 ppbv on the October 14 to 6 ppbv on October 15 and only 3 ppbv on October 16. During this latter period the weather was unsettled, with morning fog and occasional rain. After October 16 the weather improved, being mostly sunny, and the HNO_3 levels increased slowly to a maximum of 22 ppbv on October 25. After that, the daily maximum remained about 10 ppbv for the rest of the study. It should be noted that the last 5 days of the study overlapped the major forest fires in the Los Angeles area.

The daily average HNO_3 measured by the TDLAS along with the measured uncertainty is summarized in Table 4 and shown graphically in Figure 5. The 24 hr average HNO_3 mixing ratio measured by the TDLAS showed considerable variability particularly during the first two weeks of the study. As was observed with the daily maximum values, the 24 hour average value showed a minimum value on October 16. Prior to that, the levels varied between ~ 9 ppbv and 4 ppbv although a general decrease was observed on a daily basis after October 12. The daily average increased again after the October 16 maximizing at about 5 ppbv over the period October 22 through October 25 after which it again slowly decreased.

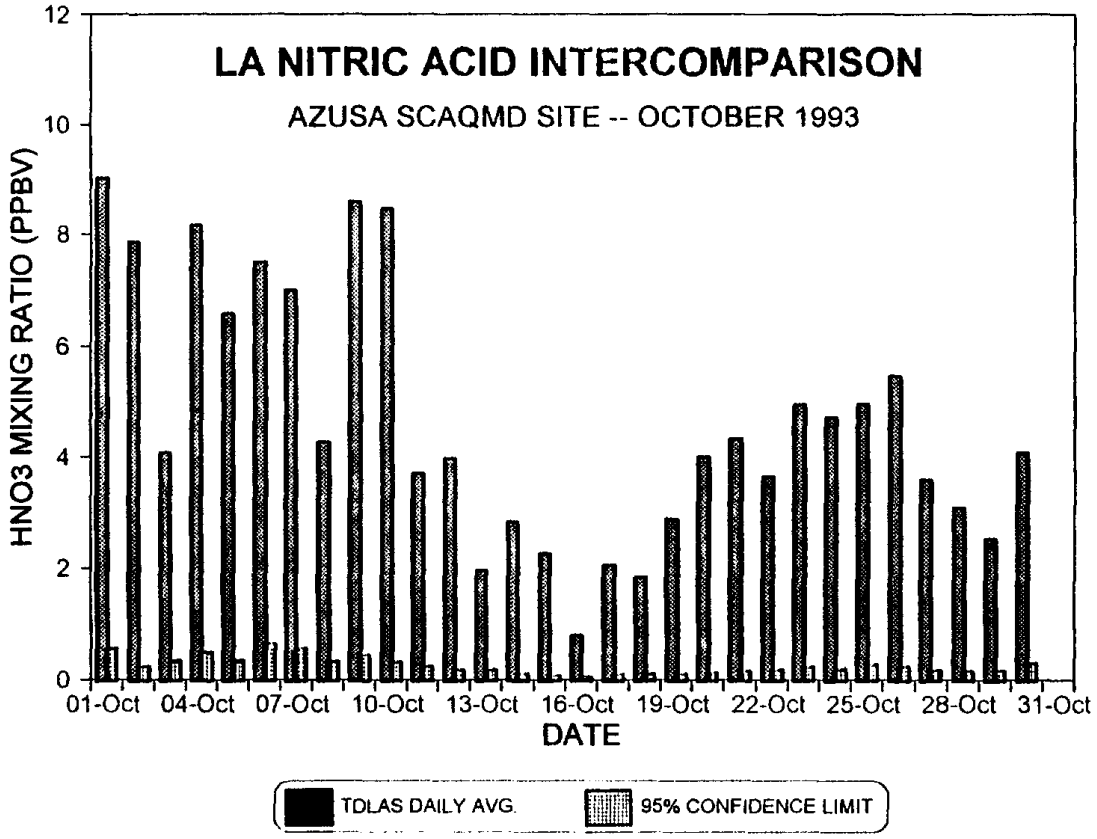

Figure 5: Daily average HNO_3 mixing ratios measured by the TDLAS during the period 00:00, October 1, 1993, through 24:00, October 30, 1993. The lower trace is the calculated daily average confidence limit which is comparable to the minimum detection limit for that period

The average HNO_3 mixing ratios and the 95% confidence limits measured during the daytime period, 10:00 through 18:00 PDT, are summarized in Table 5. The results are shown graphically in Figure 6. The daytime averages showed much the same behavior as the daily averages. The maximum value of ~20 ppbv was reached on October 4 and the minimum value of 1.5 ppbv for the daytime average was observed on October 16. The HNO_3 daytime mixing ratio showed a decline from the highest values in early October to a minimum on the October 16 after which the

HNO_3 increased again to a high of almost 13 ppbv on October 25. After October 25 the HNO_3 again slowly decreased.

Table 6 shows the average HNO_3 measured during the non-comparison "nighttime" period 18:00 at night through 10:00 the next morning for each 24 hour period. Also shown is the ratio of the nighttime to daytime measurements. This ratio varies from a high of 59% on October 27 to a minimum of 4% on October 13. There is no correlation in the ratio with maximum daily mixing ratio. Furthermore, there does not appear to be a correlation with weather conditions insofar as humidity, precipitation and solar radiation are concerned. It suggests that air circulation, wind direction, wind speed and air trajectory must be the cause of the variation in this ratio and the higher nighttime mixing ratios observed on occasion. The meteorological data, however, is not currently available for comparison and possible confirmation of this hypothesis.

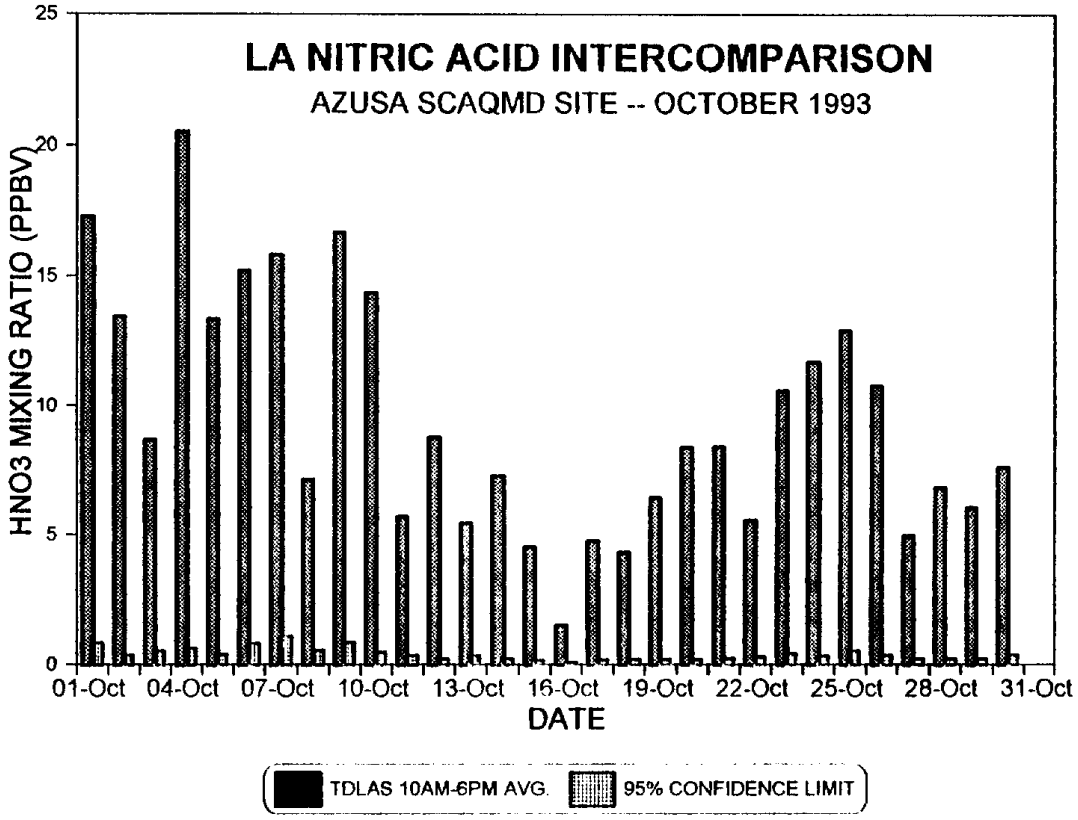

Figure 6: Daytime (10:00 -- 18:00) average HNO_3 mixing ratios measured by the TDLAS during the period 00:00, October 1, 1993, through 24:00, October 30, 1993. The lower trace is the calculated daytime average confidence limit which is comparable to the minimum detection limit for that period

Table 4 Daily average HNO_3 mixing ratio measured by the TDLAS during the LA Acid Precipitation Intercomparison Study October 1 -- 30, 1993 at the Azusa SCAQMD site.

DATE DD-MM	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	COMMENTS
01-Oct	00:00	23:59	9.01	0.56	
02-Oct	00:00	23:59	7.86	0.24	
03-Oct	00:00	23:59	4.08	0.32	DATA MISSING 14:00 -- 24:00
04-Oct	00:00	23:59	8.16	0.49	
05-Oct	00:00	23:59	6.58	0.33	
06-Oct	00:00	23:59	7.50	0.64	
07-Oct	00:00	23:59	7.01	0.57	
08-Oct	00:00	23:59	4.26	0.33	
09-Oct	00:00	23:59	8.58	0.44	DATA MISSING 08:00 -- 09:00
10-Oct	00:00	23:59	8.46	0.31	DATA MISSING 07:00 -- 09:16
11-Oct	00:00	23:59	3.70	0.23	
12-Oct	00:00	23:59	3.97	0.18	
13-Oct	00:00	23:59	1.95	0.18	
14-Oct	00:00	23:59	2.83	0.11	
15-Oct	00:00	23:59	2.27	0.08	
16-Oct	00:00	23:59	0.78	0.06	
17-Oct	00:00	23:59	2.06	0.10	
18-Oct	00:00	23:59	1.83	0.10	
19-Oct	00:00	23:59	2.88	0.11	
20-Oct	00:00	23:59	3.99	0.13	
21-Oct	00:00	23:59	4.33	0.17	DATA MISSING 09:00 -- 11:14
22-Oct	00:00	23:59	3.64	0.19	
23-Oct	00:00	23:59	4.94	0.22	
24-Oct	00:00	23:59	4.71	0.20	
25-Oct	00:00	23:59	4.95	0.27	
26-Oct	00:00	23:59	5.46	0.23	
27-Oct	00:00	23:59	3.59	0.17	
28-Oct	00:00	23:59	3.07	0.15	
29-Oct	00:00	23:59	2.52	0.16	
30-Oct	00:00	23:59	4.08	0.29	STUDY END 24:00

Table 5 Daytime (10:00 -- 18:00) average HNO_3 mixing ratio measured by the TDLAS during the LA Acid Precipitation Intercomparison Study October 1 -- 30, 1993 at the Azusa SCAQMD site.

DATE DD-MM	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	COMMENTS
01-Oct	10:00	18:00	17.25	0.81	
02-Oct	10:00	18:00	13.40	0.31	
03-Oct	10:00	18:00	8.64	0.51	DATA MISSING 14:00 -- 18:00
04-Oct	10:00	18:00	20.48	0.59	
05-Oct	10:00	18:00	13.32	0.37	
06-Oct	10:00	18:00	15.18	0.79	
07-Oct	10:00	18:00	15.80	1.07	
08-Oct	10:00	18:00	7.09	0.53	
09-Oct	10:00	18:00	16.66	0.83	
10-Oct	10:00	18:00	14.34	0.44	
11-Oct	10:00	18:00	5.67	0.32	
12-Oct	10:00	18:00	8.72	0.20	
13-Oct	10:00	18:00	5.44	0.31	
14-Oct	10:00	18:00	7.22	0.19	
15-Oct	10:00	18:00	4.52	0.14	
16-Oct	10:00	18:00	1.49	0.05	
17-Oct	10:00	18:00	4.75	0.15	
18-Oct	10:00	18:00	4.30	0.17	
19-Oct	10:00	18:00	6.37	0.16	
20-Oct	10:00	18:00	8.32	0.17	
21-Oct	10:00	18:00	8.34	0.22	DATA MISSING 10:00 -- 11:14
22-Oct	10:00	18:00	5.52	0.26	
23-Oct	10:00	18:00	10.55	0.40	
24-Oct	10:00	18:00	11.65	0.31	
25-Oct	10:00	18:00	12.86	0.50	
26-Oct	10:00	18:00	10.74	0.32	
27-Oct	10:00	18:00	4.94	0.19	
28-Oct	10:00	18:00	6.76	0.18	
29-Oct	10:00	18:00	6.00	0.20	
30-Oct	10:00	18:00	7.56	0.36	STUDY END 24:00

Table 6 Average HNO_3 mixing ratio for the non-daytime averaging period (18:00 -- 10:00) measured by the TDLAS during the LA Acid Precipitation Intercomparison Study October 1 -- 30, 1993 at the Azusa SCAQMD site.

DATE DD-MM	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	RATIO 18:00 - 10:00 / 10:00 - 18:00
01-Oct	18:00	10:00	4.89	0.43	0.28
02-Oct	18:00	10:00	5.09	0..20	0.38
03-Oct	18:00	10:00	2.25	0.25	0.26
04-Oct	18:00	10:00	2.00	0.44	0.10
05-Oct	18:00	10:00	3.21	0.31	0.24
06-Oct	18:00	10:00	3.66	0.57	0.23
07-Oct	18:00	10:00	2.61	0.32	0.17
08-Oct	18:00	10:00	2.85	0.23	0.40
09-Oct	18:00	10:00	4.28	0.23	0.26
10-Oct	18:00	10:00	5.10	0.23	0.36
11-Oct	18:00	10:00	2.71	0.26	0.48
12-Oct	18:00	10:00	1.59	0.17	0.18
13-Oct	18:00	10:00	0.21	0.11	0.04
14-Oct	18:00	10:00	0.64	0.07	0.09
15-Oct	18:00	10:00	1.14	0.05	0.25
16-Oct	18:00	10:00	0.42	0.07	0.28
17-Oct	18:00	10:00	0.71	0.07	0.15
18-Oct	18:00	10:00	0.60	0.07	0.14
19-Oct	18:00	10:00	1.14	0.09	0.18
20-Oct	18:00	10:00	1.83	0.11	0.22
21-Oct	18:00	10:00	2.45	0.14	0.29
22-Oct	18:00	10:00	2.70	0.15	0.49
23-Oct	18:00	10:00	2.14	0.13	0.20
24-Oct	18:00	10:00	1.24	0.14	0.11
25-Oct	18:00	10:00	1.00	0.15	0.08
26-Oct	18:00	10:00	2.82	0.18	0.26
27-Oct	18:00	10:00	2.92	0.16	0.59
28-Oct	18:00	10:00	1.23	0.14	0.18
29-Oct	18:00	10:00	0.78	0.14	0.13
30-Oct	18:00	10:00	2.35	0.25	0.31

4. CONCLUSIONS

Measurements of HNO_3 by the TDLAS were made during the period 12:00, September 30, 1993 through 24:00, October 30, 1993 inclusive. Data was obtained over 1 minute averaging periods. The results were reduced to 1 hour average values and Daytime average value (10:00 -- 18:00) for comparison with measurements made by the ARB denuder samplers. Data coverage was better than 98% and detection limits of better than 0.2 ppbv were obtained for the one hour averages.

The diurnal behavior of HNO_3 was quite regular. The maximum concentrations generally occurred between 14:00 and 16:00 each day. The HNO_3 daily maximum varied between 3 ppbv (during wet weather) and 30 ppbv (hot dry weather) with the median value of about 15 ppbv for the entire period. The values calculated for the period 10:00 -- 18:00 (the denuder sampling period) were on average twice the nighttime (18:00 -- 10:00) values and represented ~75% of the total daily HNO_3 burden. This indicates that, on most occasions, the denuders should capture a major fraction of the HNO_3 produced during a 24 hour period.

Tests performed during the field study indicated that there were no significant losses of HNO_3 in the sampling line, the sampling integrity was good and the scrubbing efficiency of the Nylon filters used to remove HNO_3 from ambient air to allow background noise determinations was adequate for HNO_3 levels below ~5 ppbv. Furthermore, there was no evidence for any large particle nitrate (>2 μm) dissociation from the particulate matter collected on the inlet filter contributing to the HNO_3 signal measured by the TDLAS. While it could not be completely ruled out, dissociation of small nitrate particles (<2 μm) (which passed through the filter) in the White cell was not obvious and the results indicate that it could contribute at most 10% of the measured signal at any time.

5. REFERENCES

1. The Atmospheric Acidity Protection Program: Annual Report to the Governor and the Legislature, (1992)

2. H. I. Schiff, G. W. Harris, G. I. Mackay, "Tunable Diode Laser Absorption Spectrometry as a Reference Method for Tropospheric Measurements", Commission of the European Communities Air Pollution Research Reports: Monitoring of Gaseous Pollutants by Tunable Diode Lasers-II, Mainz, FRG, (October 1988)

3. D. R. Hastie, H. I. Schiff, G. I. Mackay, T. Iguchi, B. A. Ridley, "Tunable Diode Laser Systems for Measuring Trace Gases in Tropospheric Air", Environmental Science and Technology 17, 352 (1984)

4. Unisearch Final Report to the State of California Air Resources Board contract number A5-189-32 (1987)

5. G. I. Mackay, L. K. Mayne, H. I. Schiff, "Measurements of H_2O_2 and HCHO by Tunable Diode Laser Absorption Spectroscopy During the 1986 Carbonaceous Species Methods Comparison Study in Glendora, California" Aerosol Sci. & Technol. 12, 56-63 (1990)

APPENDIX A

1 Hour average HNO_3 mixing ratios

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
30-Sep	00:00	01:00				
30-Sep	01:00	02:00				
30-Sep	02:00	03:00				
30-Sep	03:00	04:00				
30-Sep	04:00	05:00				
30-Sep	05:00	06:00				
30-Sep	06:00	07:00				
30-Sep	07:00	08:00				
30-Sep	08:00	09:00				
30-Sep	09:00	10:00				
30-Sep	10:00	11:00				
30-Sep	11:00	12:00				
30-Sep	12:00	13:00	12.297	0.679	0.97	MEASUREMENTS BEGAN @ 12:00
30-Sep	13:00	14:00	15.063	1.101	0.95	
30-Sep	14:00	15:00	17.537	0.955	0.97	
30-Sep	15:00	16:00	15.535	0.719	0.98	
30-Sep	16:00	17:00	10.211	0.867	0.93	
30-Sep	17:00	18:00	6.081	0.301	0.97	
30-Sep	18:00	19:00	7.055	0.486	0.95	
30-Sep	19:00	20:00	7.847	0.306	0.98	
30-Sep	20:00	21:00	7.782	0.580	0.95	
30-Sep	21:00	22:00	4.202	0.267	0.96	
30-Sep	22:00	23:00	4.914	0.133	0.99	
30-Sep	23:00	24:00	4.787	0.336	0.95	
01-Oct	00:00	01:00	3.972	0.233	0.97	
01-Oct	01:00	02:00	6.617	0.437	0.96	
01-Oct	02:00	03:00	6.549	0.401	0.96	
01-Oct	03:00	04:00	5.524	0.376	0.95	
01-Oct	04:00	05:00	4.088	0.475	0.88	
01-Oct	05:00	06:00	0.656	0.220	0.54	
01-Oct	06:00	07:00	2.573	0.684	0.63	
01-Oct	07:00	08:00	4.748	0.580	0.87	CALIBRATION 07:34 - 07:57
01-Oct	08:00	09:00	2.515	0.254	0.81	
01-Oct	09:00	10:00	6.807	0.431	0.91	
01-Oct	10:00	11:00	9.971	1.008	0.96	
01-Oct	11:00	12:00	12.663	0.553	0.91	
01-Oct	12:00	13:00	14.735	0.515	0.98	CALIBRATION 12:42 - 12:49
01-Oct	13:00	14:00	23.432	0.682	0.99	
01-Oct	14:00	15:00	30.096	1.199	0.99	
01-Oct	15:00	16:00	24.421	1.023	0.98	
01-Oct	16:00	17:00	15.201	0.806	0.98	
01-Oct	17:00	18:00	7.474	0.667	0.97	
01-Oct	18:00	19:00	5.628	1.140	0.92	
01-Oct	19:00	20:00	5.944	0.479	0.73	CALIBRATION 19:36 - 19:47
01-Oct	20:00	21:00	9.248	0.483	0.94	
01-Oct	21:00	22:00	7.755	0.246	0.97	
01-Oct	22:00	23:00	4.484	0.184	0.99	
01-Oct	23:00	24:00	1.128	0.248	0.98	

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
02-Oct	00:00	01:00	2.716	0.134	0.98	NOISY SIGNAL
02-Oct	01:00	02:00	2.716	0.134	0.98	AVERAGE 00:00 - 08:00
02-Oct	02:00	03:00	2.716	0.134	0.98	
02-Oct	03:00	04:00	2.716	0.134	0.98	
02-Oct	04:00	05:00	2.716	0.134	0.98	
02-Oct	05:00	06:00	2.716	0.134	0.98	
02-Oct	06:00	07:00	2.716	0.134	0.98	
02-Oct	07:00	08:00	2.716	0.134	0.98	CALIBRATION 07:39 - 07:55
02-Oct	08:00	09:00	3.905	0.304	0.95	
02-Oct	09:00	10:00	6.327	0.135	1.00	
02-Oct	10:00	11:00	6.733	0.183	0.99	
02-Oct	11:00	12:00	9.334	0.220	0.99	
02-Oct	12:00	13:00	10.299	0.269	0.99	
02-Oct	13:00	14:00	14.594	0.240	1.00	
02-Oct	14:00	15:00	21.013	0.509	0.99	
02-Oct	15:00	16:00	23.128	0.495	1.00	
02-Oct	16:00	17:00	13.613	0.348	0.99	
02-Oct	17:00	18:00	8.467	0.256	0.99	
02-Oct	18:00	19:00	9.499	0.185	1.00	
02-Oct	19:00	20:00	11.878	0.149	1.00	
02-Oct	20:00	21:00	9.611	0.265	0.99	
02-Oct	21:00	22:00	6.847	0.338	0.98	
02-Oct	22:00	23:00	4.190	0.275	0.96	
02-Oct	23:00	24:00	7.378	0.480	0.96	
03-Oct	00:00	01:00	3.235	0.491	0.82	CALIBRATION 00:50 - 01:02
03-Oct	01:00	02:00	4.429	0.231	0.97	
03-Oct	02:00	03:00	1.890	0.421	0.70	
03-Oct	03:00	04:00	0.524	0.369	0.29	
03-Oct	04:00	05:00	0.324	0.143	0.44	
03-Oct	05:00	06:00	1.919	0.182	0.92	
03-Oct	06:00	07:00	2.376	0.115	0.98	
03-Oct	07:00	08:00	2.159	0.163	0.94	
03-Oct	08:00	09:00	1.732	0.203	0.88	
03-Oct	09:00	10:00	3.897	0.164	0.98	CALIBRATION 09:26 - 09:34
03-Oct	10:00	11:00	4.773	0.424	0.93	
03-Oct	11:00	12:00	9.187	0.382	0.98	
03-Oct	12:00	13:00	9.620	0.971	0.91	
03-Oct	13:00	14:00	10.993	0.277	0.99	CALIBRATION 13:44 - 14:13
03-Oct	14:00	15:00				SYSTEM LEFT IN CALIBRATION
03-Oct	15:00	16:00				MODE. NO DATA 14:00-24:00
03-Oct	16:00	17:00				
03-Oct	17:00	18:00				
03-Oct	18:00	19:00				
03-Oct	19:00	20:00				
03-Oct	20:00	21:00				
03-Oct	21:00	22:00				
03-Oct	22:00	23:00				
03-Oct	23:00	24:00				

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
04-Oct	00:00	01:00	0.857	0.403	0.43	CALIBRATION LEFT ON
04-Oct	01:00	02:00	0.857	0.403	0.43	AVERAGE DATA 00:00 - 09:00
04-Oct	02:00	03:00	0.857	0.403	0.43	
04-Oct	03:00	04:00	0.857	0.403	0.43	
04-Oct	04:00	05:00	0.857	0.403	0.43	
04-Oct	05:00	06:00	0.857	0.403	0.43	
04-Oct	06:00	07:00	0.857	0.403	0.43	
04-Oct	07:00	08:00	0.857	0.403	0.43	CALIBRATION 07:51 - 08:39
04-Oct	08:00	09:00	0.857	0.403	0.43	
04-Oct	09:00	10:00	4.139	0.245	0.97	
04-Oct	10:00	11:00	15.250	0.801	0.94	
04-Oct	11:00	12:00	17.216	0.530	0.97	
04-Oct	12:00	13:00	17.768	0.661	0.99	
04-Oct	13:00	14:00	27.221	0.616	0.99	
04-Oct	14:00	15:00	28.024	0.523	1.00	
04-Oct	15:00	16:00	24.134	0.671	0.99	
04-Oct	16:00	17:00	19.045	0.426	0.99	
04-Oct	17:00	18:00	15.169	0.501	0.99	
04-Oct	18:00	19:00	12.359	0.614	0.98	
04-Oct	19:00	20:00	3.697	0.576	0.82	
04-Oct	20:00	21:00	1.014	0.482	0.42	AVERAGE VALUE 20:00 - 24:00
04-Oct	21:00	22:00	1.014	0.482	0.42	
04-Oct	22:00	23:00	1.014	0.482	0.42	CALIBRATION 22:35 -23:03
04-Oct	23:00	24:00	1.014	0.482	0.42	
05-Oct	00:00	01:00	1.161	0.181	0.75	
05-Oct	01:00	02:00	1.529	0.294	0.67	
05-Oct	02:00	03:00	2.528	0.446	0.70	
05-Oct	03:00	04:00	6.017	0.470	0.91	
05-Oct	04:00	05:00	5.034	0.321	0.94	
05-Oct	05:00	06:00	5.058	0.326	0.94	
05-Oct	06:00	07:00	5.404	0.280	0.96	
05-Oct	07:00	08:00	6.362	0.267	0.97	CALIBRATION 07:41 - 07:57
05-Oct	08:00	09:00	5.819	0.213	0.98	
05-Oct	09:00	10:00	5.585	0.213	0.98	
05-Oct	10:00	11:00	8.605	0.149	1.00	
05-Oct	11:00	12:00	15.070	0.208	1.00	
05-Oct	12:00	13:00	18.782	0.198	1.00	
05-Oct	13:00	14:00	19.168	0.499	0.99	
05-Oct	14:00	15:00	17.130	0.630	0.98	
05-Oct	15:00	16:00	12.978	0.570	0.97	
05-Oct	16:00	17:00	9.469	0.418	0.97	
05-Oct	17:00	18:00	5.376	0.302	0.95	CALIBRATION 17:23 - 17:42
05-Oct	18:00	19:00	3.082	0.131	0.97	
05-Oct	19:00	20:00	1.640	0.166	0.87	
05-Oct	20:00	21:00	0.501	0.566	0.15	
05-Oct	21:00	22:00	1.211	0.510	0.38	
05-Oct	22:00	23:00	-0.072	0.322	-0.04	CALIBRATION 22:30 - 22:43
05-Oct	23:00	24:00	0.485	0.228	0.35	

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
06-Oct	00:00	01:00	1.260	0.700	0.66	AVERAGE 00:00 - 09:00
06-Oct	01:00	02:00	1.260	0.700	0.66	
06-Oct	02:00	03:00	1.260	0.700	0.66	
06-Oct	03:00	04:00	1.260	0.700	0.66	
06-Oct	04:00	05:00	1.260	0.700	0.66	
06-Oct	05:00	06:00	1.260	0.700	0.66	
06-Oct	06:00	07:00	1.260	0.700	0.66	
06-Oct	07:00	08:00	1.260	0.700	0.66	CALIBRATION 07:44 - 08:10
06-Oct	08:00	09:00	1.260	0.700	0.66	
06-Oct	09:00	10:00	9.206	0.621	0.95	
06-Oct	10:00	11:00	6.718	0.689	0.90	
06-Oct	11:00	12:00	11.615	0.262	0.99	
06-Oct	12:00	13:00	18.300	0.477	0.99	
06-Oct	13:00	14:00	18.065	1.060	0.96	
06-Oct	14:00	15:00	21.493	1.356	0.96	
06-Oct	15:00	16:00	21.421	1.492	0.95	
06-Oct	16:00	17:00	16.684	0.507	0.99	
06-Oct	17:00	18:00	7.166	0.473	0.96	
06-Oct	18:00	19:00	11.979	0.735	0.96	CALIBRATION 18:02 - 18:23
06-Oct	19:00	20:00	5.009	0.206	0.98	
06-Oct	20:00	21:00	6.199	0.223	0.99	
06-Oct	21:00	22:00	6.448	0.379	0.96	
06-Oct	22:00	23:00	4.446	0.302	0.95	CALIBRATION 22:50 - 23:05
06-Oct	23:00	24:00	3.879	0.298	0.94	
07-Oct	00:00	01:00	4.192	0.193	0.98	
07-Oct	01:00	02:00	1.265	0.237	0.76	
07-Oct	02:00	03:00	0.517	0.276	0.38	
07-Oct	03:00	04:00	1.395	0.408	0.60	
07-Oct	04:00	05:00	1.433	0.428	0.59	
07-Oct	05:00	06:00	2.333	0.280	0.88	
07-Oct	06:00	07:00	1.319	0.182	0.84	
07-Oct	07:00	08:00	1.898	0.093	0.98	CALIBRATION 07:33 - 07:53
07-Oct	08:00	09:00	1.808	0.172	0.92	
07-Oct	09:00	10:00	4.988	0.133	0.99	
07-Oct	10:00	11:00	12.086	0.999	0.93	
07-Oct	11:00	12:00	16.576	1.224	0.95	
07-Oct	12:00	13:00	20.792	1.304	0.96	
07-Oct	13:00	14:00	17.961	0.839	0.98	
07-Oct	14:00	15:00	17.591	0.769	0.98	
07-Oct	15:00	16:00	19.392	1.136	0.97	
07-Oct	16:00	17:00	14.813	1.385	0.92	
07-Oct	17:00	18:00	7.168	0.907	0.86	
07-Oct	18:00	19:00	4.375	0.878	0.94	CALIBRATION 18:05 - 18:23
07-Oct	19:00	20:00	3.482	0.265	0.99	CALIBRATION GAS LEFT ON
07-Oct	20:00	21:00	1.719	0.437	0.98	18:23 - 22:27
07-Oct	21:00	22:00	2.859	0.376	0.99	CALIBRATION GAS SUBTRACTED
07-Oct	22:00	23:00	3.850	0.395	0.96	
07-Oct	23:00	24:00	4.351	0.344	0.94	

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
08-Oct	00:00	01:00	4.317	0.182	0.98	
08-Oct	01:00	02:00	2.680	0.167	0.96	
08-Oct	02:00	03:00	1.722	0.177	0.90	
08-Oct	03:00	04:00	1.103	0.267	0.67	
08-Oct	04:00	05:00	0.906	0.254	0.61	
08-Oct	05:00	06:00	2.397	0.222	0.92	
08-Oct	06:00	07:00	4.147	0.233	0.97	
08-Oct	07:00	08:00	4.500	0.138	0.99	CALIBRATION 07:43 - 08:10
08-Oct	08:00	09:00	3.711	0.342	0.92	
08-Oct	09:00	10:00	4.762	0.304	0.96	
08-Oct	10:00	11:00	2.382	0.412	0.78	
08-Oct	11:00	12:00	5.507	0.349	0.96	
08-Oct	12:00	13:00	9.443	0.590	0.96	
08-Oct	13:00	14:00	9.572	0.589	0.96	
08-Oct	14:00	15:00	5.220	0.741	0.84	
08-Oct	15:00	16:00	7.520	0.554	0.95	
08-Oct	16:00	17:00	8.755	0.760	0.93	
08-Oct	17:00	18:00	8.336	0.206	0.99	
08-Oct	18:00	19:00	0.935	0.407	0.45	CALIBRATION 18:11 - 18:20
08-Oct	19:00	20:00	3.030	0.198	0.96	
08-Oct	20:00	21:00	3.364	0.222	0.96	
08-Oct	21:00	22:00	2.715	0.203	0.95	
08-Oct	22:00	23:00	2.556	0.108	0.98	CALIBRATION 22:35 - 22:53
08-Oct	23:00	24:00	2.674	0.227	0.93	
09-Oct	00:00	01:00	1.883	0.112	0.97	
09-Oct	01:00	02:00	2.292	0.107	0.98	
09-Oct	02:00	03:00	2.954	0.107	0.99	
09-Oct	03:00	04:00	2.677	0.110	0.98	
09-Oct	04:00	05:00	2.239	0.091	0.98	
09-Oct	05:00	06:00	3.432	0.151	0.98	
09-Oct	06:00	07:00	3.828	0.154	0.98	
09-Oct	07:00	08:00	3.771	0.146	0.98	CALIBRATIONS AND RE-ALIGNMENT
09-Oct	08:00	09:00				07:31 - 08:43
09-Oct	09:00	10:00	7.946	0.726	0.92	
09-Oct	10:00	11:00	15.116	0.898	0.97	
09-Oct	11:00	12:00	14.710	0.809	0.97	
09-Oct	12:00	13:00	15.341	0.819	0.97	
09-Oct	13:00	14:00	16.173	0.837	0.97	
09-Oct	14:00	15:00	17.764	0.955	0.97	
09-Oct	15:00	16:00	19.448	0.919	0.98	
09-Oct	16:00	17:00	18.148	0.704	0.98	
09-Oct	17:00	18:00	16.546	0.739	0.98	
09-Oct	18:00	19:00	8.819	0.550	0.96	
09-Oct	19:00	20:00	5.036	0.299	0.97	CALIBRATIONS 19:53 - 20:33
09-Oct	20:00	21:00	4.572	0.217	0.98	
09-Oct	21:00	22:00	3.108	0.215	0.95	
09-Oct	22:00	23:00	4.859	0.304	0.96	
09-Oct	23:00	24:00	6.778	0.156	0.99	

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
10-Oct	00:00	01:00	4.832	0.272	0.97	
10-Oct	01:00	02:00	0.003	0.179	0.00	
10-Oct	02:00	03:00	6.102	0.232	0.98	
10-Oct	03:00	04:00	6.845	0.258	0.98	
10-Oct	04:00	05:00	6.586	0.334	0.97	
10-Oct	05:00	06:00	4.872	0.259	0.97	
10-Oct	06:00	07:00	5.915	0.250	0.98	
10-Oct	07:00	08:00				RE-ALIGN OPTICS
10-Oct	08:00	09:00				CALIBRATIONS 08:08 - 09:16
10-Oct	09:00	10:00	1.626	0.243	0.82	
10-Oct	10:00	11:00	9.581	0.336	0.99	
10-Oct	11:00	12:00	13.903	0.322	0.99	
10-Oct	12:00	13:00	16.501	0.504	0.99	
10-Oct	13:00	14:00	16.709	0.801	0.98	
10-Oct	14:00	15:00	16.581	0.493	0.99	
10-Oct	15:00	16:00	17.597	0.534	0.99	
10-Oct	16:00	17:00	12.332	0.298	0.98	
10-Oct	17:00	18:00	11.509	0.227	1.00	
10-Oct	18:00	19:00	11.058	0.295	0.99	
10-Oct	19:00	20:00	5.873	0.176	0.99	
10-Oct	20:00	21:00	7.030	0.230	0.99	
10-Oct	21:00	22:00	4.647	0.130	0.99	CALIBRATION 21:30 - 21:39
10-Oct	22:00	23:00	3.202	0.215	0.95	
10-Oct	23:00	24:00	2.842	0.165	0.96	
11-Oct	00:00	01:00	2.782	0.284	0.86	
11-Oct	01:00	02:00	2.967	0.275	0.88	
11-Oct	02:00	03:00	3.962	0.294	0.92	
11-Oct	03:00	04:00	2.092	0.205	0.87	
11-Oct	04:00	05:00	0.530	0.207	0.41	
11-Oct	05:00	06:00	-0.234	0.330	-0.12	
11-Oct	06:00	07:00	2.359	0.234	0.92	
11-Oct	07:00	08:00	3.611	0.279	0.95	
11-Oct	08:00	09:00	1.824	0.412	0.69	CALIBRATION 08:57 - 09:07
11-Oct	09:00	10:00	3.003	0.137	0.98	
11-Oct	10:00	11:00	4.145	0.118	0.99	
11-Oct	11:00	12:00	1.765	0.186	0.90	
11-Oct	12:00	13:00	3.437	0.111	0.99	
11-Oct	13:00	14:00	7.839	0.547	0.95	
11-Oct	14:00	15:00	8.051	0.448	0.97	
11-Oct	15:00	16:00	4.818	0.140	0.99	
11-Oct	16:00	17:00	6.610	0.477	0.95	
11-Oct	17:00	18:00	8.715	0.496	0.97	
11-Oct	18:00	19:00	6.321	0.330	0.97	CALIBRATION 18:58 - 19:09
11-Oct	19:00	20:00	2.342	0.169	0.95	
11-Oct	20:00	21:00	3.965	0.407	0.90	
11-Oct	21:00	22:00	2.017	0.242	0.87	
11-Oct	22:00	23:00	3.176	0.236	0.95	
11-Oct	23:00	24:00	2.703	0.181	0.96	

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
12-Oct	00:00	01:00	2.600	0.079	0.99	
12-Oct	01:00	02:00	-0.064	0.086	-0.16	
12-Oct	02:00	03:00	0.469	0.160	0.54	
12-Oct	03:00	04:00	0.566	0.175	0.57	
12-Oct	04:00	05:00	-0.187	0.350	-0.11	
12-Oct	05:00	06:00	-0.409	0.187	-0.43	
12-Oct	06:00	07:00	1.567	0.140	0.92	CALIBRATION 08:33 - 08:50
12-Oct	07:00	08:00	2.942	0.133	0.98	
12-Oct	08:00	09:00	1.870	0.063	0.99	
12-Oct	09:00	10:00	3.284	0.176	0.97	
12-Oct	10:00	11:00	4.386	0.079	1.00	
12-Oct	11:00	12:00	9.982	0.290	0.99	CALIBRATION 11:33 - 11:40
12-Oct	12:00	13:00	14.410	0.208	1.00	
12-Oct	13:00	14:00	11.451	0.297	0.99	
12-Oct	14:00	15:00	13.614	0.169	1.00	
12-Oct	15:00	16:00	6.362	0.151	0.99	
12-Oct	16:00	17:00	6.549	0.187	0.99	
12-Oct	17:00	18:00	3.039	0.234	0.92	
12-Oct	18:00	19:00	3.107	0.110	0.99	CALIBRATION 18:36 - 18:56
12-Oct	19:00	20:00	3.814	0.073	1.00	CLEAN INLET PLUMBING
12-Oct	20:00	21:00	3.135	0.102	0.99	CALIBRATION 20:13 - 20:24
12-Oct	21:00	22:00	3.714	0.127	0.99	
12-Oct	22:00	23:00	-0.750	0.327	-0.45	
12-Oct	23:00	24:00	-0.276	0.439	-0.14	
13-Oct	00:00	01:00	-0.135	0.122	-0.23	ETALON NOISE ON SYSTEM
13-Oct	01:00	02:00	-0.135	0.122	-0.23	AVERAGE 00:00 - 09:00
13-Oct	02:00	03:00	-0.135	0.122	-0.23	
13-Oct	03:00	04:00	-0.135	0.122	-0.23	
13-Oct	04:00	05:00	-0.135	0.122	-0.23	
13-Oct	05:00	06:00	-0.135	0.122	-0.23	
13-Oct	06:00	07:00	-0.135	0.122	-0.23	
13-Oct	07:00	08:00	-0.135	0.122	-0.23	
13-Oct	08:00	09:00	-0.135	0.122	-0.23	CALIBRATION 08:37 - 08:48
13-Oct	09:00	10:00	-0.149	0.248	-0.13	CALIBRATION 08:51 - 09:27
13-Oct	10:00	11:00	0.612	0.244	0.48	BACKGROUND EVERY 10 MIN
13-Oct	11:00	12:00	1.167	0.257	0.70	TO IMPROVE NIGHTTIME DATA
13-Oct	12:00	13:00	2.921	0.147	0.97	
13-Oct	13:00	14:00	4.533	0.267	0.96	
13-Oct	14:00	15:00	5.587	0.302	0.97	
13-Oct	15:00	16:00	8.486	0.414	0.98	
13-Oct	16:00	17:00	11.436	0.463	0.98	
13-Oct	17:00	18:00	8.807	0.407	0.98	
13-Oct	18:00	19:00	3.271	0.228	0.95	
13-Oct	19:00	20:00	0.692	0.035	0.97	
13-Oct	20:00	21:00	0.585	0.037	0.96	CALIBRATION 20:39 - 20:47
13-Oct	21:00	22:00	0.113	0.055	0.41	
13-Oct	22:00	23:00	-0.046	0.015	-0.55	
13-Oct	23:00	24:00	0.044	0.044	0.21	

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
14-Oct	00:00	01:00	0.170	0.043	0.65	
14-Oct	01:00	02:00	0.411	0.062	0.82	
14-Oct	02:00	03:00	0.386	0.048	0.87	
14-Oct	03:00	04:00	0.202	0.056	0.61	
14-Oct	04:00	05:00	0.255	0.061	0.67	
14-Oct	05:00	06:00	0.372	0.057	0.82	
14-Oct	06:00	07:00	-0.027	0.105	-0.06	
14-Oct	07:00	08:00	0.095	0.117	0.17	
14-Oct	08:00	09:00	0.355	0.111	0.57	CALIBRATION 08:33 - 08:41
14-Oct	09:00	10:00	0.410	0.184	0.43	
14-Oct	10:00	11:00	1.045	0.087	0.93	
14-Oct	11:00	12:00	1.666	0.077	0.98	
14-Oct	12:00	13:00	4.530	0.213	0.98	
14-Oct	13:00	14:00	7.317	0.129	1.00	
14-Oct	14:00	15:00	10.950	0.252	0.99	
14-Oct	15:00	16:00	15.818	0.316	1.00	
14-Oct	16:00	17:00	10.304	0.183	1.00	
14-Oct	17:00	18:00	6.119	0.245	0.98	
14-Oct	18:00	19:00	3.535	0.109	0.99	
14-Oct	19:00	20:00	1.009	0.052	0.97	CALIBRATION 19:13 - 19:23
14-Oct	20:00	21:00	0.957	0.039	0.98	
14-Oct	21:00	22:00	0.782	0.043	0.97	
14-Oct	22:00	23:00	0.917	0.029	0.99	
14-Oct	23:00	24:00	0.359	0.069	0.75	
15-Oct	00:00	01:00	0.663	0.037	0.97	
15-Oct	01:00	02:00	0.887	0.035	0.98	
15-Oct	02:00	03:00	0.682	0.071	0.90	
15-Oct	03:00	04:00	0.927	0.046	0.97	
15-Oct	04:00	05:00	1.511	0.064	0.98	
15-Oct	05:00	06:00	2.330	0.040	1.00	
15-Oct	06:00	07:00	2.285	0.049	1.00	
15-Oct	07:00	08:00	1.090	0.026	0.99	
15-Oct	08:00	09:00	1.316	0.025	1.00	CALIBRATION 08:28 - 08:38
15-Oct	09:00	10:00	1.467	0.032	0.99	
15-Oct	10:00	11:00	2.210	0.061	0.99	
15-Oct	11:00	12:00	5.216	0.043	1.00	
15-Oct	12:00	13:00	4.740	0.074	1.00	
15-Oct	13:00	14:00	5.981	0.139	0.99	
15-Oct	14:00	15:00	5.564	0.215	0.98	
15-Oct	15:00	16:00	4.184	0.190	0.98	
15-Oct	16:00	17:00	3.698	0.131	0.99	
15-Oct	17:00	18:00	4.367	0.242	0.97	
15-Oct	18:00	19:00	2.198	0.041	1.00	CALIBRATION 18:33 - 18:42
15-Oct	19:00	20:00	0.929	0.104	0.89	
15-Oct	20:00	21:00	0.741	0.067	0.92	
15-Oct	21:00	22:00	0.728	0.039	0.97	
15-Oct	22:00	23:00	0.178	0.029	0.80	
15-Oct	23:00	24:00	0.328	0.035	0.90	

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
16-Oct	00:00	01:00	0.266	0.051	0.75	
16-Oct	01:00	02:00	0.280	0.045	0.80	
16-Oct	02:00	03:00	0.319	0.053	0.79	
16-Oct	03:00	04:00	0.216	0.092	0.45	
16-Oct	04:00	05:00	0.578	0.035	0.96	
16-Oct	05:00	06:00	0.295	0.257	0.24	
16-Oct	06:00	07:00	0.275	0.037	0.85	
16-Oct	07:00	08:00	0.463	0.090	0.74	
16-Oct	08:00	09:00	0.481	0.098	0.73	CALIBRATION 08:56 - 09:04
16-Oct	09:00	10:00	0.465	0.038	0.94	
16-Oct	10:00	11:00	0.427	0.044	0.90	
16-Oct	11:00	12:00	1.244	0.068	0.97	
16-Oct	12:00	13:00	1.829	0.048	0.99	
16-Oct	13:00	14:00	2.716	0.050	1.00	
16-Oct	14:00	15:00	2.077	0.046	0.99	
16-Oct	15:00	16:00	1.352	0.071	0.97	
16-Oct	16:00	17:00	1.125	0.039	0.99	
16-Oct	17:00	18:00	1.126	0.032	0.99	
16-Oct	18:00	19:00	0.848	0.022	0.99	
16-Oct	19:00	20:00	0.874	0.041	0.98	
16-Oct	20:00	21:00	0.627	0.033	0.97	CALIBRATION 20:30 - 20:40
16-Oct	21:00	22:00	0.133	0.073	0.37	
16-Oct	22:00	23:00	0.320	0.061	0.75	
16-Oct	23:00	24:00	0.335	0.038	0.88	
17-Oct	00:00	01:00	0.202	0.049	0.66	
17-Oct	01:00	02:00	0.488	0.091	0.76	
17-Oct	02:00	03:00	0.553	0.051	0.92	
17-Oct	03:00	04:00	0.640	0.063	0.91	
17-Oct	04:00	05:00	0.332	0.082	0.66	
17-Oct	05:00	06:00	0.760	0.152	0.74	
17-Oct	06:00	07:00	0.208	0.111	0.38	
17-Oct	07:00	08:00	0.572	0.058	0.91	
17-Oct	08:00	09:00	0.642	0.100	0.81	CALIBRATION 08:46 - 08:45
17-Oct	09:00	10:00	1.428	0.060	0.98	
17-Oct	10:00	11:00	1.860	0.059	0.99	
17-Oct	11:00	12:00	3.637	0.101	0.99	
17-Oct	12:00	13:00	6.197	0.229	0.99	
17-Oct	13:00	14:00	5.329	0.137	0.99	
17-Oct	14:00	15:00	6.529	0.160	0.99	
17-Oct	15:00	16:00	5.589	0.172	0.99	
17-Oct	16:00	17:00	4.936	0.214	0.98	
17-Oct	17:00	18:00	3.902	0.119	0.99	
17-Oct	18:00	19:00	1.510	0.039	0.99	
17-Oct	19:00	20:00	1.299	0.041	0.99	
17-Oct	20:00	21:00	1.116	0.043	0.98	
17-Oct	21:00	22:00	0.981	0.034	0.99	CALIBRATION 21:25 - 21:34
17-Oct	22:00	23:00	0.298	0.083	0.61	
17-Oct	23:00	24:00	0.345	0.058	0.79	

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
18-Oct	00:00	01:00	0.352	0.026	0.95	
18-Oct	01:00	02:00	0.347	0.068	0.74	
18-Oct	02:00	03:00	0.679	0.165	0.66	
18-Oct	03:00	04:00	0.012	0.084	0.03	
18-Oct	04:00	05:00	0.820	0.099	0.87	
18-Oct	05:00	06:00	0.118	0.053	0.43	
18-Oct	06:00	07:00	0.353	0.075	0.71	
18-Oct	07:00	08:00	0.288	0.145	0.40	
18-Oct	08:00	09:00	0.447	0.104	0.68	CALIBRATIONS 08:42 - 08:53
18-Oct	09:00	10:00	0.432	0.093	0.71	
18-Oct	10:00	11:00	1.502	0.042	0.99	
18-Oct	11:00	12:00	2.580	0.047	1.00	
18-Oct	12:00	13:00	3.985	0.107	0.99	
18-Oct	13:00	14:00	4.265	0.077	1.00	
18-Oct	14:00	15:00	6.743	0.164	0.99	
18-Oct	15:00	16:00	7.144	0.242	0.99	
18-Oct	16:00	17:00	4.720	0.324	0.95	
18-Oct	17:00	18:00	3.431	0.335	0.91	
18-Oct	18:00	19:00	1.311	0.047	0.99	
18-Oct	19:00	20:00	1.005	0.039	0.98	
18-Oct	20:00	21:00	0.926	0.028	0.99	
18-Oct	21:00	22:00	1.321	0.033	0.99	CALIBRATIONS 21:25 - 21:35
18-Oct	22:00	23:00	0.902	0.068	0.94	
18-Oct	23:00	24:00	0.238	0.047	0.74	
19-Oct	00:00	01:00	0.416	0.059	0.84	
19-Oct	01:00	02:00	0.730	0.058	0.94	
19-Oct	02:00	03:00	0.266	0.053	0.74	
19-Oct	03:00	04:00	0.510	0.040	0.94	
19-Oct	04:00	05:00	0.514	0.049	0.92	
19-Oct	05:00	06:00	0.236	0.097	0.47	
19-Oct	06:00	07:00	-0.114	0.095	-0.25	
19-Oct	07:00	08:00	-0.076	0.139	-0.12	
19-Oct	08:00	09:00	-0.134	0.185	-0.16	
19-Oct	09:00	10:00	1.651	0.094	0.97	CALIBRATION 09:09 - 09:21
19-Oct	10:00	11:00	3.937	0.227	0.97	NO TEFLON FILTER IN LINE
19-Oct	11:00	12:00	7.078	0.242	0.99	SAMPLING AT VAN ROOF LEVEL
19-Oct	12:00	13:00	7.587	0.184	0.99	
19-Oct	13:00	14:00	6.374	0.050	1.00	
19-Oct	14:00	15:00	6.245	0.109	1.00	
19-Oct	15:00	16:00	6.553	0.149	0.99	
19-Oct	16:00	17:00	7.010	0.192	0.99	
19-Oct	17:00	18:00	6.158	0.145	0.99	
19-Oct	18:00	19:00	4.556	0.262	0.97	
19-Oct	19:00	20:00	2.086	0.093	0.98	
19-Oct	20:00	21:00	1.902	0.058	0.99	
19-Oct	21:00	22:00	1.561	0.045	0.99	CALIBRATION 20:59 - 21:08
19-Oct	22:00	23:00	2.551	0.057	0.99	
19-Oct	23:00	24:00	1.617	0.075	0.98	

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
20-Oct	00:00	01:00	1.347	0.069	0.97	
20-Oct	01:00	02:00	1.382	0.058	0.98	
20-Oct	02:00	03:00	0.687	0.049	0.95	
20-Oct	03:00	04:00	0.864	0.025	0.99	
20-Oct	04:00	05:00	0.909	0.039	0.98	
20-Oct	05:00	06:00	0.813	0.085	0.90	
20-Oct	06:00	07:00	1.142	0.038	0.99	
20-Oct	07:00	08:00	0.384	0.202	0.38	
20-Oct	08:00	09:00	0.822	0.090	0.89	
20-Oct	09:00	10:00	2.414	0.059	1.00	CALIBRATION 09:01 - 09:18
20-Oct	10:00	11:00	5.215	0.286	0.97	
20-Oct	11:00	12:00	7.807	0.147	1.00	
20-Oct	12:00	13:00	8.896	0.057	1.00	
20-Oct	13:00	14:00	8.795	0.173	1.00	
20-Oct	14:00	15:00	7.921	0.118	1.00	BACKGROUND 14:40 - 14:52
20-Oct	15:00	16:00	8.305	0.172	1.00	
20-Oct	16:00	17:00	9.633	0.167	1.00	
20-Oct	17:00	18:00	10.020	0.242	0.99	
20-Oct	18:00	19:00	6.309	0.377	0.96	
20-Oct	19:00	20:00	5.032	0.214	0.98	
20-Oct	20:00	21:00	3.332	0.258	0.94	
20-Oct	21:00	22:00	1.203	0.080	0.96	
20-Oct	22:00	23:00	1.466	0.099	0.95	
20-Oct	23:00	24:00	1.114	0.077	0.95	
21-Oct	00:00	01:00	1.229	0.023	1.00	
21-Oct	01:00	02:00	2.418	0.087	0.99	
21-Oct	02:00	03:00	2.576	0.067	0.99	
21-Oct	03:00	04:00	2.556	0.041	1.00	
21-Oct	04:00	05:00	1.718	0.051	0.99	
21-Oct	05:00	06:00	2.460	0.031	1.00	
21-Oct	06:00	07:00	2.366	0.037	1.00	
21-Oct	07:00	08:00	1.393	0.191	0.85	
21-Oct	08:00	09:00	0.197	0.200	0.21	
21-Oct	09:00	10:00				CALIBRATION 09:11 - 09:22
21-Oct	10:00	11:00				SYSTEM CHECKS 09:00 - 11:14
21-Oct	11:00	12:00	5.547	0.199	0.99	
21-Oct	12:00	13:00	7.804	0.053	1.00	
21-Oct	13:00	14:00	7.860	0.242	0.99	
21-Oct	14:00	15:00	8.206	0.133	1.00	
21-Oct	15:00	16:00	9.115	0.136	1.00	
21-Oct	16:00	17:00	11.470	0.312	0.99	
21-Oct	17:00	18:00	8.388	0.436	0.97	
21-Oct	18:00	19:00	8.239	0.273	0.99	
21-Oct	19:00	20:00	5.009	0.534	0.90	
21-Oct	20:00	21:00	1.750	0.116	0.96	
21-Oct	21:00	22:00	0.877	0.189	0.71	CALIBRATION 21:40 - 21:50
21-Oct	22:00	23:00	1.232	0.164	0.85	
21-Oct	23:00	24:00	2.778	0.109	0.98	

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
22-Oct	00:00	01:00	1.597	0.056	0.99	
22-Oct	01:00	02:00	1.745	0.092	0.97	
22-Oct	02:00	03:00	2.579	0.133	0.97	
22-Oct	03:00	04:00	2.425	0.080	0.99	
22-Oct	04:00	05:00	2.002	0.147	0.95	
22-Oct	05:00	06:00	2.631	0.070	0.99	
22-Oct	06:00	07:00	1.022	0.247	0.67	
22-Oct	07:00	08:00	1.343	0.088	0.96	
22-Oct	08:00	09:00	1.428	0.087	0.96	CALIBRATION 08:36 - 08:47
22-Oct	09:00	10:00	2.677	0.085	0.99	
22-Oct	10:00	11:00	6.295	0.105	1.00	
22-Oct	11:00	12:00	7.094	0.256	0.99	
22-Oct	12:00	13:00	5.668	0.174	0.99	
22-Oct	13:00	14:00	2.310	0.279	0.87	
22-Oct	14:00	15:00	3.264	0.388	0.88	
22-Oct	15:00	16:00	3.076	0.245	0.94	
22-Oct	16:00	17:00	7.025	0.395	0.97	
22-Oct	17:00	18:00	9.430	0.272	0.99	CALIBRATION 17:16 - 17:27
22-Oct	18:00	19:00	7.808	0.298	0.98	
22-Oct	19:00	20:00	6.859	0.283	0.98	
22-Oct	20:00	21:00	4.923	0.249	0.97	
22-Oct	21:00	22:00	2.589	0.104	0.98	
22-Oct	22:00	23:00	1.351	0.075	0.97	
22-Oct	23:00	24:00	0.229	0.327	0.15	
23-Oct	00:00	01:00	0.387	0.260	0.31	
23-Oct	01:00	02:00	1.038	0.092	0.93	
23-Oct	02:00	03:00	1.797	0.092	0.97	
23-Oct	03:00	04:00	1.494	0.059	0.98	
23-Oct	04:00	05:00	1.652	0.141	0.93	
23-Oct	05:00	06:00	1.466	0.038	0.99	
23-Oct	06:00	07:00	0.670	0.188	0.61	
23-Oct	07:00	08:00	1.695	0.145	0.93	CALIBRATION 07:12 - 07:23
23-Oct	08:00	09:00	2.326	0.065	0.99	
23-Oct	09:00	10:00	2.564	0.085	0.99	
23-Oct	10:00	11:00	7.052	0.292	0.98	
23-Oct	11:00	12:00	8.118	0.285	0.99	
23-Oct	12:00	13:00	9.742	0.375	0.98	
23-Oct	13:00	14:00	10.476	0.438	0.98	BACKGROUND TEST 13:14 - 13:35
23-Oct	14:00	15:00	11.737	0.419	0.99	
23-Oct	15:00	16:00	13.974	0.440	0.99	
23-Oct	16:00	17:00	13.308	0.534	0.98	
23-Oct	17:00	18:00	10.008	0.411	0.98	
23-Oct	18:00	19:00	6.847	0.275	0.98	
23-Oct	19:00	20:00	5.192	0.208	0.98	
23-Oct	20:00	21:00	3.452	0.131	0.98	
23-Oct	21:00	22:00	1.326	0.078	0.97	CALIBRATION 21:05 - 21:19
23-Oct	22:00	23:00	1.211	0.123	0.91	BACKGROUND TEST 21:19 - 21:28
23-Oct	23:00	24:00	1.072	0.073	0.95	

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
24-Oct	00:00	01:00	0.727	0.135	0.76	
24-Oct	01:00	02:00	0.395	0.183	0.42	
24-Oct	02:00	03:00	0.505	0.041	0.94	
24-Oct	03:00	04:00	0.510	0.228	0.44	
24-Oct	04:00	05:00	0.737	0.078	0.90	
24-Oct	05:00	06:00	0.231	0.209	0.23	
24-Oct	06:00	07:00	0.478	0.081	0.79	
24-Oct	07:00	08:00	0.680	0.112	0.80	
24-Oct	08:00	09:00	0.129	0.172	0.16	
24-Oct	09:00	10:00	0.346	0.159	0.43	CALIBRATION 09:01 - 09:12
24-Oct	10:00	11:00	0.510	0.119	0.68	
24-Oct	11:00	12:00	6.882	0.302	0.98	
24-Oct	12:00	13:00	14.066	0.281	1.00	
24-Oct	13:00	14:00	15.149	0.350	0.99	
24-Oct	14:00	15:00	17.103	0.409	0.99	
24-Oct	15:00	16:00	18.827	0.486	0.99	BACKGROUND 15:40 - 15:51
24-Oct	16:00	17:00	12.913	0.352	0.99	
24-Oct	17:00	18:00	7.760	0.188	0.99	
24-Oct	18:00	19:00	6.808	0.282	0.98	
24-Oct	19:00	20:00	4.839	0.182	0.99	CALIBRATION 19:35 - 19:47
24-Oct	20:00	21:00	1.226	0.049	0.98	
24-Oct	21:00	22:00	0.663	0.161	0.67	
24-Oct	22:00	23:00	0.692	0.100	0.83	
24-Oct	23:00	24:00	0.909	0.060	0.96	
25-Oct	00:00	01:00	0.551	0.073	0.85	
25-Oct	01:00	02:00	0.694	0.095	0.84	
25-Oct	02:00	03:00	0.487	0.147	0.57	
25-Oct	03:00	04:00	0.317	0.126	0.47	
25-Oct	04:00	05:00	0.015	0.127	0.03	
25-Oct	05:00	06:00	0.037	0.162	0.05	
25-Oct	06:00	07:00	-0.060	0.177	-0.07	
25-Oct	07:00	08:00	0.440	0.170	0.48	
25-Oct	08:00	09:00	-0.007	0.212	-0.01	
25-Oct	09:00	10:00	0.308	0.336	0.19	CALIBRATION 09:06 - 09:18
25-Oct	10:00	11:00	-0.066	0.690	-0.02	
25-Oct	11:00	12:00	5.531	0.342	0.96	
25-Oct	12:00	13:00	10.269	0.437	0.98	
25-Oct	13:00	14:00	13.952	0.354	0.99	
25-Oct	14:00	15:00	20.371	0.679	0.99	
25-Oct	15:00	16:00	22.164	0.858	0.98	
25-Oct	16:00	17:00	18.134	0.496	0.99	
25-Oct	17:00	18:00	12.518	0.163	1.00	
25-Oct	18:00	19:00	5.995	0.137	0.99	
25-Oct	19:00	20:00	3.253	0.100	0.99	
25-Oct	20:00	21:00	2.139	0.111	0.97	CALIBRATION 20:35 - 20:43
25-Oct	21:00	22:00	0.565	0.114	0.73	
25-Oct	22:00	23:00	0.818	0.238	0.59	
25-Oct	23:00	24:00	0.451	0.106	0.67	

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
26-Oct	00:00	01:00	0.205	0.171	0.26	
26-Oct	01:00	02:00	0.443	0.164	0.51	
26-Oct	02:00	03:00	0.758	0.131	0.79	
26-Oct	03:00	04:00	0.580	0.134	0.69	
26-Oct	04:00	05:00	0.416	0.122	0.60	
26-Oct	05:00	06:00	0.609	0.109	0.78	
26-Oct	06:00	07:00	0.373	0.068	0.77	
26-Oct	07:00	08:00	0.335	0.103	0.58	
26-Oct	08:00	09:00	0.263	0.206	0.27	CALIBRATION 08:23 - 08:42
26-Oct	09:00	10:00	0.890	0.130	0.83	CALIBRATION 08:59 - 09:09
26-Oct	10:00	11:00	8.211	0.343	0.98	
26-Oct	11:00	12:00	13.321	0.345	0.99	
26-Oct	12:00	13:00	12.799	0.224	1.00	BACKGROUND 12:47 - 13:00
26-Oct	13:00	14:00	9.465	0.409	0.98	
26-Oct	14:00	15:00	11.295	0.387	0.99	
26-Oct	15:00	16:00	10.529	0.247	0.99	
26-Oct	16:00	17:00	9.868	0.308	0.99	
26-Oct	17:00	18:00	10.397	0.292	0.99	
26-Oct	18:00	19:00	8.585	0.391	0.98	
26-Oct	19:00	20:00	8.031	0.340	0.98	
26-Oct	20:00	21:00	8.883	0.316	0.99	CALIBRATION 20:25 - 20:37
26-Oct	21:00	22:00	8.179	0.194	0.99	
26-Oct	22:00	23:00	3.583	0.192	0.97	
26-Oct	23:00	24:00	2.961	0.073	0.99	
27-Oct	00:00	01:00	4.523	0.242	0.97	
27-Oct	01:00	02:00	4.835	0.263	0.97	
27-Oct	02:00	03:00	4.638	0.136	0.99	
27-Oct	03:00	04:00	3.954	0.141	0.99	
27-Oct	04:00	05:00	4.418	0.129	0.99	
27-Oct	05:00	06:00	4.845	0.183	0.99	
27-Oct	06:00	07:00	3.740	0.153	0.98	
27-Oct	07:00	08:00	2.488	0.190	0.94	
27-Oct	08:00	09:00	4.161	0.117	0.99	
27-Oct	09:00	10:00	3.474	0.290	0.94	CALIBRATION 09:27 - 09:39
27-Oct	10:00	11:00	3.419	0.085	0.99	
27-Oct	11:00	12:00	3.004	0.161	0.97	
27-Oct	12:00	13:00	3.625	0.085	0.99	
27-Oct	13:00	14:00	4.727	0.117	0.99	
27-Oct	14:00	15:00	7.442	0.218	0.99	
27-Oct	15:00	16:00	10.090	0.424	0.98	
27-Oct	16:00	17:00	5.502	0.223	0.98	
27-Oct	17:00	18:00	1.671	0.212	0.87	
27-Oct	18:00	19:00	0.951	0.088	0.92	
27-Oct	19:00	20:00	0.900	0.139	0.82	
27-Oct	20:00	21:00	1.062	0.110	0.90	CALIBRATION 20:34 - 20:45
27-Oct	21:00	22:00	1.503	0.054	0.99	
27-Oct	22:00	23:00	0.505	0.180	0.52	
27-Oct	23:00	24:00	0.655	0.080	0.88	

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
28-Oct	00:00	01:00	1.181	0.115	0.91	
28-Oct	01:00	02:00	0.938	0.187	0.74	
28-Oct	02:00	03:00	1.047	0.126	0.88	
28-Oct	03:00	04:00	0.678	0.213	0.57	
28-Oct	04:00	05:00	1.108	0.093	0.93	
28-Oct	05:00	06:00	1.137	0.169	0.83	
28-Oct	06:00	07:00	0.471	0.203	0.45	
28-Oct	07:00	08:00	0.337	0.083	0.67	
28-Oct	08:00	09:00	0.835	0.148	0.78	
28-Oct	09:00	10:00	0.221	0.078	0.53	CALIBRATION 09:31 - 09:43
28-Oct	10:00	11:00	3.138	0.080	0.99	
28-Oct	11:00	12:00	4.232	0.170	0.98	
28-Oct	12:00	13:00	5.563	0.133	0.99	
28-Oct	13:00	14:00	7.002	0.154	1.00	
28-Oct	14:00	15:00	8.424	0.172	1.00	
28-Oct	15:00	16:00	10.756	0.294	0.99	
28-Oct	16:00	17:00	8.831	0.250	0.99	
28-Oct	17:00	18:00	6.130	0.221	0.99	
28-Oct	18:00	19:00	3.637	0.325	0.93	
28-Oct	19:00	20:00	1.965	0.076	0.98	
28-Oct	20:00	21:00	1.476	0.064	0.98	
28-Oct	21:00	22:00	1.608	0.141	0.93	CALIBRATION 21:38 - 21:52
28-Oct	22:00	23:00	1.690	0.051	0.99	
28-Oct	23:00	24:00	1.333	0.095	0.95	
29-Oct	00:00	01:00	1.257	0.060	0.98	
29-Oct	01:00	02:00	1.367	0.225	0.80	
29-Oct	02:00	03:00	0.787	0.126	0.81	
29-Oct	03:00	04:00	0.474	0.176	0.51	
29-Oct	04:00	05:00	0.106	0.115	0.20	
29-Oct	05:00	06:00	0.044	0.164	0.06	
29-Oct	06:00	07:00	0.219	0.096	0.45	
29-Oct	07:00	08:00	0.513	0.219	0.46	
29-Oct	08:00	09:00	0.554	0.076	0.85	
29-Oct	09:00	10:00	0.303	0.149	0.41	CALIBRATION 09:14 - 09:29
29-Oct	10:00	11:00	1.782	0.091	0.97	
29-Oct	11:00	12:00	3.507	0.092	0.99	
29-Oct	12:00	13:00	4.462	0.209	0.98	
29-Oct	13:00	14:00	8.019	0.247	0.99	CALIBRATION 12:56 - 13:18
29-Oct	14:00	15:00	9.128	0.328	0.99	
29-Oct	15:00	16:00	8.595	0.232	0.99	
29-Oct	16:00	17:00	8.862	0.261	0.99	
29-Oct	17:00	18:00	3.668	0.151	0.98	
29-Oct	18:00	19:00	1.363	0.148	0.90	
29-Oct	19:00	20:00	1.018	0.076	0.95	
29-Oct	20:00	21:00	1.443	0.063	0.98	
29-Oct	21:00	22:00	0.827	0.265	0.57	
29-Oct	22:00	23:00	0.966	0.242	0.67	CALIBRATION 22:15 - 22:26
29-Oct	23:00	24:00	1.277	0.108	0.94	

STUDY NAME: LA ACID PRECIPITATION INTERCOMPARISON STUDY
LOCATION: AZUSA SCAQMD AIR MONITORING STATION
INSTRUMENT: TDLAS
SPECIES: HNO3 - 1 HOUR AVERAGES
PERIOD: SEPTEMBER 30 - OCTOBER 30, 1993

DATE DD-MMM-YY	START TIME PDT	END TIME PDT	MIXING RATIO (PPBV)	95% LIMIT (PPBV)	CORR. COEFF.	COMMENTS
30-Oct	00:00	01:00	2.192	0.204	0.92	
30-Oct	01:00	02:00	0.153	0.127	0.26	
30-Oct	02:00	03:00	0.344	0.126	0.52	
30-Oct	03:00	04:00	0.544	0.138	0.66	
30-Oct	04:00	05:00	0.840	0.165	0.75	
30-Oct	05:00	06:00	-0.065	0.160	-0.09	
30-Oct	06:00	07:00	0.833	0.095	0.89	
30-Oct	07:00	08:00	0.256	0.172	0.31	
30-Oct	08:00	09:00	-0.103	0.259	-0.09	CALIBRATION 08:29 - 08:40
30-Oct	09:00	10:00	0.748	0.314	0.46	
30-Oct	10:00	11:00	2.703	0.185	0.95	
30-Oct	11:00	12:00	7.109	0.320	0.98	CALIBRATION 10:57 - 11:18
30-Oct	12:00	13:00	6.410	0.305	0.98	
30-Oct	13:00	14:00	7.705	0.406	0.97	
30-Oct	14:00	15:00	8.287	0.392	0.98	
30-Oct	15:00	16:00	10.020	0.368	0.99	
30-Oct	16:00	17:00	8.672	0.462	0.97	
30-Oct	17:00	18:00	9.585	0.428	0.98	CALIBRATION 17:48 - 17:59
30-Oct	18:00	19:00	4.998	0.437	0.93	
30-Oct	19:00	20:00	6.126	0.441	0.95	
30-Oct	20:00	21:00	6.060	0.312	0.98	
30-Oct	21:00	22:00	6.256	0.604	0.92	
30-Oct	22:00	23:00	4.201	0.199	0.98	
30-Oct	23:00	24:00	4.153	0.255	0.97	END OF STUDY

NOTES

NOTES