JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 95, NO. D7, PAGES 10,089–10,102, JUNE 20, 1990

An Intercomparison of Airborne Nitric Acid Measurements

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Results from an airborne intercomparison of techniques to measure tropospheric levels of nitric acid are discussed. The intercomparison was part of the National Aeronautics and Space Administration's Global Tropospheric Experiment and was conducted during the summer of 1986. Instruments intercompared included a denuder tube collection system (DENUDER) with chemiluminescent detection, a nylon filter collection system (FILTER) with ion chromatography detection, and a tunable diode laser (TDLAS) multipath absorption system. Intercomparison of investigators' calibration standards were also performed as part of the test protocol. While results were somewhat "soft" and data sparse, these tests suggested that the TDLAS measurements might be high compared to the other techniques. Airborne intercomparisons were conducted predominately in the free troposphere and included encounters with marine and continental air masses. While the intercomparisons included mixing ratios to 1000 parts per trillion by volume (pptv), the majority of the results were for mixing ratios of <300 pptv. The TDLAS participated in an intercomparison of NO_2 instruments (major focus) that was also conducted during the same flights. As a result the TDLAS data set is limited. Further, a significant fraction of the nitric acid measurements were below the TDLAS detection limit (75 pptv as configured for these tests). While the lack of simultaneous measurements from the three instruments limits the conclusions that can be drawn, it is clear that there can be substantial disagreement among the three techniques, even at mixing ratios above their respective detection limits. Equally clear is that at mixing ratios below 150 pptv there is very little correlation between their results. Based on these observations, an overall conclusion from the intercomparison is that none of the HNO_3 techniques can be identified to unambiguously (e.g., 20% accuracy) provide measurements of HNO_3 at levels often encountered in the free troposphere (e.g., 100 pptv). However, at the more elevated levels of HNO_3 (e.g., >150 pptv), both the FILTER and DENUDER techniques reported the same levels of nitric acid, while as suggested by the results from the standards intercomparison, the TDLAS reported higher nitric acid values than the other two techniques.

INTRODUCTION

The wet and dry deposition of nitric acid represents one of the major pathways by which odd nitrogen species are removed from the troposphere [*Levy*, 1972; *Logan et al.*, 1981; *Logan*, 1983]. Because of the detrimental impact that acid deposition has on the natural environment the formation and removal of nitric acid (as well as sulfuric acid) has been the subject of intense studies. The measurement of nitric acid is difficult because of its tendency to absorb on nearly all surfaces and its involvement in reversible vapor-to-solid reactions, which can result in a positive or negative contribution to its vapor phase concentration [*Spicer et al.*, 1982; *Anlauf et al.*, 1985, 1986; *Mulawa and Cadle*, 1985]. To date, the use of nylon filters for collection of nitric acid vapor has provided the bulk of the tropospheric measurements [e.g., *Goldan et al.*, 1983; *Parrish et al.*, 1986; *Fahey et al.*, 1986; *Galasyn et al.*, 1987]. Sampling time for this method increases with decreasing nitric acid concentration. For mixing ratios often observed in remote tropospheric environments (e.g., <100 parts per trillion by volume (pptv)), sampling times of 1–2 hours are not uncommon. At these low mixing ratios and long sampling times the absorption and phase change characteristics of nitric acid make its measurement difficult. Recently, alternative methods, the tunable diode laser and denuder, have been used for ambient nitric acid measurements [*Anlauf et al.*, 1986, 1987]. Recent attempts [*Fahey et al.*, 1986] to balance measurements of the major odd nitrogen constituents (e.g., nitric oxide, nitrogen dioxide, peroxyacetyl nitrate (PAN), and nitric acid) with a measurement of total odd nitrogen have raised questions about our understanding of tropospheric nitrogen chemistry and/or the measurement techniques for the various constituents. As part of the National Aeronautics and Space Administration's (NASA) Tropospheric Chemistry Program a field mission was conducted in August 1986 to address issues related to both the ability to measure key odd nitrogen species and the understanding of the chemistry of tropospheric odd nitrogen.

The August 1986 mission was the second to be initiated by NASA to evaluate state-of-the-art capability for measuring key tropospheric species [*McNeal et al.*, 1983; *Beck et al.*, 1987]. The evaluation was based upon intercomparison of aircraft measurements obtained in a common air mass by instruments employing different detection principles. These intercomparisons, designated as Chemical Instrumentation Test and Evaluation (CITE), were conducted as part of NASA's Global Tropospheric Experiment (GTE). The primary objective of the first CITE was the evaluation of the capability for measurements of background levels of carbon monoxide (CO), nitric oxide (NO), and the hydroxyl (OH). In particular, CITE 1 demonstrated that the capability now exists for aircraft measurements of NO in remote environ-

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Paper number 89JD03103.
0148-0227/90/89JD-03103$05.00

ments [*Hoell et al.*, 1987]. Results from CITE 2 evaluate the current capability for airborne measurements of the remaining nitrogen species postulated to have a major role in tropospheric chemistry. The overall objectives of CITE 2 were (1) to evaluate instrumentation for measuring nitrogen dioxide (NO_2), HNO_3, and PAN and (2) to determine for various tropospheric environments the relative abundances and partition among the major nitrogen species. This paper reports on the intercomparison results for HNO_3. The results for the NO_2 and PAN intercomparisons and the relative abundance, partition, and other issues related to the chemistry of tropospheric odd nitrogen are addressed in companion papers.

EXPERIMENTAL DESCRIPTION

HNO_3 Instrumentation

CITE 2 instrumentation for the nitric acid intercomparisons included a denuder tube collection system with chemiluminescent detection, a nylon filter collection system with ion chromatography detection, and a tunable diode laser multipath absorption system. Each instrument as applied during CITE 2 is briefly discussed below.

The denuder system (DENUDER) utilized a denuder tube, fabricated from a 35-cm length of 6-mm (OD) quartz tube, vacuum deposited with an interior coating of tungsten oxide (WO_3) [*Braman et al.*, 1982, 1986; *LeBel et al.*, 1985]. Nitric acid and ammonia (NH_3) in an air sample drawn through the denuder tube are chemisorbed on the WO_3 surface. After a sample has been collected, heat is applied to the denuder tube with a carrier gas (ultrazero grade air) flowing. Collected HNO_3 and NH_3 are thermally desorbed; NH_3 is desorbed as NH_3 and is recollected on an in-line WO_3 denuder tube, which serves to separate NH_3 from HNO_3. Nitric acid is desorbed as NO and is detected by chemiluminescent reaction of NO with ozone. The net integrated desorption curve is related to the HNO_3 concentration by calibration with a HNO_3 permeation tube/dilution system. During CITE 2 the DENUDER system was calibrated before each flight. The inlet system consisted of a forward-facing Teflon-lined probe mounted external (free stream) to the Electra aircraft. Air samples flowing through this Teflon-lined manifold were sampled approximately 1 m from the inlet entrance using a 6-cm length of Teflon tube attached to the denuder tube. Sample collection time was approximately 10 min followed by a 10-min analysis period. (At the higher nitric acid mixing ratios a few samples of 5-min duration were reported.) The DENUDER system was configured such that collection by a second denuder tube was initiated during the analysis phase of the first tube with the intent of providing nearly contiguous 10-min samples; however, data from only one tube were reported. The unreported measurements were stated to have a large artifact which could not be resolved during the mission and which was apparently caused by a leak in the inlet manifold of one of the samplers. The denuder tube system was stated to have a detection limit of about 20 pptv for a 10-min sample with an accuracy of 15–20% and precision of about 8%.

The nylon filter system (FILTER) [*Goldan et al.*, 1983] consisted of a serial pair of 90-mm-diameter filters. The first filter, a Teflon prefilter (Gelman Zeflour), retained aerosols while passing HNO_3 vapor; HNO_3 vapor was adsorbed on the second, nylon filter (Gelman Nylasorb). Typical collection times were of the order of 30 min to 2 hours, during which 5–20 kg of air were filtered. A carbon-vane pump was used for ground-based tests; a venturi pump attached to one of the aircraft engines was used for flight operations. The mass flow of the air sample was continuously monitored using a mass flowmeter. Analysis of each filter was generally performed within 48 hours of collection. Analyses included washing the nylon filter with a carbonate/bicarbonate buffer followed by nitrate analyses of the resulting solutions by ion chromatography. During CITE 2, calibration was based upon injection of known concentrations of nitrate in solution into the ion chromatograph. The ambient air concentration of HNO_3 was calculated from the ratio of nitrate (on the nylon filter) to the sampled air mass. The detection limit was stated to be about 8 pptv for a 15-kg sample of air (90-min sample). For most remote tropospheric sampling conditions, accuracy and precision are estimated at about 20% and 10%, respectively. However, as noted by the principal investigator, accuracy and precision are somewhat dependent upon the effects of artifacts (e.g., NO_2, ammonium nitrate aerosols, and sulfuric acid aerosols). The degree to which these artifacts affect the accuracy and precision of the technique is dependent on the composition of the air being sampled and to some extent the amount of nitric acid collected. During CITE 2, measurements were made to verify the precision of the FILTER technique. Nine sets of duplicate FILTER samples were reported, with seven at mixing ratios below 150 pptv. These seven duplicates exhibited an averaged 1σ variability of <10 pptv (or 17%). The 1σ variability in the two sets above 150 pptv was also <10 pptv (or 4%).

The tunable diode laser system (TDLAS) utilized infrared absorption in a multipass absorption cell (1.5-m length, 100 passes) through which the air sample was drawn [*Hastie et al.*, 1983; *Schiff et al.*, 1987]. The radiation source was a Pb salt semiconductor laser operated at cryogenic temperatures. The TDLAS instrument participated in both the NO_2 [*Gregory et al.*, this issue] and HNO_3 intercomparisons. For NO_2 a different Pb salt laser was required, and thus during each intercomparison flight the TDLAS system was dedicated to the detection of either NO_2 or HNO_3. The HNO_3 absorption feature employed during CITE 2 was centered at approximately 1722 cm^{-1}. The change in radiation transmitted through the cell is proportional to the concentration of HNO_3 in the cell. The air inlet was constructed of Teflon. The details of the aircraft system used for this study are described by *Schiff et al.* [this issue].

Laboratory studies with this system indicated a minimum detection limit of about 75 pptv for a 3-min sampling time. However, no laboratory tests were performed on the sampling integrity of the system or the time required to reach steady state at concentrations in the 100-pptv range. With this "caveat" the accuracy and precision of the technique were estimated to be 15% and 10%, respectively, for mixing ratios greater than 300 pptv. At lower mixing ratios the precision degrades with decreasing mixing ratio, approaching 100% at the detection limit of 75 pptv. During flight, changes in the instrument calibration were typically monitored by passing an air mixture containing approximately 1 part per million by volume (ppmv) of HNO_3 in nitrogen through a 10-cm cell placed in the optical path while ambient air scrubbed of HNO_3 by a nylon filter was passed through the White cell. The ratio of the length of the short cell to that

of the multipath length in the White cell, multiplied by the mixing ratio in the short cell, served as a secondary calibration mixing ratio. Because of the time required for the TDLAS system to reach steady state, calibration by standard addition was performed only once per flight by adding known concentrations of HNO_3 to the ambient air in the White cell. For either calibration method a permeation system was used to provide the HNO_3. The flight data were reported as 2- to 3-min averages referenced to the standard addition calibration performed once per flight.

The experimental layout of the three HNO_3 instruments, as well as other supporting instrumentation aboard the NASA aircraft, is discussed in the overview paper [*Hoell et al.*, this issue].

Data Protocol

The CITE 2 HNO_3 activities included intercomparison of calibration standards as well as ambient measurements. All measurements were conducted blind with no exchange of information between the investigator teams prior to or after submittal of their results. Final results from the standard tests were submitted to the GTE project office during the field operations, typically 48 hours after each test. Preliminary results from the airborne measurements were also submitted to the project office during the field operations. The results from the standards and field measurements were analyzed by project personnel to monitor progress of the tests and to provide guidance for subsequent tests.

The standards exchange and the flight tests were conducted as separate intercomparisons. The final results from the standards exchange were discussed jointly with the HNO_3 investigators during the field activities but after submittal of all standards data. Only a qualitative assessment of the progress of the results from the flight measurements was provided to the investigators in the field. Each investigator group elected not to modify final flight data (submitted 3 months after the field work) based on the standards results revealed while in the field.

Detailed results of the HNO_3 intercomparisons (first release of the flight results) were discussed during a data workshop convened approximately 6 months after the field mission. It is noted here that after the workshop, the DENUDER team reported that postmission analysis had indicated a nonlinearity in extrapolation of calibrations performed at low HNO_3 mixing ratios to the higher mixing ratios that were encountered during one flight. Subsequent correction of this nonlinearity resulted in a change of two mixing ratio values for this flight. The corrected mixing ratios increased by 15–20% (e.g., 570 pptv to 670 pptv and 730 pptv to 910 pptv) and are used in these analyses.

RESULTS FROM INTERCOMPARISON OF STANDARDS

The standards intercomparison was performed by having each instrument sample from the output of a portable HNO_3 reference source provided by the GTE project office. The methodology of the tests was based upon providing each instrument a constant mixing ratio of HNO_3 from a reference source with an independent assessment of the HNO_3 output from the source. This methodology inherently couples any uncertainties associated with the measurement technique and those associated with the respective calibration procedures. When differences occur, it is not possible to partition them between instrument or calibration source. However, in the absence of differences the methodology provides a strong indication of agreement between the calibration sources used by the respective instruments.

The GTE reference source utilized a HNO_3 permeation device housed in a temperature-controlled oven with a carrier gas continuously flowing through the oven followed by two stages of dilution. The carrier and dilution flow was zero air filtered through charcoal and drying filters. The output from the final dilution stage was directed into a 2.5-cm (ID) by 30-cm pyrex manifold having four 0.6-cm (ID) sampling ports along its length. Each instrument sampled from the pyrex manifold, using a Teflon tube attached to one of the ports. In each case the Teflon sample line was provided by the respective investigator. For the DENUDER and TDLAS systems this tube was that normally used between the aircraft inlet and the instrument.

At the outset of CITE 2 it was determined that it would be impractical to design a reference system to accommodate the range of sample flow rates used by the three instruments during flight. These flow rates ranged from 1 liter per minute (L/min) to more than 250 L/min. As a compromise the system was designed to deliver a maximum flow rate of 10 L/min with HNO_3 mixing ratios that could be varied from about 200 pptv to 1000 pptv. With this flow rate range the DENUDER system could sample from the reference system at the flow rate normally used to acquire a sample in-flight (1 L/min) with sufficient flow remaining to allow an independent measurement of the HNO_3 (discussed below) to be made at the same time. In order to also obtain a similar independent sample the TDLAS was required to sample at 5 L/min, half the sample flow rate normally used. The more significant deviation between flight sample flow rate and the flow rate used during the standards tests occurred for the FILTER system. Recall that the FILTER system normally operates with a sampling flow rate up to 250 L/min for 30 min to 2 hours. During the standards tests the FILTER system sampled at 5 L/min for approximately 30 hours of continuous sampling to accumulate the desired amount of HNO_3. Independent samples were also acquired during the FILTER test.

A sampling method (OSHA Test Method ID-165SG) employing silica gel collection followed by ion chromatography analysis was selected as the technique to provide the independent measurements of the HNO_3 mixing ratio from the reference source. Premission testing of the reference system was performed to characterize the output of the reference system and to define a set of operational procedures (reference system and silica gel collection) that could be used in the field. The tests included studies to define (1) the passivation time required to stabilize the system output, (2) key operational parameters controlling the stability and absolute concentration of the output, and (3) the composition of the perm tube emissions (e.g., HNO_3, H_2SO_4, and H_2O). Tests also included various matrix studies to define precision and accuracy of the permeation system/silica gel system. Results from these tests indicated that the HNO_3 reference system, properly set up and passivated, could provide HNO_3/air mixtures in the 200- to 1000-pptv range with an accuracy of 20% and a precision (stability over several hours) of better than 10%.

The standards tests were conducted in the field after

TABLE 1. Nitric Acid Standard Results

Date	Project Data		DENUDER[a]	FILTER[b]	TDLAS[a]	Ratio PI/Project
	Sample 1	Sample 2				
Aug. 7[c]						...
Aug. 20	359	375	340			0.93
Aug. 21	266	193		236		1.03
Aug. 27	no samples taken		200		none[d]	...

Measurements are in parts per trillion by volume.
[a]Tests performed aboard aircraft.
[b]Tests performed in laboratory.
[c]Invalid tests: project reference source unstable.
[d]TDLAS detected no HNO_3 at a stated detection limit for the tests of 100 pptv.

integration and checkout of each instrument aboard the aircraft. The DENUDER and TDLAS tests were performed aboard the aircraft using the flight instrumentation, while the FILTER test was performed in a laboratory with prototype hardware similar to that used in-flight. The procedures ultimately adopted for the tests involved setting up the reference system aboard the aircraft, 8–12 hours prior to the tests, with the output conditions that were planned for the actual test. For the FILTER test a similar procedure was used in the laboratory. The DENUDER and TDLAS tests were performed independently and typically conducted over a 2-hour period; the FILTER test, as already noted, required about 30 hours.

Table 1 summarizes results from the standards tests. The first took place at the Wallops Flight Facility (WFF) on August 7 prior to the start of the intercomparison flights. Results from this test were declared invalid because of the lack of stability exhibited by the project reference system. The variability was noted in both the results from the silica gel samples obtained during the test and the reported TDLAS measurements. This variability was attributed to inadequate time for the reference system equilibration after being moved from the laboratory to the aircraft. The remaining standard tests took place at Ames Research Center (ARC) on August 20, 21, and 27. These were conducted with revised procedures which allowed 8–12 hours for the reference system to equilibrate. During the tests conducted on August 20 and 21, two silica gel samples were taken. The ratio of the HNO_3 mixing ratio reported by the DENUDER and FILTER systems to the average of the silica gel results for each test is given in the last column of Table 1. As the result of logistical problems, no silica gel samples were taken during the tests conducted on August 27.

The TDLAS investigators reported that no HNO_3 was detected during their test on August 27. Immediately after completing the TDLAS test the reference system was moved, without loss of power or dilution flow, to the DENUDER location on the aircraft to initiate measurements by this system. After approximately 1 hour of equilibration the DENUDER reported a mixing ratio of 200 pptv. Even though no independent measurements (e.g., silica gel sample) of the reference source were made during the TDLAS test, the DENUDER results could be considered as a "transfer standard" for the TDLAS system. If the DENUDER results are accepted as such, then the August 27 results suggest the TDLAS detection limit was above 200 pptv or that a significant difference exists between the DENUDER and TDLAS instruments, calibration sources/procedures, or both. It is noted that during these tests, 1600 pptv of nitric acid (from the TDLAS internal standard) added to the above project's nitric acid reference was detected at the TDLAS-stated 15% uncertainty level.

The standards tests were performed in order to access the degree to which the flight results might be affected by differences associated with the various calibrations standards. It is recognized that extrapolations of the results from these tests to flight results should be done cautiously, particularly in view of the sparsity of results. With this in mind the results suggest that the calibration sources/techniques used by DENUDER and FILTER are in agreement and therefore any differences that might appear in their flight measurements cannot be attributed to calibration differences. Extrapolation of the standards results for the TDLAS is more tenuous in that the DENUDER standards must serve as a transfer standard. However, the results suggest that differences between flight results from the TDLAS and DENUDER and FILTER might be expected.

FLIGHT INTERCOMPARISONS

Aircraft Flights

All tests were conducted aboard the NASA Wallops Flight Facility (WFF) Electra aircraft. A total of 16 flights, each nominally of $5\frac{1}{2}$ hours duration, were conducted as part of the CITE 2 program. The first three flights based at the WFF were designated as "shakedown" flights, and as such no intercomparison data were requested. The remaining 13 flights, including the four ferry flights (two each way) between WFF, Virginia, and ARC, California, were intercomparison flights. As noted above, the TDLAS instrument participated in both the NO_2 and HNO_3 intercomparisons and was configured for nitric acid in only four of the 13 intercomparison flights. (As decided by the CITE 2 science team, the TDLAS measurements were focused toward the NO_2 intercomparisons. As the result of the spectroscopic nature of the TDLAS measurement it was deemed desirable to include it in the HNO_3 intercomparisons, realizing that its data would not be available for all flights and that its detection limit was about 75 pptv for nitric acid.) During two of these flights, TDLAS reported detecting no HNO_3. Nitric acid measurements were reported by the other two instruments for each of the 13 intercomparison flights. The nine flights based at ARC sampled a variety of air masses, including tropical and nontropical, maritime, and continental. Flight altitudes ranged from 150 to 5000 m above ground

TABLE 2. CITE 2 Flight Summary

Date	Flight	Type of Flight	Takeoff, GMT	Land, GMT	Altitudes, km	HNO_3 Range, pptv
Aug. 11	4	Ferry, day	1257	1714	4.8	10–560
Aug. 11	5	Ferry, day	1811	2301	4.8	70–700
Aug. 15	6	Oceanic, day	1824	2335	4.8	180–760
Aug. 19	7	Oceanic, day	1718	2238	4.8–0.15	40–200
Aug. 21	8	Oceanic, day	1721	2214	4.8	10–140
Aug. 24	9	Continental, night	0349	0847	4.8	120–380
Aug. 26*	10	Oceanic, day	1725	2230	4.8–0.15	30–140†
Aug. 28*	11	Continental, day	1728	2315	4.7–2.6	20–1370
Aug. 30	12	Oceanic, day	1723	2227	1.0–5.0	40–160
Aug. 31	13	Continental, day	1744	2253	4.8	10–220
Sept, 2	14	Continental, day	1700	2224	6.1–2.3	10–120
Sept. 5*	15	Ferry, day	1431	1911	5.2	10–160
Sept. 5*	16	Ferry, day	2040	0035	5.2	20–130†

*Denotes that TDLAS was configured for nitric acid intercomparison.
†TDLAS detected no HNO_3 (i.e., below detection limits).

level (AGL). All flights were during daylight hours except for one nighttime flight. Table 2 summarizes the flights, the study areas, flight times and altitudes, and the nominal range of HNO_3 values reported. An asterisk with the mission date indicates those flights in which the TDLAS was configured for nitric acid, and a dagger with the HNO_3 range column indicates those flights in which TDLAS reported that nitric acid was below detection. Details of the flights, type of air masses, and meteorological scenarios are discussed in detail by *Shipham et al.* [this issue].

Intercomparison Data Sets

Table 3 summarizes the intercomparison data bases that were constructed from the measurements reported. Data base 1 contains measurements reported by all three instruments; data base 2, measurements from DENUDER and FILTER; data base 3, from DENUDER and TDLAS; and data base 4, from FILTER and TDLAS. In each case the intercomparison data used in the analyses were obtained by defining a "simultaneous" measurement as one having an overlap between any two portions of the sample period reported by the investigators. For each data base the instrument with the longest integration time was used to initiate the overlapping data period, and as such only a single measurement from that instrument is used for the overlap period. Where more than one value of nitric acid was reported by any one of the remaining instruments during the overlap, the arithmetic average of those measurements was used as the intercomparison value. In a few cases, duplicate samples were provided from the FILTER instrument, and

TABLE 3. Summary of Overlapped Data Bases: Nitric Acid

		Number of Overlapped Data Periods			
Date	Flight	Data Base 1	Data Base 2	Data Base 3	Data Base 4
Aug. 11	4	NA	1	NA	NA
Aug. 11	5	NA	2	NA	NA
Aug. 15	6	NA	4	NA	NA
Aug. 19	7	NA	4	NA	NA
Aug. 21	8	NA	3 (2)	NA	NA
Aug. 24	9	NA	6	NA	NA
Aug. 26	10	none*	3	none*	none*
Aug. 28	11	8 (7)	10	13 (9)	8 (7)
Aug. 30	12	NA	4	NA	NA
Aug. 31	13	NA	4 (1)	NA	NA
Sept. 2	14	NA	2 (1)	NA	NA
Sept. 5	15	1	4 (3)	2	1
Sept. 5	16	none†	3	none†	none†
Total CITE 2 overlaps		9	50	15	9
Overlaps excluding less-than data		2	43	6	2

Data base 1 constructed by determining overlaps among all three instruments. Data base 2 constructed by determining overlaps between DENUDER and FILTER techniques. Data base 3 constructed by determining overlaps between DENUDER and TDLAS techniques. Data base 4 constructed by determining overlaps between FILTER and TDLAS techniques. NA, not appropriate as TDLAS technique was not configured for nitric acid. Numbers in parentheses are the number of overlap periods excluded from the analyses because they included data reported as less-than values.
*TDLAS detected no nitric acid at a detection limit of 200 pptv.
†TDLAS detected no nitric acid at a detection limit of 120 pptv.

these were treated as independent samples rather than averaged to a single value. Measurements reported as upper limits (referred to as less-than values) were included in the initial construction of each data base. The number of overlap periods which included less-than values is given in parentheses in Table 3. The total number of overlap periods considered in the quantitative analyses (i.e., less-than overlaps have been excluded) are also shown in the table. The less-than values in each data base are discussed only from the consideration as to whether they were consistent with the other investigators' values reported for the particular overlapping period.

Analyses Methods

Three methods of analysis were employed to evaluate the level of agreement among the measurements in data bases 2 and 3. Data bases 1 and 4, containing only two overlaps each, are discussed as special cases. The first method of analysis is based upon the numerical difference, δ, between the investigators' values for each overlap period. This approach is useful for identifying constant biases between instruments. A constant δ, for example, would suggest that the disagreement may be the result of contaminants in zero gas, instrument artifact, and/or interference effects that are independent of the HNO_3 mixing ratio. A disadvantage of the δ approach is that it does not normalize instrument agreement with respect to the HNO_3 mixing ratio at which the measurement was made.

The second method of analysis compliments the δ approach in that it considers the percentage difference (% diff) between overlapping measurements normalized to the average of the mixing ratio for the overlapping period. The % diff is evaluated as

$$\%\ \text{diff} = 100^*(X - Y)/\text{ave} \quad (1)$$

where X and Y are the HNO_3 mixing ratios reported by instruments X and Y during an overlap period and ave is the arithmetic average of the two instrument values for the overlap period.

The third analysis approach is based upon the correlation parameters obtained from an unweighted linear regression of the results from one instrument against the results from a second instrument. The parameters characterizing the linear regression line include the intercept (A), the slope (B), the correlation coefficient (r), the number of samples contained in the data set (N), and the standard deviation on A and B (σ_A and σ_B, respectively). The correlation coefficient provides a measure of the likelihood that the instruments have observed the same parameter. The intercept provides a measure of any constant bias existing between the respective data sets, and the slope provides a measure of any existing proportional bias. An advantage of the regression analysis is its statistical approach in providing an estimate of both proportional and constant bias over a range of mixing ratios. A disadvantage is its sensitivity to a few data points at the higher mixing ratios. As such, one must ensure that the regression analyses are not biased by a few high-value data points which do not reflect the majority of the data.

Using the procedures just described, data bases 2 and 3 were initially examined for the presence of measurements that might tend to bias the overall results, to identify data categories (i.e., subsets) under which intercomparison results should be stated independently, and to identify outlying events for which results are not representative of the base data. In particular, each data set was examined to evaluate the influence of (1) the degree of temporal overlap (i.e., the ratio of common sample time of any one instrument measurement to the total overlap period), (2) systematic day-to-day variability, and (3) the distribution of HNO_3 mixing ratios.

Typical Flight Data

Figures 1 and 2 illustrate HNO_3 measurements reported for two flights. The flight on August 28 (Figure 1) was specifically flown as a HNO_3 intercomparison flight with the TDLAS configured for HNO_3 and the flight path directed along the San Joaquin Valley in order to obtain higher levels of HNO_3 than had been observed during previous flights. The flight on August 24 (Figure 2), the only night flight, was flown specifically to test the NO_2 instruments including the TDLAS, and therefore only FILTER and DENUDER HNO_3 measurements were made. In each figure, measurements from the DENUDER, TDLAS, and FILTER instruments are indicated by the circles, asterisks, and squares, respectively. The length of the horizontal bar associated with each symbol corresponds to the length of the sampling period. Data without bars have sampling periods less than the length of the data symbol. Data reported as upper limits or less-than values are flagged and are plotted at half value. Note that Figure 1*b* is plotted with an expanded time and mixing ratio scale to show the measurements from 2200 hours to 2300 hours. The ordinate scale of Figure 1*a* precludes displaying these data.

DENUDER/FILTER Intercomparison Results

Data base 2 (DENUDER/FILTER) contains the largest number of overlapping measurements. Seven of the 50 overlapping periods contained less-than values reported by the DENUDER instrument. As noted earlier, these values have not been included in the quantitative analyses discussed below. Figure 3 illustrates the general characteristics of data set 2. Figure 3*a* shows the frequency distribution of the mixing ratios as a function of the average (ave) of the mixing ratios reported for each overlap period. All overlaps included only a single FILTER sample; the DENUDER value was obtained from one to seven samples with most DENUDER values calculated as the average of three to five 10-min samples obtained during the FILTER sample period. While the mixing ratios included ave values as high as 1000 pptv, most of the overlap periods (38) are for values of <300 pptv, and approximately 60% are for mixing ratios of <150 pptv. (The 1000-pptv value is not shown on Figure 3*a*.) Thus the intercomparison results should be particularly meaningful for evaluating the ability for HNO_3 measurements in clean, remote environments. The significance of the shaded portion of the histogram shown in Figure 3*a* will be discussed later. Figure 3*b* shows the distribution of the overlap time period for data base 2. The abscissa is the ratio of the common overlap time to the total overlap period encompassed by the two techniques (defined as time ratio). Time ratios are typically greater than 0.3. The effect of the temporal overlap was evaluated by analyzing two subsets of the base set—one for measurements having a time ratio of

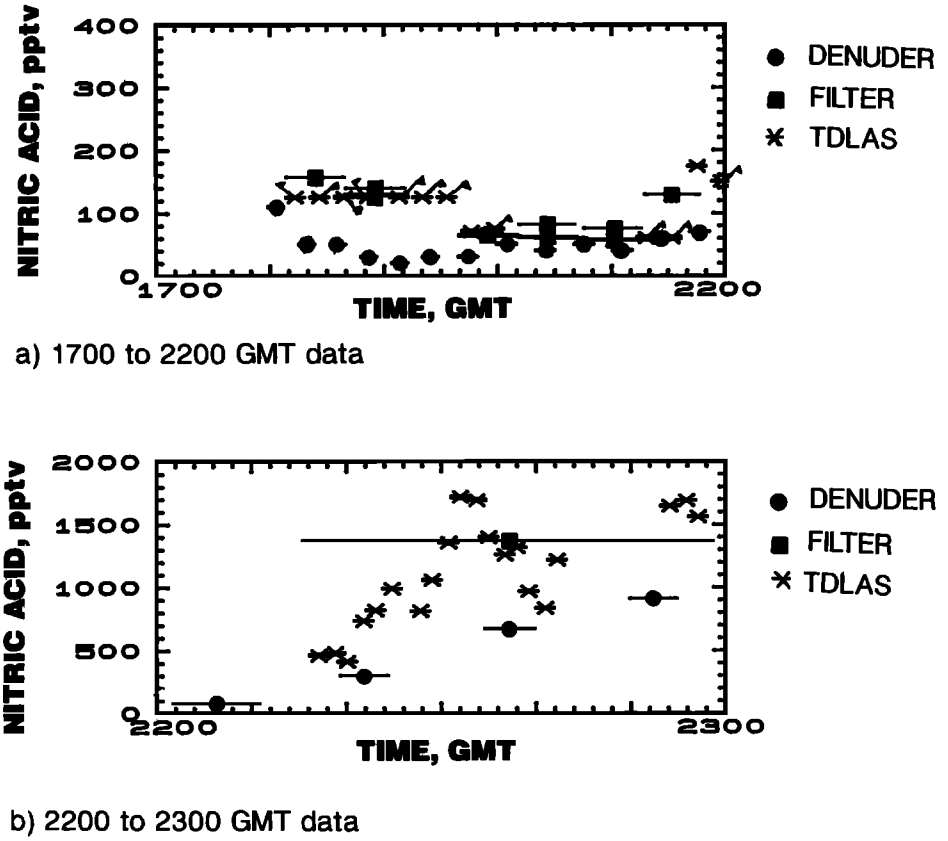


Fig. 1. Flight data of August 28, 1986.

≥0.4 and one for measurements having a time ratio of <0.4. The two subsets contained 35 and 8 samples, respectively. No significant difference existed between the analysis parameters obtained for the two subsets.

Changes in instrument performance associated with environmental factors or calibration may produce systematic day-to-day offsets between data sets. To examine the data for such effects, data sets were intercompared on a flight-to-flight basis. Figure 4 shows the comparison of the average of % diff, (FILTER−DENUDER)/ave, evaluated for each flight and that obtained from the average of the entire data set. The shaded area represents the 1σ limits obtained for the average of the % diff calculated for all 43 measurements contained in data set 2. The symbols give the averaged results for each flight with the vertical bars on each symbol representing the 1σ variation for that flight. The number of overlapping measurements for each flight is indicated by the number shown next to each symbol. Figure 4 shows a sizeable flight-to-flight variation in % diff. However, there is no obvious correlation between this variability and factors such as the variation in ambient species (e.g., NO, NO_2, PAN, CO, H_2O, and O_3), temporal overlap of the two measurements, the HNO_3 mixing ratio at which the measurements were made, or variations in test conditions such as altitude or air mass type (e.g., marine versus continental). It is always possible that such variability may be indicative of an influence from ambient variability in HNO_3 coupled with the different sampling periods used by each instrument as the time ratios for all overlaps were <0.6 (see Figure 3*b*). However, generally, the multiple denuder samples used in

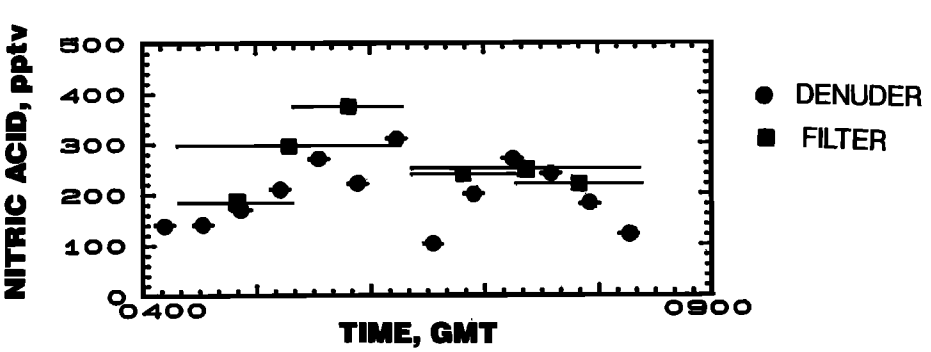


Fig. 2. Flight data of August 24, 1986.

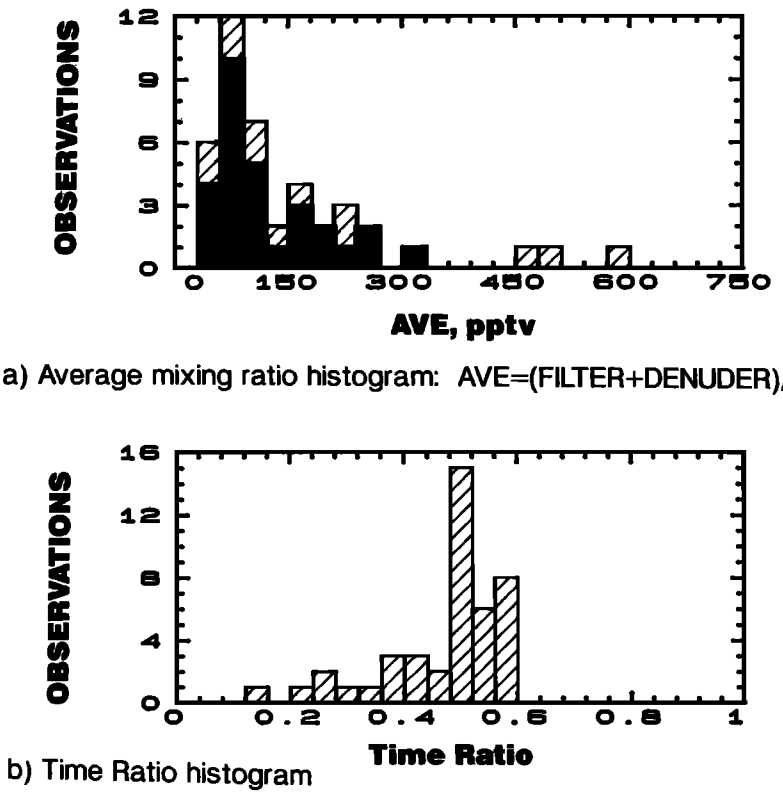


Fig. 3. Frequency histograms: DENUDER/FILTER data base 2.

arriving at an averaged DENUDER value for each overlap period would suggest that ambient variability is probably not a major factor. Note also that during the early flights (i.e., 4–8) there is a tendency for the FILTER technique to be low compared to the DENUDER with the reverse tendency for flights 9–16. Here again, this trend does not appear to be correlated with any ambient specie or test condition. In summary, there is no clear evidence to suggest a cause for any flight-to-flight bias.

Figure 5 shows the scatter diagram of DENUDER versus FILTER measurements for data base 2. Note that measurements from one overlap period (circled in Figure 5*a*) are clearly suspect. This measurement originates from the August 28 flight data shown in Figure 1*b*. The measurements

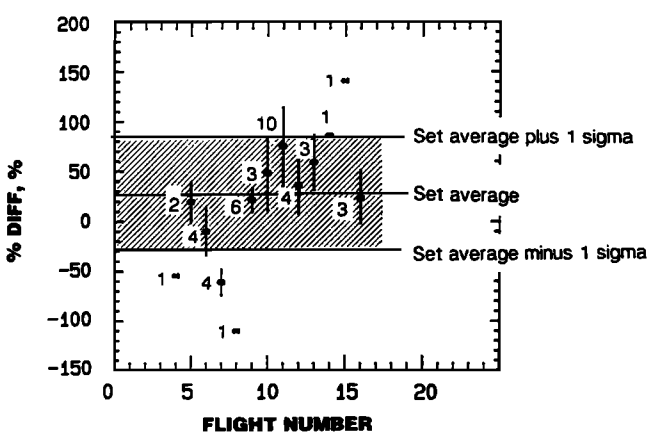


Fig. 4. Flight-by-flight comparison: DENUDER/FILTER data base 2.

reported by TDLAS for this flight suggest a high degree of variability in ambient HNO_3, which, given the difference in the sampling time between DENUDER and FILTER (time ratio is 0.35), may have contributed to the anonymously different values obtained by these two systems during this time period. Further discussion regarding measurements from this flight will be given below. At this point, however, Figure 5*a* clearly indicates that with respect to this data base the circled measurement should be considered an "outlyer" and hence is omitted from further analyses. The resulting base data set is composed of 42 samples representing mixing ratios of <600 pptv.

Figure 5 also shows the results of the linear regression analyses (solid line) of the FILTER data against the DENUDER data for the 42-sample data base (Figure 5*a*), the subset for mixing ratios of <300 pptv (Figure 5*b*), and the subset for mixing ratios of <150 pptv (Figure 5*c*). The regression slope and intercept with their respective sigmas, the corresponding correlation coefficient, and the number of samples for each case are given in Figures 5*a* and 5*b*. The slope, intercept, and sigmas are not given for the lower mixing ratio range (Figure 5*c*), since these parameters have little significance for a correlation coefficient of −0.01. For comparison the 1:1 correlation is shown as a dashed line in each panel. Within the mixing ratio ranges illustrated in Figures 5*a* and 5*b* the regression slopes (intercepts), plus or minus the respective sigmas, include 1 (0), suggesting no statistical difference between the measurements from these two instruments. Note, however, that as the range of mixing ratios is reduced the correlation between the FILTER and DENUDER measurements deteriorates, with a correlation coefficient of +0.89 for mixing ratios up to 600 pptv, 0.65 for

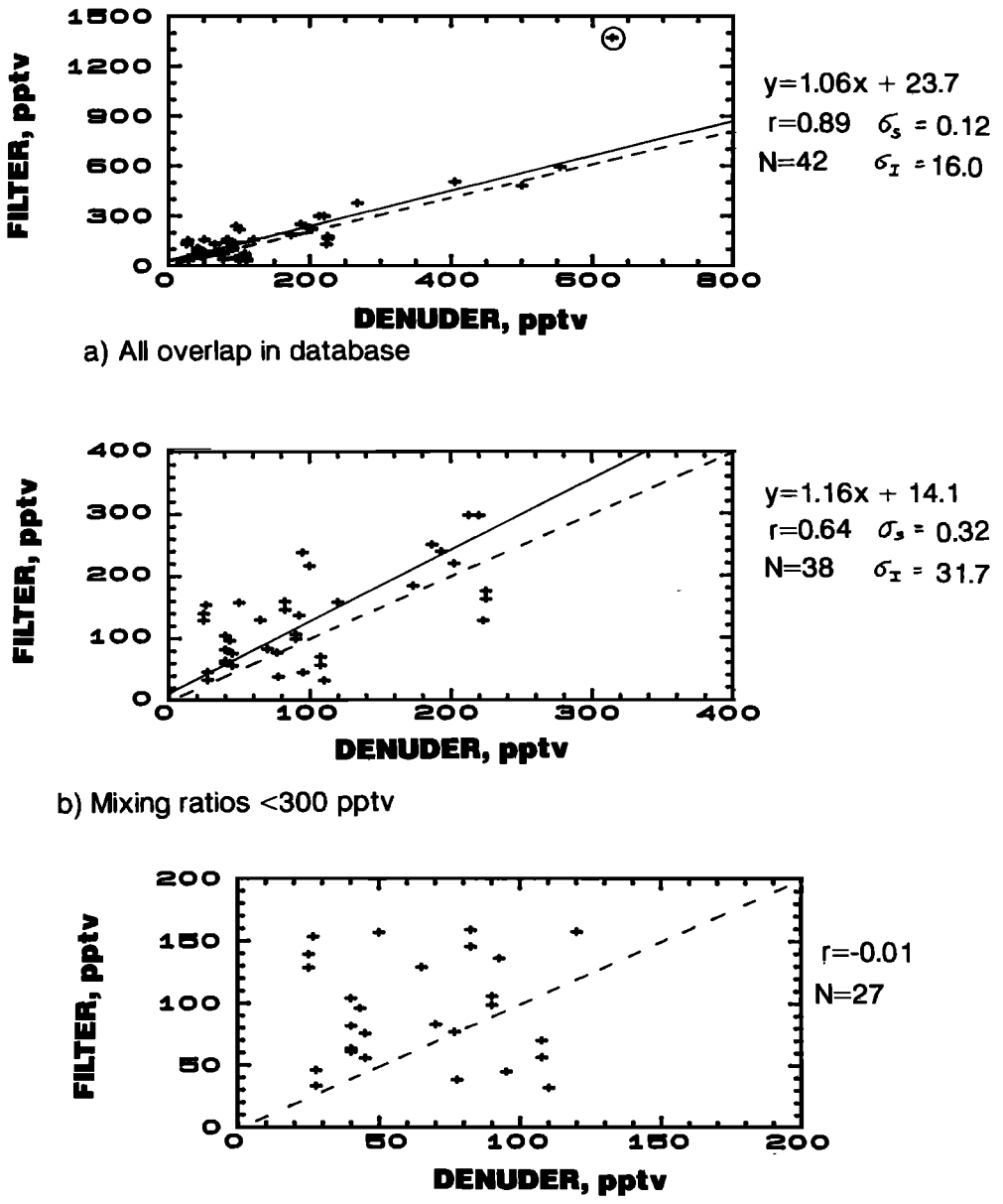


Fig. 5. Scatter plot for overlapped results for DENUDER/FILTER data base 2.

mixing ratios below 300 pptv, and −0.01 for mixing ratios below 150 pptv. While one expects a poorer correlation at the lower mixing ratios, since both techniques give detection limits in the 8- to 20-pptv range, the scatter diagram in Figure 5*c* suggests little or no correlation between these two instruments below about 150 pptv. Again this lack of correlation between the instruments could not be attributed to any ambient or test condition.

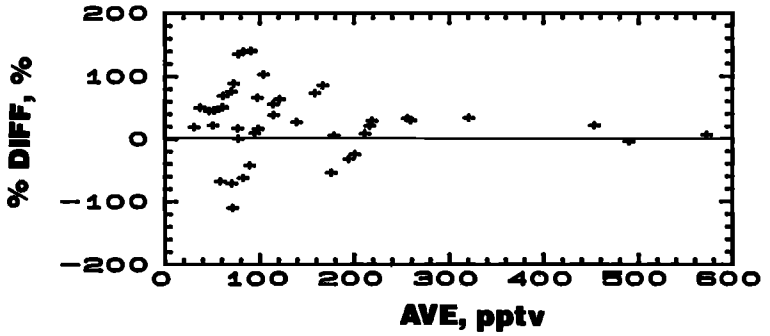
Figures 6*a* and 6*b* show the % diff and the δ between FILTER and DENUDER as a function of the average HNO_3 reported for each overlap period in data base 2. As suggested earlier by Figure 5, the % diff between FILTER and DENUDER shows sizeable variability at mixing ratios of <150 pptv. The results shown in Figure 6, while far from definitive, do suggest a tendency for a systematic offset between the instruments, the FILTER results being higher than those from the DENUDER for 75% of the overlaps of data base 2.

It is of interest to estimate the number of overlapping measurements for which the difference between the FILTER and DENUDER measurements are greater than that expected based on stated instrument uncertainties. Recall that the accuracy and precision estimated for the DENUDER and FILTER techniques are approximately 20% and 10%, respectively. If these estimates are assumed to be valid throughout the mixing ratio range reported here, an estimate of the "expected" uncertainty, E, in the difference between two measurements can be obtained from equation (2):

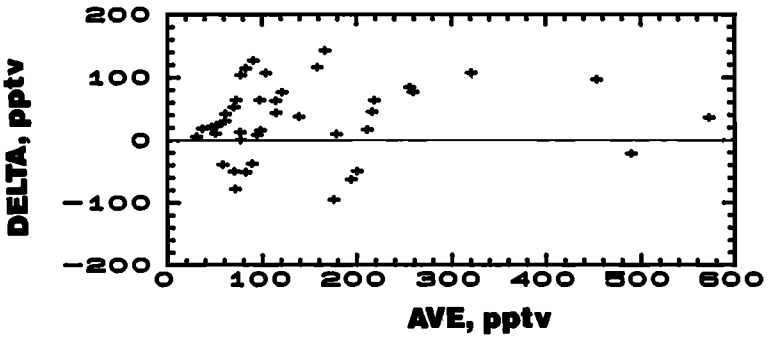
$$E = (\sigma_{F1}^2 + \sigma_{F2}^2 + \sigma_{D1}^2 + \sigma_{D2}^2)^{1/2} \quad (2)$$

where:

σ_{F1} = uncertainty associated with the FILTER measurement as the result of accuracy, i.e., 0.2 times the reported FILTER value;



a) % DIFF analyses: % DIFF=(FILTER-DENUDER)/AVE



b) DELTA analyses: DELTA=(FILTER-DENUDER)

Fig. 6. Instrument agreement for DENUDER/FILTER data base 2.

σ_{F2} = uncertainty associated with the FILTER measurement as the result of precision, i.e., 0.1 times the reported FILTER value;
σ_{D1} = uncertainty associated with the DENUDER measurement as the result of accuracy, i.e., 0.2 times the reported DENUDER value;
σ_{D2} = uncertainty associated with the DENUDER measurement as the result of precision, i.e., 0.1 times the reported DENUDER value.

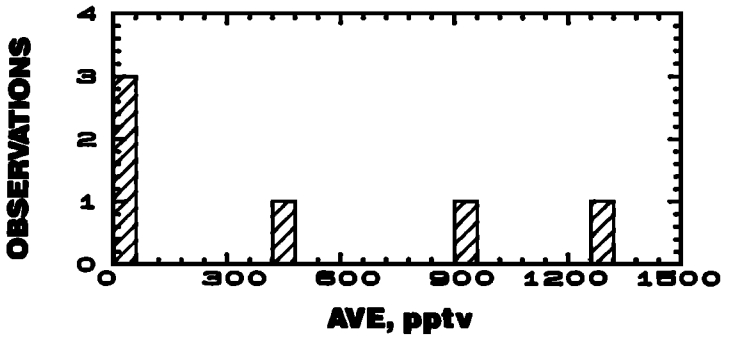
When δ (based upon measurements) is $>E$, then the difference between the two measurements is greater than expected. The shaded portion of the histogram given in Figure 3*a* illustrates the number of overlapping measurements having δ greater than E. The shaded area represents approximately 70% of the data set. It is recognized that equation (2) does not represent a rigorous statistical formulation for the expected error in the difference between these measurements. Nevertheless, it is felt that this formulation does provide a reasonable estimate and serves to illustrate that a large percentage of observations included δ values much larger than expected.

The final observations relative to data base 2 concern the relative agreement associated with the seven less-than values reported by DENUDER. For three of these the FILTER values were lower than the DENUDER less-than values and therefore can be considered to be consistent with the DENUDER values. For the other four, all at mixing ratios of <100 pptv and all for which DENUDER reported the mixing ratio to be <20 or 25 pptv, the FILTER mixing ratios were significantly higher (e.g., typically >70 pptv).

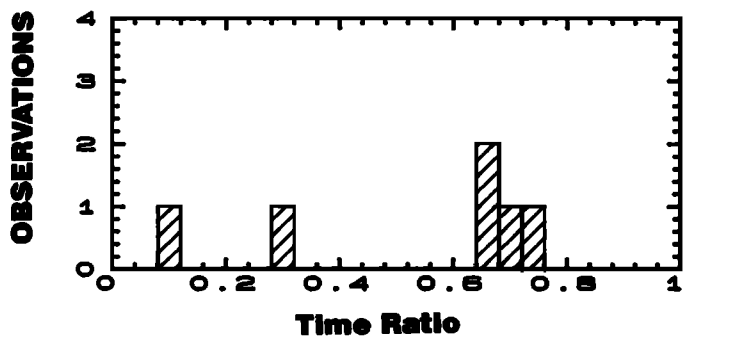
DENUDER/TDLAS Intercomparison Data Set

Data base 3 contains 15 overlap periods between TDLAS and DENUDER, of which nine have measurements reported as less-than values—seven from TDLAS and two from DENUDER. In all cases the DENUDER values were less than the upper limit implied by the TDLAS data. Excluding the less-than values, data base 3 contains six overlap periods, four of which are from the measurements shown in Figures 1*a* and 1*b*. Figures 7*a* and 7*b* illustrate general characteristics of these six overlapping measurements. Figure 7*a* illustrates the distribution of the mixing ratios showing ave mixing ratios as high as 1280 pptv. Half of the overlaps are for ave < 100 pptv. Figure 7*b* illustrates that all but two overlaps (1280 and 44 pptv) have a temporal overlap of sampling times of 60% or greater.

Figure 8 shows the scatter diagram for this data base. The solid line is the linear regression line from an unweighted fit of TDLAS data against the DENUDER data. The dashed line, shown for reference, represents a 1:1 correlation. The slope and intercept along with respective σ values and correlation coefficient are given on the figure. The correlation coefficient is almost unity, and the σ on the slope is small (0.08) relative to the slope. There is a rather large σ associated with the intercept, suggesting that the high correlation is being forced by the upper three values. These three higher mixing ratios are from overlaps constructed from the measurements of Figure 1*b* and are those data that were incorporated into the FILTER/DENUDER overlap identified as an outlyer in the previous data set. We note that in contrast to the outlyer measurement in the DENUDER/



a) Average mixing ratio histogram: AVE=(TDLAS+DENUDER)/2



b) Time Ratio histogram

Fig. 7. Frequency histograms: DENUDER/TDLAS data base 3.

FILTER data set that originated from this flight there is no evidence that the TDLAS/DENUDER data set contains similar outlyers. The high correlation between TDLAS and DENUDER suggests that possible effects associated with ambient variability (discussed with data base 2) may have been minimized by the shorter sampling periods (approximately 5 min set by DENUDER) as compared to the single and longer overlap period set by the FILTER in data base 2. The time ratio for two of these measurements is >0.6, and that for the third is >0.3. Because only six values are contained in this data set, further dissection with respect to mixing ratios was not felt to be warranted.

Figures 9*a* and 9*b* show, respectively, δ (TDLAS-DENUDER) and the % diff between the two instruments for each overlap in data base 3 as a function of the average mixing ratio. The results shown here exhibit a δ that tends to increase with HNO_3 mixing ratio and a percentage difference (at the higher mixing ratios) of about 70%. For comparison purposes a slope of 1.8 (Figure 8) at an ave of 1000 pptv translates to a % diff of 57%. The % diff at about 1000 pptv in Figure 9*b* is about 60%. Although the number of measurements at the low mixing ratios is too small to warrant a detailed analysis, the results shown in Figure 9 suggest much poorer correlation and agreement at the lower mixing ratios. A poorer correlation would be expected as stated instrument detection limits are approached (i.e., TDLAS of 75 pptv and DENUDER of 20 pptv).

The results shown in Figures 8 and 9, albeit only a few measurements, suggest a proportional bias between the TDLAS and DENUDER which could be attributed to the possible difference between calibration standards or a loss of HNO_3 in one or both sampling systems. The HNO_3 loss, if present, could be expected to be a function of the ambient level of HNO_3, as well as ambient conditions such as temperature and water vapor. This proportional bias is apparent at mixing ratios well above stated detection limits and is significant at the 2σ level as from Figure 8, the slope $\pm 2\sigma$ on the slope does not include 1. While results are somewhat scattered, even at mixing ratios that approach the stated detection limits for each instrument, the TDLAS measurements continue to be higher (or DENUDER lower). Last, it is noted that δ for all six overlaps is greater than the expected error in δ calculated from equation (2), assuming 20% and 10% accuracy and precision, respectively, for each instrument.

DENUDER/FILTER/TDLAS and FILTER/TDLAS Intercomparison Data Set

Seven of the nine overlaps for data bases 1 and 4 include less-than data reported by TDLAS during the August 28 flight (Figure 1*a*). Because of the high percentage of less-than values, quantitative analysis using the three methods described above was not performed. The remaining two measurements in each data base are from the same measurement periods, and thus observations from data base 4 are identical to those noted below for data base 1. The seven less-than values in data base 1 (all reported by TDLAS) are quantitatively in agreement with the measurements reported by both DENUDER and FILTER.

While definitive conclusions cannot be drawn from such a sparse data set, several observations are of interest, since they represent the only periods during which all three

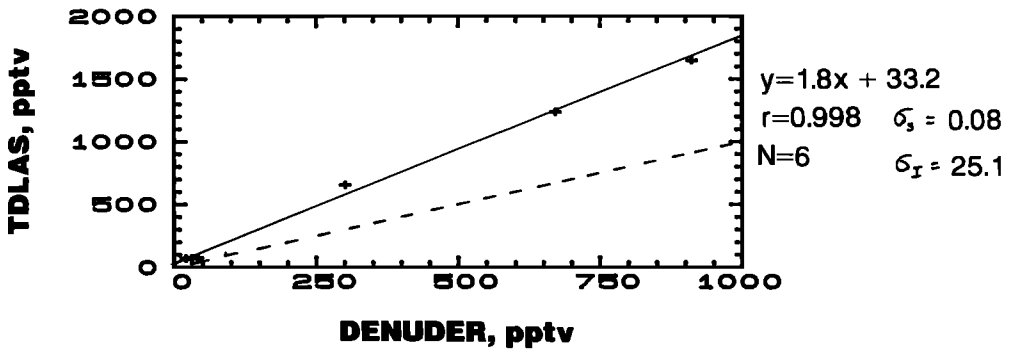


Fig. 8. Scatter plot for overlapped results for DENUDER/TDLAS data base 3.

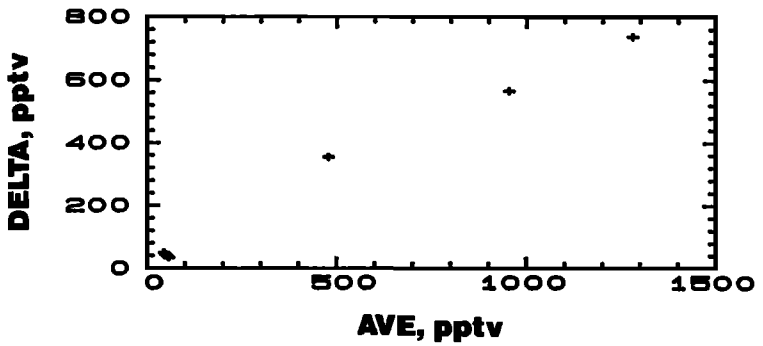
instruments reported measurements. The overlapping measurements for the two periods are given in Table 4. The uncertainty for the DENUDER and TDLAS is the larger of (1) the 1σ on the average of their individual measurements reported for the overlap period or (2) the largest uncertainty stated for an individual measurement during the overlap period. For the FILTER measurements the uncertainty is that quoted by the investigator for that particular measurement. For these two measurement periods there is a general consistency in the relative agreement among the instruments with FILTER high and DENUDER low relative to TDLAS, although FILTER and TDLAS are basically in agreement during flight 11 (Figure 1*b*). The flight 11 overlap is of particular interest. One possible interpretation of this data point is that FILTER and TDLAS agree and are about a factor of 2 higher compared to DENUDER. However, and limiting discussions to mixing ratios of >150 pptv (i.e., well above the instruments' detection limits), this flight 11 overlap is the only CITE 2 data that suggest the above conclusions. Data base 2 (DENUDER/FILTER, 15 overlaps at mixing ratios of >150 pptv) consistently showed with a high level of correlation that DENUDER and FILTER results generally agree. Data base 3 (DENUDER/TDLAS, three overlaps at mixing ratios of >150 pptv) also showed high correlation among the data and TDLAS (or DENUDER) to be high (low) relative to the other. Thus for this overlap it is noted that (1) the DENUDER/FILTER measurement from flight 11 was clearly identified as an outlyer during the discussion of the DENUDER/FILTER data base (e.g., the circled data in Figure 5*a*), (2) there was no evidence to suggest that the DENUDER/TDLAS measurements from this same period were an outlyer in the DENUDER/TDLAS data base, and (3) the TDLAS measurements from this flight and time period (Figure 1*b*) suggested significant ambient HNO_3 variability. In addition, the filter method, as an integrating technique, by definition has 100% data coverage. The temporal coverage values (time ratio) of the TDLAS and DENUDER measurements relative to FILTER during this period are 0.5 and 0.35, respectively. Given the HNO_3 variability and limited temporal coverage, any agreement during this period should be considered fortuitous. Even so, it is noted that the relative agreement between the integrating technique (FILTER) and the average mixing ratio obtained from the more discrete sampling techniques is intuitively consistent. In particular, the TDLAS average, containing more measurements ($N = 21$) with a time ratio of 0.5, is in closer agreement with FILTER than the DENUDER average with only three measurements and a time ratio of 0.35. For the flight 15 data of Table 4 the impact of ambient variability on the measurements appears to be minimal. While the mixing ratio reported by the FILTER technique is approximately a factor of 9 greater than its estimated detection limit (for the quantity of air sampled), the results from TDLAS and DENUDER are at or below their stated detection limits. Thus again, some care must be taken in interpreting the relative agreement among the three instruments.

SUMMARY

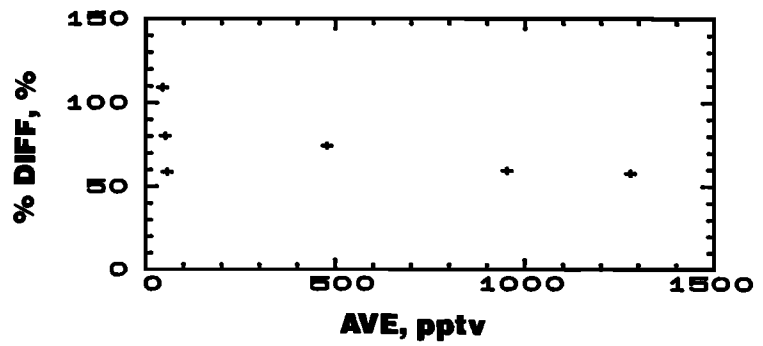
The CITE 2 activities included intercomparison of the HNO_3 calibration standards and airborne measurements from three different measurement techniques. The three techniques included a nylon filter collection (FILTER), a tungstic oxide denuder (DENUDER), and a diode laser absorption (TDLAS) system. The standards intercomparison was performed by having each instrument sample from the output of a portable HNO_3 reference source provided by the GTE project office. The conclusions from these tests, while somewhat "soft" because of the sparsity of test results, suggest that differences in flight measurements between DENUDER and FILTER should not be attributed to standards and that the TDLAS measurements might be higher than the other two.

The airborne intercomparisons were conducted predominately in the free troposphere and included encounters with marine and continental air masses. The TDLAS also participated in an intercomparison of NO_2 instruments that was conducted during the same flights. During any particular flight the TDLAS was configured to measure either HNO_3 or NO_2. Accordingly, the data base obtained for the DENUDER/FILTER overlapping measurements was significantly larger than that obtained for any combination involving the TDLAS. Further, a significant fraction of the TDLAS measurements and some of the DENUDER measurements were reported as upper limits (e.g., less-than values) on HNO_3. These less-than values were excluded from any quantitative analysis. The data base for the quantitative analyses consisted of 42 simultaneous measurements for the DENUDER/FILTER data base; six for the DENUDER/TDLAS data base; and two each for the FILTER/TDLAS and DENUDER/FILTER/TDLAS data bases.

The DENUDER/FILTER measurements presented a consistent view of the relative agreement between these two techniques. In general, the FILTER measurements were high relative to those reported by the DENUDER, although some tendency for DENUDER to be high was noted during the first few flights. At mixing ratios greater than 300 pptv the agreement was well within the accuracy and precision



a) DELTA analyses: DELTA=(TDLAS-DENUDER)



b) % DIFF analyses: % DIFF=(TDLAS-DENUDER)/AVE

Fig. 9. Instrument agreement for DENUDER/TDLAS data base 3.

stated for these two instruments. For mixing ratios below 300 pptv, linear regression analysis showed the FILTER to be high (slope of 1.16). The correlation coefficient for the analysis was to 0.64 compared to 0.89 for the data set of mixing ratios of <600 pptv. At mixing ratios of <150 pptv (27 samples) the correlation coefficient for an unweighted linear regression was −0.01, indicating no correlation between the instruments. Closer examination of the data indicates that this poor correlation not only is the result of a high number of measurements near the detection limit of the instruments (e.g., 20 pptv) but also occurs at mixing ratios of 100 pptv. Below 300 pptv the difference between simultaneous measurements was found to be greater than expected (based upon the accuracy/precision stated for each instrument) for more than 75% of the measurements.

The results from the DENUDER/TDLAS data set also exhibited a consistent view of the agreement between these two instruments. The six measurements included mixing ratios ranging from below 100 pptv to about 1280 pptv. Throughout this range the TDLAS measurements were consistently higher than those reported by the DENUDER. For average mixing ratios greater than about 300 pptv (three samples) the TDLAS results were systematically about a factor of 2 higher than the DENUDER measurements. At mixing ratios below about 100 pptv the TDLAS continued to be high relative to DENUDER but with more scatter associated with the difference. These measurements were at or very near the stated detection limits of the instruments of 20 pptv (DENUDER) and 75 pptv (TDLAS).

The DENUDER/FILTER/TDLAS data set consisted of only two simultaneous measurements. During one overlap the reported HNO_3 mixing ratios ranged from about 533 pptv to 1370 pptv. The measurements from TDLAS and FILTER were in agreement, while the DENUDER measurements were approximately a factor of 2 lower. During this period there was evidence that ambient variability could have been an influencing factor on any stated level of agreement among the instruments. The DENUDER system had only a 35% overlap (three samples) of the approximate 45-min FILTER sample. The TDLAS had substantially more measurements during this period (21 samples, 50% overlap), and accordingly, the average mixing ratio might be expected to approximate more closely the value from the FILTER technique. The mixing ratios reported for the second overlapping period in this data base ranged from about 27 pptv to 153 pptv with the FILTER measurements about a factor of 2.5 higher than TDLAS and TDLAS about a factor of 2 higher than DENUDER. We note, however, that for this last period the measurements from both the DENUDER and TDLAS were at or below their stated detection limits.

The lack of simultaneous measurements from the three instruments involved in this intercomparison has limited the conciseness of the conclusions that can be drawn. The implementation of the TDLAS technique during CITE 2 lacked the sensitivity for measurements at mixing ratios that were often encountered. It is clear, however, that there can be substantial disagreement among the three techniques, even at mixing ratios above their respective detection limits. Equally clear is that at mixing ratios below 150 pptv there is very little correlation between their results. Based on these observations, an overall conclusion from this intercomparison is that none of the HNO_3 techniques participating in

TABLE 4. Summary of Measurements in Data Base 1 (FILTER/DENUDER/TDLAS)

Flight	FILTER, pptv	DENUDER, pptv	TDLAS, pptv
11	1370 ± 69.2 (N = 1)	627.1 ± 251.3 (N = 21)	1120.5 ± 418.2 (N = 3)
15	153.4 ± 13.8 (N = 1)	26.7 ± 9.4 (N = 3)	68.0 ± 4.1 (N = 3)

CITE 2 can be identified to unambiguously provide measurements of HNO_3 at levels often encountered in the free troposphere (e.g., 100 pptv). However, at the more elevated levels of HNO_3 (e.g., >150 pptv), both the FILTER and DENUDER techniques report the same levels of nitric acid.

Acknowledgments. The authors would like to acknowledge all CITE 2 participants and express thanks for cooperation, support, and professionalism displayed throughout CITE 2. Special recognition is extended to the Wallops Electra flight and ground crews under the direction of Roger Navarro for the long hours spent in the field, preparing and flying the aircraft while at the Ames Research Center. To the hangar crew at Wallops, their support and helpful suggestions during installation of equipment and test flights at Wallops are appreciated. We also acknowledge the support and hospitality of the Ames aircraft/hangar personnel during the Ames-based portion of the field program. Last, we acknowledge the efforts of Eddie Winstead for his contributions to the premission and field operations of the project's HNO_3 reference calibration system and Robert Talbot for his analyses efforts of the project's nitric acid samples taken while at Ames.

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(Received December 6, 1988;
revised September 29, 1989;
accepted September 29, 1989.)