

Airborne tunable diode laser measurements of formaldehyde

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Abstract

Accurate measurements of formaldehyde (CH₂O) in the atmosphere are essential to further our understanding of various atmospheric cycles involving hydrogen and carbon-containing species. Comparisons among independent measurements of this gas and between measurements and model calculations have raised numerous questions regarding the veracity of both endeavors. The present paper describes a long-term effort by our group to develop and employ tunable diode laser absorption spectroscopy (TDLAS) for highly accurate measurements of this gas on both ground-based and aircraft platforms. A highly sensitive and selective TDLAS system, which has successfully flown on three different aircraft campaigns, will be described. Many new hardware and software features, which have been implemented, now make it possible to detect ambient CH₂O concentrations as low as 55 parts-per-trillion employing a 20-s integration time. This paper will also discuss the many aspects associated with high accuracy and its verification, including a brief discussion of our aircraft sampling system and inlet surface effects. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Tunable diode laser absorption spectroscopy; Accurate measurements; Formaldehyde

1. Introduction

Advances in our understanding of the earth's lower atmosphere, the troposphere, require highly sensitive and selective measurements from both ground-based and aircraft platforms. Aircraft measurements are particularly valuable in this regard; such platforms carrying a variety of instruments allow one to simultaneously measure the distributions of a large suite of photochemically related species over a wide range of horizon-

tal and vertical scales in various layers of the atmosphere. Airborne platforms, however, present rather stringent measurement challenges; not only must airborne instruments be highly sensitive and selective, but also fast, insensitive to aircraft vibrations and changing conditions of ambient pressures and temperatures, insensitive to varying cabin pressures and temperatures, and immune to variable input voltages and frequencies. Weight and size are also important aspects of aircraft instruments. Tunable diode laser systems can be designed to meet these stringent demands. The present paper gives an overview of a highly sensi-

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tive airborne system developed and employed by the National Center for Atmospheric Research (NCAR) to measure the concentrations of formaldehyde (CH_2O) during recent aircraft measurement campaigns.

Formaldehyde is the most abundant atmospheric gas-phase carbonyl compound. This long-lived intermediate is formed by the oxidation of most biogenic and anthropogenic hydrocarbons initiated by reactions with the hydroxyl (OH) radical or O_3 . Decomposition of CH_2O produces both the reactive peroxy hydrogen radical (HO_2) and CO. HO_2 radicals in conjunction with OH (collectively known as odd hydrogen radicals, HO_x) play a major role in the oxidizing capacity of the atmosphere. During twilight and low solar zenith angles, Fried et al. [1] have shown that CH_2O decomposition becomes a significant HO_x radical source in the lower atmosphere. In air masses not influenced by local pollution, CH_2O decomposition also becomes the major source of CO.

Accurate ambient measurements of CH_2O are thus important in understanding the budgets of, and the cycling among, various hydrogen, nitrogen, and carbon-containing species in the atmosphere. As many hydrocarbon reactions proceed via CH_2O as an intermediate, this gas is also important in constraining and validating current photochemical models of the troposphere. Because of its importance, a relatively large number of techniques have been developed and employed for ambient measurements of CH_2O , and numerous intercomparison studies have been carried out. The interested reader is referred to the Gilpin et al. study [2] for a very recent summary of these intercomparisons carried out on the ground. Unfortunately, the level of agreement in these campaigns has varied from quite good to quite poor. Comparison measurements carried out during the second Mauna Loa Observatory Photochemistry Experiment (MLOPEX 2) study reflect this fact. There were times when three independent techniques (tunable diode laser absorption spectroscopy; a flowing enzyme system; and a continuous scrubbing coil method) were in agreement, and times of extreme disagreement by as much as a factor of 8 [3,4].

In addition to measurement uncertainties, considerable uncertainty exists regarding CH_2O measurement-modeling comparisons in the remote troposphere. Measurements are typically lower by a factor of 2–3 [1] than those predicted by photochemical models. While there is the possibility that the measurements are systematically low, this discrepancy may also reflect model errors due to an overestimation of CH_2O sources, an underestimation of sinks, and/or the presence of additional oxidation mechanisms which do not produce CH_2O .

Because of the importance of CH_2O and the issues above, our group at NCAR has embarked upon a long term effort to develop and employ tunable diode laser absorption spectroscopy (TDLAS) for highly accurate measurements of this gas on both ground-based and aircraft platforms. A major focus of this effort is measurement accuracy and its verification. Measurement accuracy encompasses many instrumental issues such as: selectivity, calibration, instrument precision, assessment of instrumental background, and assessment of inlet surface effects. The present paper will briefly summarize laboratory and field studies dealing with these aspects. In addition, hardware and software features incorporated for high sensitivity, will also be discussed. This will be followed by a brief discussion of recent airborne measurements employing the TDLAS system.

2. Aircraft tunable diode laser system

2.1. Optical system

The basic airborne TDLAS instrument has been described previously in detail by Wert et al. [5] and by Fried et al. [6], and only a brief overview will be given here. Fig. 1 schematically shows the optical system employed. Up to four downward-emitting lead-salt diode lasers are mounted on a temperature-controlled stage within a liquid nitrogen dewar. The IR radiation emitted from one selected laser is collected by a 90° off-axis ellipsoidal mirror (OAE), refocused at the iris/chopper assembly shown, and expands onto a second 90° OAE mirror. A lifting stage in front of

the iris/chopper assembly periodically blocks the laser beam (approximately once a minute) for measurements of detector background levels to allow accurate laser power measurements. The second OAE directs the beam off an entrance flat into the center of a multipass astigmatic Herriott cell (Aerodyne Incorporated) in approximately an $f^{\#}/90$ converging cone. The IR beam, which traces out a Lissajous pattern, utilizes nearly the entire surface of both cell mirrors [7]. This attribute allows an optical pathlength of 100 m to be achieved (55 cm base path) in only a 3 l cell volume. As will be discussed, the small sampling volume is critical for using rapid background subtraction and for fast time response required for aircraft operation.

After 182 reflections, the beam becomes re-entrant and exits the Herriott cell through the same aperture as it entered only at a different angle. The exit beam is reflected off two flats and focused onto an InSb detector using an $f^{\#}/1$ BaF₂ plano-convex lens. Approximately 10% of the beam is split off by a BaF₂ window and is directed onto a second InSb detector (reference detector) through a 15 cm reference cell containing a few Torr of formaldehyde.

The sample gas is continuously drawn through the Herriott cell at a reduced pressure of 25 Torr

using flow rates around 7.5 l min^{-1} (slm, standard conditions of $P = 760 \text{ Torr}$, and $T = 273.15 \text{ K}$). The inlet sampling system will be discussed in detail in a later section.

2.2. Data acquisition

Data are acquired utilizing sweep integration coupled with second harmonic detection [8]. The diode laser is repetitively scanned across absorption features of interest using a 200 point sawtooth ramp at a frequency of 50 Hz. A 50 kHz synchronous modulation waveform, either triangle or quasi-square wave, is simultaneously applied to the laser tuning current. Both the sample and wavelength reference channels (200 data points each) are demodulated at twice this frequency (100 kHz) employing commercial lock-in amplifiers. The amplifier outputs are then digitized and co-averaged by computer. The line center of the wavelength reference, which has a very high S/N, is determined on every scan.

Each scan is appropriately shifted in memory to align the peak centers before co-averaging, a procedure that is extremely important for high instrument performance. Upon completion of each scan cycle, typically 20 s for ambient measurements (1000 scans), the wavelength reference line center

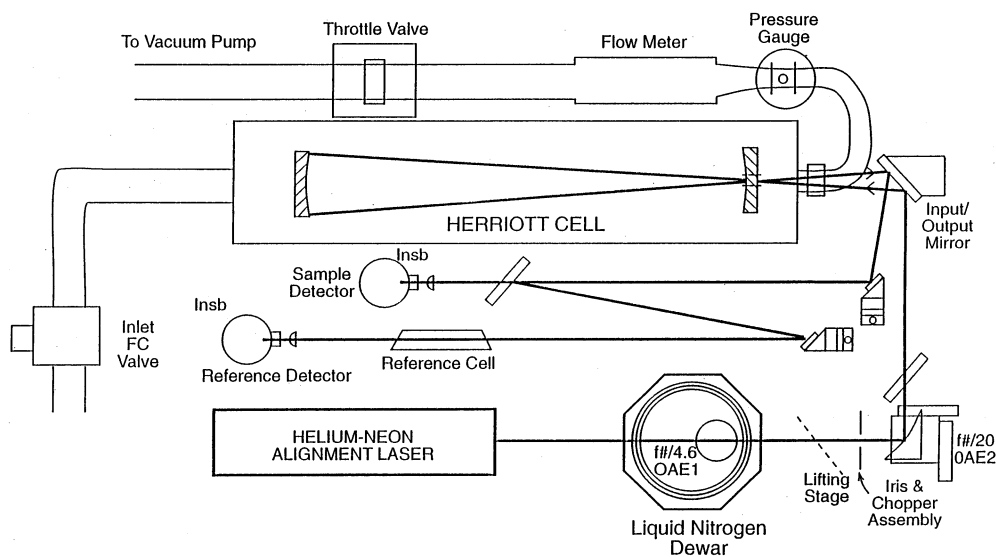


Fig. 1. Schematic of optical and sampling systems employed in the aircraft TDLAS system.

is determined using a polynomial fit, and an appropriate correction voltage is applied to the laser controller to keep the absorption feature centered in the scan window. In addition, the mean value for the amplitude of each scan is forced through zero before co-averaging. This procedure effectively removes small scan-to-scan dc variability and thus improves the co-averaging effectiveness. The co-averaged spectrum at the end of each scan cycle is then transformed into the frequency domain employing a Fast Fourier Transform algorithm, bandpass filtered, and transformed back into the time domain. This approach helps to reduce both high and low frequency noise without appreciably affecting the net results of the fitting procedure.

By far the most dramatic improvement in instrument performance has been achieved using rapid background subtraction. Fried et al. [6,9], Zahniser et al. [7], and Werle et al. [10] among others have presented the merits of this approach for TDLAS. If carried out correctly, rapid background subtraction effectively captures and removes optical noise which ultimately limits the performance of most, if not all, tunable diode laser instruments. Such noise is frequently caused by light scattering from various optical elements, and this generates a somewhat random undulating background structure. Often such structure contains multiple frequencies, amplitudes, and time constants originating from multiple scattering sources. In rapid background subtraction, background measurements are acquired before and after each ambient measurement. Typically, two 10 s background acquisition periods are acquired within approximately a 1 min time frame. Background spectra are thus acquired within a time period before the optical noise has significantly changed; repeated Allan variance measurements have shown stability periods ranging between 40 and 87 s, with the longer periods being more typical [6].

The backgrounds surrounding each 20 s ambient acquisition are averaged and subtracted point by point from the ambient. The wavelength reference arm is employed here to ensure that the line center for both backgrounds appears at the same channel number as the ambient spectrum. Here-

after, the terms background spectrum and ambient spectrum refer to data acquired and processed in the above manner. The average background is employed since in most cases it more effectively captures the true background underlying the ambient spectrum than a single background, resulting in improved replicate stability. Each background-subtracted ambient spectrum thus acquired is fit in real time to a high concentration background-subtracted calibration spectrum typically acquired every 20–30 min. Formaldehyde calibration standards in the 5–12 parts-per-billion (1 ppbv = 10^{-9} volume mixing ratio) concentration range are used for this purpose, and this will be discussed later. More comprehensive details of the Allan variance tests and the data acquisition sequence can be found in Fried et al. [6].

Fitting is achieved by a real-time multiple linear regression approach employing singular value decomposition (SVD), as described by Sewell et al. [11]. The SVD approach provides a robust means for fitting background spectra to a calibration. This procedure provides information regarding the nature of the background structure, an important aspect when employing background subtraction [5]. During background acquisition, the laser power at each of the 200 scan ramp channels is measured by recording the sample detector dc output voltage and the average value over the central 50 channels is determined. The detector 'dark' background is determined using the lifting stage shown in Fig. 1 to block the laser output. The average 'dark' value is then subtracted from the averaged laser power determination, and this yields a detector background-corrected laser power determination for every 20 s ambient determination. Slow laser power drifts are thus corrected by normalizing the 1 min block average laser power to that determined during the calibration.

The merit of rapid background subtraction can immediately be seen in Fig. 2. Here the TDLAS system repetitively sampled from a glass dilution manifold, placed at the entrance of our aircraft inlet (to be discussed), over a 1.5 h time period. In this particular case, a 3.714 ppbv mixture of CH₂O in zero air (air in which CH₂O has been removed) was continuously generated by diluting

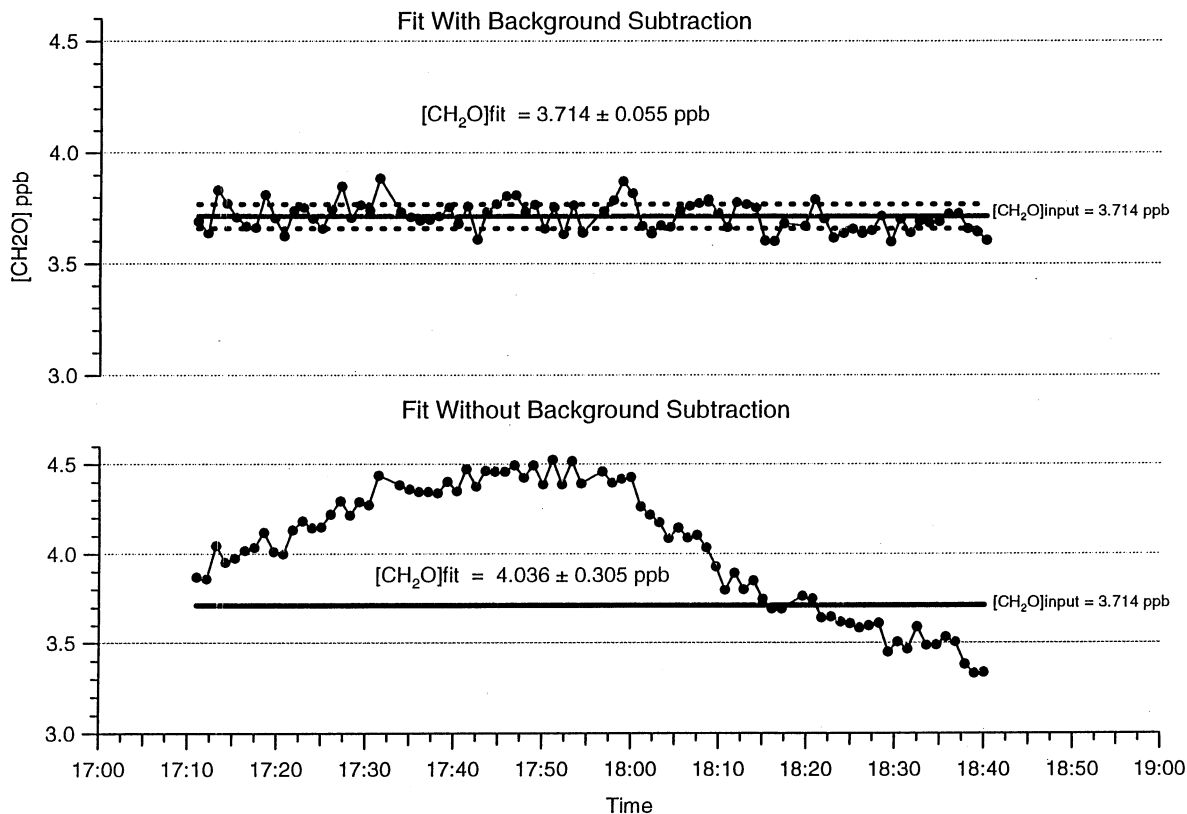


Fig. 2. (Upper panel): continuous 20 s CH₂O measurements (dark solid points) obtained by sampling a constant 3.714 ppb CH₂O in zero air mixture (dark solid horizontal line) at the entrance of our aircraft inlet system. Rapid background subtraction was employed, and the average fit concentration exactly matches the input concentration. The upper and lower dotted horizontal lines denote the $\pm 1\sigma$ levels about the mean and indicate a replicate precision of 0.055 ppbv; (Lower panel): fits of the same data set without employing rapid background subtraction. Not only is the average fit concentration (4.036 ppbv) significantly higher than the input concentration (3.714 ppbv given by the dark horizontal line), but the replicate precision (0.305 ppbv) is a factor of 5.5 worse than the upper panel.

the output of a permeation calibration system with zero air in the glass manifold. The input concentration, which falls within the typical range of CH₂O levels found in the urban troposphere, is shown in both panels of Fig. 2 by the dark solid horizontal line. The results of averaging for 20 s (which takes ≈ 60 s overall when backgrounds, cell flushing, and fitting times are included) are displayed in both figure panels by the solid points. In the upper panel, rapid background subtraction was employed, and the average fit concentration exactly matches the input concentration. Such agreement, which has been achieved in numerous time series measurements from 0.2 to 5 ppbv, demonstrates the accuracy of the fitting and back-

ground subtraction procedures employed here. The upper and lower dotted horizontal lines denote the $\pm 1\sigma$ levels of the mean, and indicate a replication precision (σ_r) of 0.055 ppbv employing rapid background subtraction. A cell pressure of 40 Torr and a quasi-square-wave modulation waveform were used in this acquisition.

The lower panel of Fig. 2, by contrast, displays the results of fitting the same data set without background subtraction. Not only is the average fit concentration significantly higher than the input concentration ($\Delta = 0.322$ ppbv), but the replication precision (0.305 ppbv) is a factor of 5.5 worse than the upper panel. In this particular case, a slow systematic drift in the background

spectra produces a drift in the retrieved values. Numerous other examples demonstrate similar improvements in precision by factors of 3–4 when rapid background subtraction is implemented.

Fig. 3, displays a representative ambient CH_2O spectrum (0.52 ppbv) acquired during an aircraft field study in 1997. The dark solid profile shows the results of fitting a 20 s ambient spectrum, with the average background subtracted, to an 11 ppbv calibration standard. Fits of the backgrounds bracketing this ambient spectrum are also shown. The background-subtracted ambient spectrum illustrates the effectiveness of removing background curvature. In this particular case, the background structure between channels 80 and 130 is very similar in shape to the ambient spec-

trum. As will be further discussed, this is caused by CH_2O outgassing from the walls of our inlet and/or sampling cell.

2.3. CH_2O absorption feature and measurement selectivity

In all cases we employed a CH_2O absorption feature at 2831.6417 cm^{-1} . The 1992 HITRAN data base [12] lists an integrated absorption cross section of $4.90 \times 10^{-20}\text{ cm}^2\text{ cm}^{-1}\text{ molecule}^{-1}$ for this line at a temperature of 30°C . However, new intensity measurements by Sams indicate that the cross sections for all CH_2O lines in the $2800\text{--}2900\text{ cm}^{-1}$ region need to be increased by an average of 11% [13]. The cross section for the CH_2O line

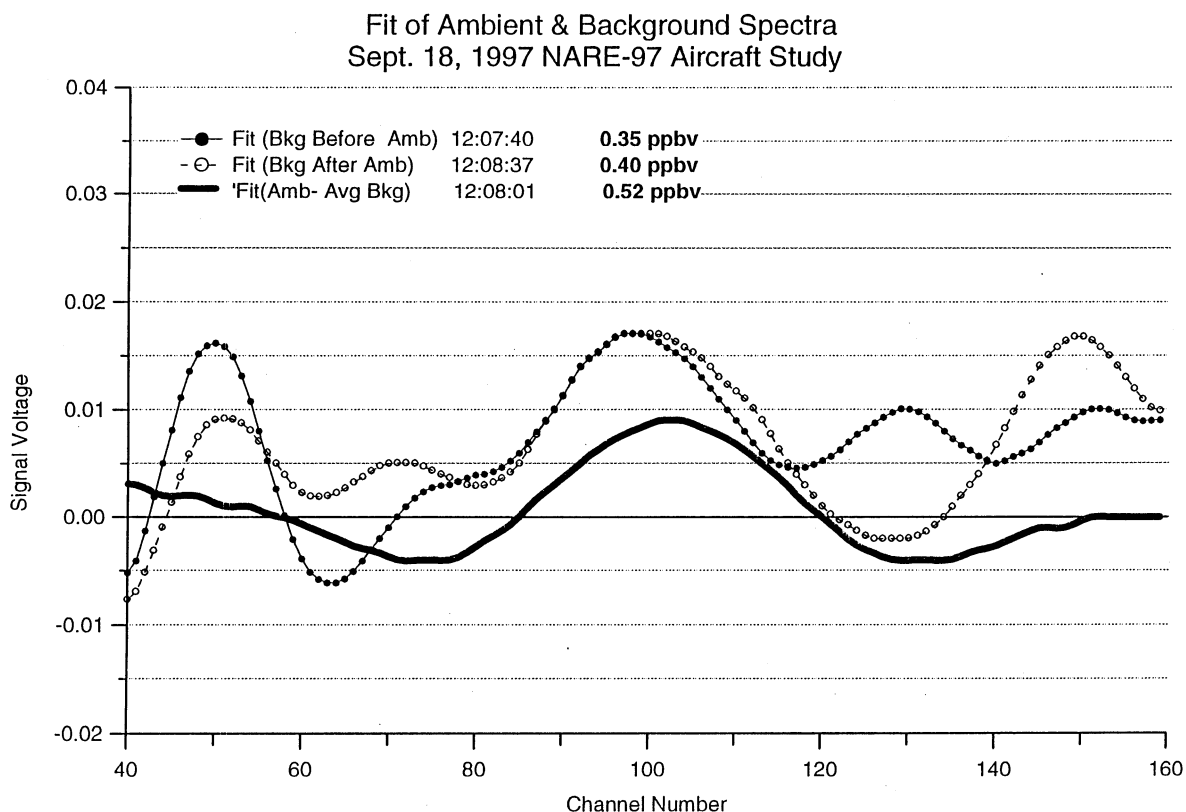


Fig. 3. Representative ambient CH_2O spectrum (20 s average) acquired during our latest aircraft study. The dark solid profile denotes the result of fitting the ambient spectrum to a 11 ppbv calibration spectrum. The background spectra before and after this ambient were first averaged and subtracted point-by-point from the ambient before fitting. Fits of both background spectra (10 s averages) are also shown.

employed in this study has thus been corrected by 11%.

As discussed by Fried et al. [9], the above CH_2O feature is clear of any known interferences. The nearest absorption line listed in the 1992 HITRAN data base [12] is 0.057 cm^{-1} higher in frequency and is due to CH_2O . The nearest interfering line is from O_3 and is 0.0787 cm^{-1} lower in frequency and over five orders of magnitude weaker in strength. The nearest H_2O line, which is 0.1993 cm^{-1} away, has an absorption cross section of $2.93 \times 10^{-24}\text{ cm}^2\text{ cm}^{-1}\text{ molecule}^{-1}$. In the direct absorption mode, high ambient H_2O concentrations of 2% would cause significant background curvature in detecting ambient CH_2O levels as low as 100 parts-per-trillion (1 pptv = 10^{-12} volume mixing ratio) using the above CH_2O line. However, employing second harmonic detection using pressures of 25 Torr completely eliminates such curvature and any consequent errors in quantifying CH_2O . Our latest measurements now use sampling pressures around 40 Torr to increase the sensitivity for a given input mixing ratio. This, however, increases the pressure-broadened linewidths for both the CH_2O and H_2O features. Since this necessitates the use of a larger modulation amplitude to capture the broader CH_2O absorption feature, there exists the possibility that the broader H_2O line may now interfere with the quantification of CH_2O . Calculations using the above mixing ratios indicate a small residual background curvature and a positive 6% error due to H_2O . However, since our present background subtraction approach maintains a relatively constant H_2O mixing ratio between ambient and background acquisition modes [14], the effects of H_2O at 40 Torr become negligible. Interference tests with other molecules like acetaldehyde and methanol, two organic molecules that exhibit broad structureless features in this region [15], indicate no response under second harmonic conditions. These features do not exhibit sharp changes in absorption coefficient with wavelength, which is a requisite for second harmonic detection. This situation is most likely the case with other larger organic molecules as well.

2.4. Minimal detectable absorbance

Employing a sampling pressure of 25 Torr, a temperature of 303 K, a 100 m pathlength (sampling conditions used in our field measurements to date), the above corrected integrated absorption cross section of $5.44 \times 10^{-20}\text{ cm}^2\text{ cm}^{-1}\text{ molecule}^{-1}$, and an air-broadening coefficient of $0.1067\text{ cm}^{-1}\text{ atm}^{-1}$, one calculates using a Voigt function that a line center absorbance of 1×10^{-6} corresponds to an ambient CH_2O mixing ratio of 35 pptv. In the case of our latest measurements using a sampling pressure around 40 Torr, an absorbance of 1×10^{-6} corresponds to a CH_2O mixing ratio of 30 pptv.

Thus the replicate precision shown in the top panel of Fig. 2 ($1\sigma = 55\text{ pptv}$) corresponds to a minimum detectable absorbance (MDA) of 1.8×10^{-6} for a 20 s integration time. This precision is very typical of what we routinely achieve in the laboratory; numerous lab-based measurements by Fried et al. [6] consistently yield NIDA values around 2.2×10^{-6} employing CH_2O standards in the range between 0 and 3.7 ppbv. Our best measurements yield MDA values around 1.3×10^{-6} . Aircraft measurements, although reasonably good, typically yield MDA values between 2.3 and 2.9×10^{-6} (81–103 pptv), and an upper limit around 4×10^{-6} (141 pptv).

The recent laboratory-based measurements are not prone to the sources of imprecision that have plagued our airborne measurements, the most important of which is precise temperature control of the entire optical system. Our laboratory measurements are now being carried out in a stable temperature environment with all cell and optical bench temperature controls shut off. These controls, which are being carefully re-engineered, were found to exacerbate the very instabilities they were designed to eliminate in the field. The stable laboratory environment has also reduced the magnitude and frequency with which laser correction voltages need to be applied. In the field, dramatic changes in aircraft cabin temperature necessitated rather frequent laser wavelength correction to keep the CH_2O absorption feature in the center of our scan window. Unfortunately, these corrections were applied too abruptly and

too frequently, resulting in subtle differences between each background and ambient [6]. In future field measurements, we plan to implement better temperature control of the laser controller and/or an improved strategy for laser wavelength correction.

Finally, we now actively couple high frequency low-amplitude vibrations, which are asynchronous with our 50 Hz data acquisition frequency, directly into our optical system to help in further suppressing optical noise. Aircraft engine-vibrations, which accomplish the same end, are not as robust since they vary too much in amplitude over the course of a flight. We hope to have these corrective measures in place for our next aircraft campaign.

2.5. Measurement calibration

All the CH₂O measurements presented herein utilized flowing gas-phase standards, in the 0.2–12 ppbv mixing ratio range, based upon permeation devices or a Henry's Law calibration system. The former used gravimetry as the absolute method of calibration while the latter employed the temperature-dependent Henry's Law coefficients together with a knowledge of the solution concentration, and measurements of flow and pressure. The two absolute calibration sources have been intercompared with one another and with direct absorption spectroscopy. In addition, two different cartridge-sampling techniques were used to further corroborate the calibration standards. Specific details of these various approaches and their interrelationships can be found in Fried et al. [9] and Gilpin et al. [2]. The four independent techniques result in equivalent CH₂O calibration concentrations within a $\pm 6\%$ range.

2.6. Inlet sampling system

Because inlet surface effects may significantly influence measurement accuracy, particularly when carrying out aircraft measurements of reactive and soluble gases like CH₂O, a great deal of effort has been expended on two fronts. First, we have designed and employed an inlet system for our recent aircraft measurements in 1997 that

attempts to minimize surface effects. Secondly, we have embarked on a series of extensive laboratory studies to characterize inlet behavior under a variety of ambient conditions of temperature, relative humidity, and pressure.

As discussed by Wert et al. [5], it is essential to understand the nature of the background structure when one employs rapid background subtraction. In the ideal case, the analyte gas under study is completely removed before each background acquisition begins. When fit to an appropriate calibration spectrum, such backgrounds will display a random fit characteristic of random optical noise. Under these circumstances one would obtain no correlation between the retrieved background values and the ambient levels of the analyte gas under study. In the case of non-reactive gases such as CO, this is typically the case. Even for reactive and soluble gases like CH₂O we often observe complete removal of the analyte gas during background acquisition when sampling relatively dry air. However, as soon as humidified air is sampled, background CH₂O measurements carried out on the ground and during our early aircraft studies in 1996 clearly show the presence of sample line outgassing [5].

If the time constant for such outgassing is long compared to the sample-background switching time (≈ 30 s), then any outgassing would in all likelihood contribute equally during the sample and background acquisition periods and cancel out. Wert et al. [5] present convincing evidence for such behavior during ground-based TDLAS measurements of CH₂O. Preliminary laboratory studies also confirm this; measurements where the inlet was unheated, purposely exposed to CH₂O concentrations in excess of 1 ppbv and high relative humidities of 85%, clearly indicated the presence of CH₂O outgassing during the background acquisition phase. These measurements, however, indicated a fairly long outgassing time constant of at least 30 min, and the retrieved CH₂O concentrations matched the input values to within the measurement precision. Thus the measurement accuracy is preserved. However, it is important to note that when background acquisition was turned off, the retrieved values were systematically high by the amount of the background out-

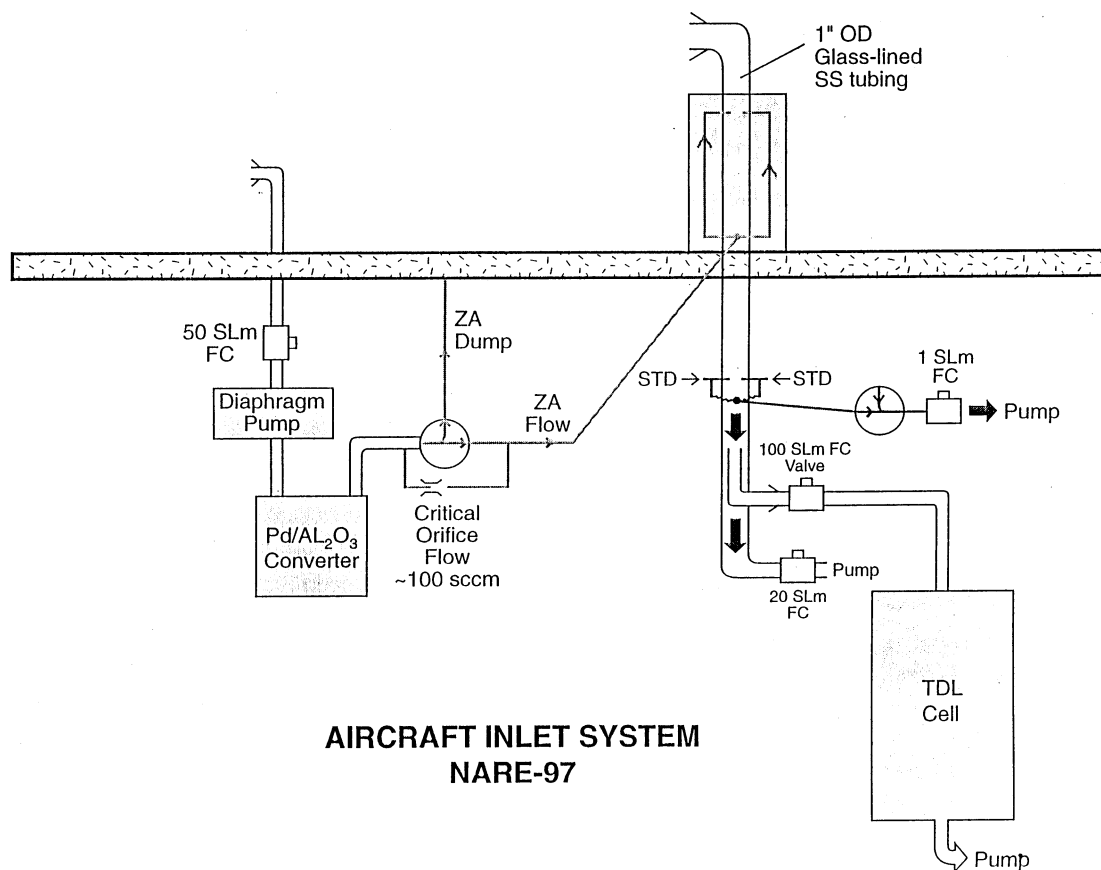


Fig. 4. Schematic of aircraft inlet system employed during the most recent measurements for the NARE 1997 studies.

gassing, 0.7–0.8 ppbv in this case. Although these laboratory studies are in the formative stages, it is becoming clearer that rapid background subtraction is not only a necessity for improved precision but also for measurement accuracy to eliminate the effects of outgassing. Comprehensive details of these laboratory inlet studies will appear in a future publication.

The inlet system employed during our most recent aircraft campaign is schematically shown in Figs. 1 and 4. As shown in Fig. 1, approximately 2 ft of 1/2 inch OD PFA grade Teflon line directs the sample flow from a mass flow control valve (100 slm) and into the Herriott cell. This valve, which is controlled by a flow meter downstream of the Herriott cell, maintains a constant cell mass flow rate even when the airplane changes altitude. This valve also maintains a nearly constant cell

pressure to within ± 4 Torr as the airplane changes altitude. Such pressure changes, however, require a pressure correction during the fitting procedure. We are presently exploring various strategies for maintaining a constant cell mass flow rate and pressure regardless of the aircraft altitude. One approach utilizes the upstream flow control valve in conjunction with the pressure transducer shown in Fig. 1 for feedback control.

As shown in Fig. 4, the inlet flow control valve samples the center portion of the flow in a 1 inch OD main sampling line. This sampling line is 24 inch long and made from glass-lined stainless steel tubing. The sampling line protrudes through the aircraft wall, through a winglet structure outside the aircraft, and is bent at 90° to face the rear of the aircraft. This together with the external protective cone shown in Fig. 4 minimizes the sam-

pling of liquid water in the inlet. The inlet, which protrudes 12 inches outside the aircraft, is well outside of the airplane boundary layer. Approximately 3.2 slm of the flow in the main sampling line (total inlet flow rate of ≈ 10.7 slm) is drawn off using a second flow controller backed by a pump. The flow velocity in the 1 inch OD main sampling line results in Reynolds numbers around 1000 for all conditions of pressure and temperature encountered during flight. Thus the inlet flow after experiencing some initial turbulence at the entrance quickly establishes a laminar flow profile. Even though turbulence is no doubt reintroduced upon sampling through the 100-slm-flow control valve, sampling through the majority of the main inlet line is accomplished with minimal wall contact. Employing the sample draw-off flow thus helps to minimize the sampling of flow that has come in close contact with the walls of the main inlet line. The entire inlet line together with the Teflon cell line and the cell itself are all heated to 30°C.

A further important modification is the method of zero air addition necessary for background subtraction. Ambient air is drawn through a second sampling inlet using a diaphragm pump as shown in Fig. 4. This air is then passed through a heated Pd/Al₂O₃ catalytic converter where most carbon-containing gases such as CO and CH₂O are oxidized completely to CO₂ and H₂O. Numerous laboratory tests have verified the efficacy of this conversion. The small additional water from this reaction is negligible compared to the much larger ambient water vapor concentration which is not significantly perturbed by the catalyst. When needed, ≈ 15 slm of zero air flow is directed into the main flow stream near the sampling entrance (within 7 inches of the entrance) via two 1/4 inch OD tubes passing through the winglet. Approximately 2–4 slm of excess zero air thus passes out the front of the inlet at all sampling altitudes in this mode. This procedure not only zeros nearly the entire sampling inlet, but also does not appreciably change the relative humidity of the inlet sample stream upon switching between ambient and zero air modes. Thus, we avoid rather dramatic relative humidity changes incurred in past measurements, a practice that may in part be responsible for the outgassing behavior previously observed. During

the ambient air mode, the zero air is dumped outside the aircraft in the boundary layer downstream of the sampling inlet. A small flow of ≈ 0.1 slm, which is controlled by a critical orifice, continuously flushes the zero air line. This dilutes the ambient samples by less than 1%.

Finally, calibration standards are added to the main flow stream using the draw-off set-up shown in Fig. 4. Here calibration flow (typically 200–400 sccm) continuously passes through an 1/8 inch Teflon T union. When not required, a three-way valve downstream of this T switches, drawing the standard flow plus approximately another 400–600 sccm of ambient sample through a 1 slm flow control valve and into a pump. The pump thus continuously draws off any outgassing in the small dead-volume between the T and the main flow stream. During calibration, the downstream three-way valve draws cabin air through the flow controller and pump and the standard flow is directed through 1/8 inch Teflon injectors mounted in the main flow stream. Results employing the above inlet modifications will be discussed in the next section.

3. Aircraft measurements of CH₂O during the 1997 NARE study

The TDLAS system discussed in this paper was mounted on board a WP3 aircraft (a four engine turboprop airplane) operated by the National Oceanic and Atmospheric Administration (NOAA) and employed on three recent field campaigns in 1996 and 1997. The TDLAS system successfully acquired ambient CH₂O measurements over 90% of the time during these campaigns. The last campaign, the 1997 North Atlantic Regional Experiment (NARE), was based out of St. Johns, Newfoundland. This study was designed to further our understanding of transport and photochemical processes resulting from the outflow of pollutants off the North American continent. Such processes have broad scale significance since they affect large-scale remote regions of the North Atlantic. This section will briefly summarize our TDLAS results for one flight during this campaign.

As discussed in the previous section, the correlation between background and ambient fit results is one means by which inlet outgassing can be spotted over the course of a flight. In Fig. 5 we plot the background fits immediately following each ambient measurement as a function of the ambient levels for one particular flight on September 16, 1997 for this purpose. As can be seen by the random scatter about the linear regression line, there is no correlation between the two variables even for ambient levels as high as 2.5 ppbv. This is further shown by the low slope (0.022 ± 0.044 at the 2σ level) and the low correlation coefficient ($R^2 = 0.003$). The upper and lower bounds of the regression fit show the 95% prediction band about the fit. Based on 298 mea-

surements, one would expect that 15 measurements should fall outside these limits for a purely random distribution, in agreement with the 15 points observed. The intercept of this regression (0.029 ± 0.026 ppbv at the 2σ level), furthermore, is in good agreement with the average background (0.04 ppbv) for this flight, and this further supports the effectiveness of the Pd/Al₂O₃ scrubber previously described. All the other flights show very similar results as Fig. 5, and this attests to the fact that the inlet discussed in the previous section works reasonably well. However, occasionally we do observe outgassing over short time intervals (typically 5 min). The background profiles of Fig. 3 are one such example.

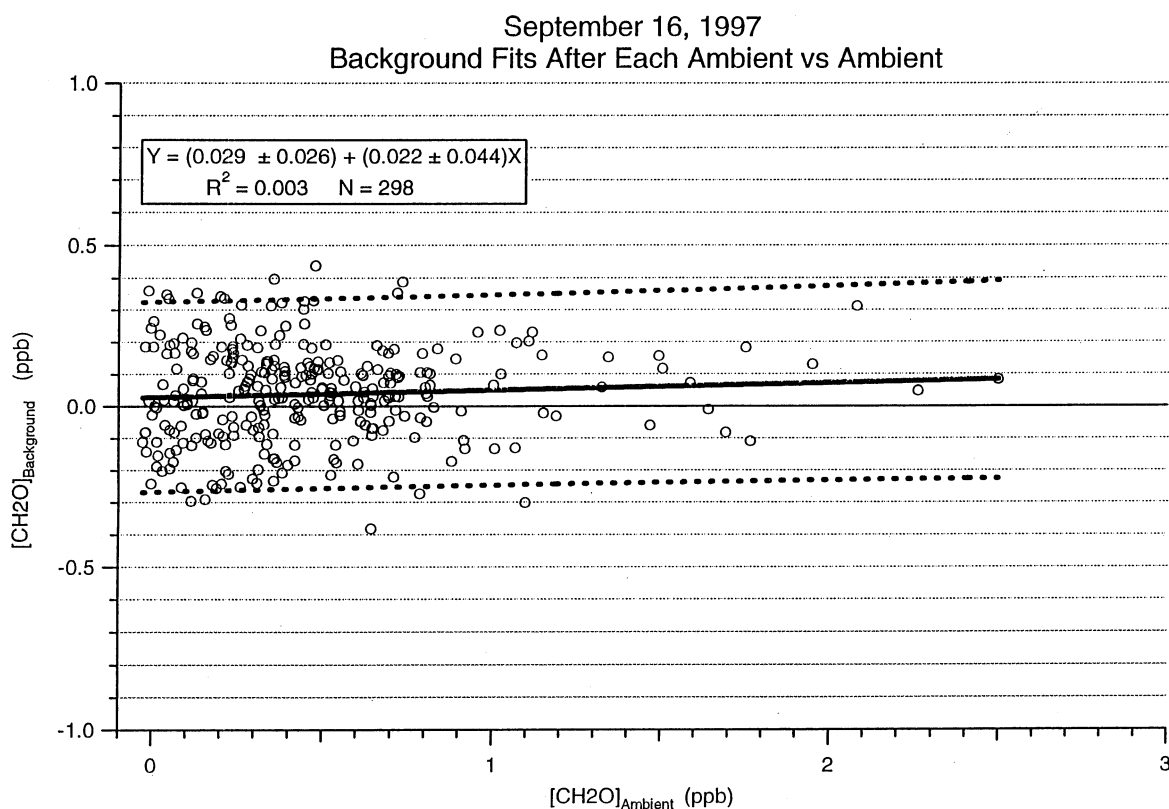


Fig. 5. Plot of background fits immediately following each ambient as a function of the ambient fits for data acquired during the September 16, 1997 NARE flight. The linear regression fit of these data and the 95% prediction interval are respectively shown, by the dark horizontal line and the two dashed horizontal lines. The linear regression equation is given in the legend along with the 2σ uncertainties. The low correlation and low slope both indicate that inlet line/sample cell outgassing of CH₂O is not prevalent here.

Typical aircraft measurements of CH_2O acquired during the NAPE-97 mission are illustrated by the September 16, 1997 data shown by the solid points in Fig. 6A. The light dashed lines show the corresponding pressure altitude profile. The black solid trace in Fig. 6B gives the entire flight track for this day, which originated and terminated in St. Johns, Newfoundland. The highlighted darkened portion of the flight track in Fig. 6B corresponds to CH_2O measurements acquired between 14:15 and 16:30 given in the shaded rectangle of Fig. 6A. As can be seen, ambient CH_2O concentrations ranged between values which averaged ≈ 100 pptv (the first high altitude leg above 5 km) to levels as high as 2.6 ppbv at low altitudes. The measurements throughout the entire NARE mission were very similar at high

altitudes, but the levels at low altitudes typically found over the remote Northern Atlantic were generally considerably lower than those of Fig. 6A.

The highly structured CH_2O profiles shown in the shaded region of 6A mimics the vertical flight profile and arises from the outflow of pollutants at low altitudes off the North American continent. Many other measurements onboard the aircraft revealed very similar concentration profiles to CH_2O . These measurements indicate that CH_2O and/or its hydrocarbon precursors are transported very effectively over long distances far removed from source regions. The analysis of data such as in Fig. 6A is presently in its formative stages. We are currently in the process of assessing the role of transport versus in situ pho-

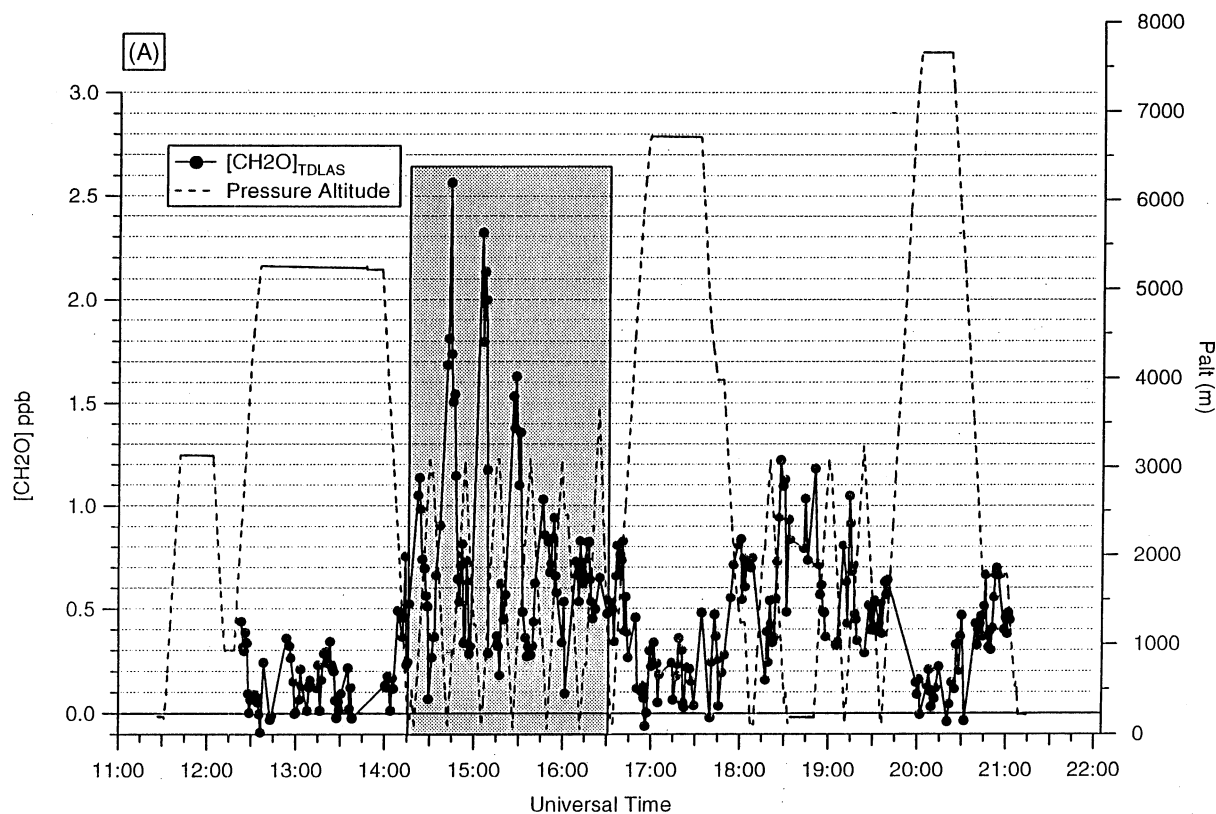


Fig. 6. (A) TDLAS measurements of CH_2O (dark solid points) acquired during the flight on September 16, 1997 as a function of the time. The pressure altitude is denoted by the dashed profile. Data in the shaded rectangle denote measurements acquired during the darkened flight leg of Fig. 6(B). We estimate a 1σ measurement precision of 87 pptv for the entire flight. (B) Flight profile for the September 16, 1997 mission.

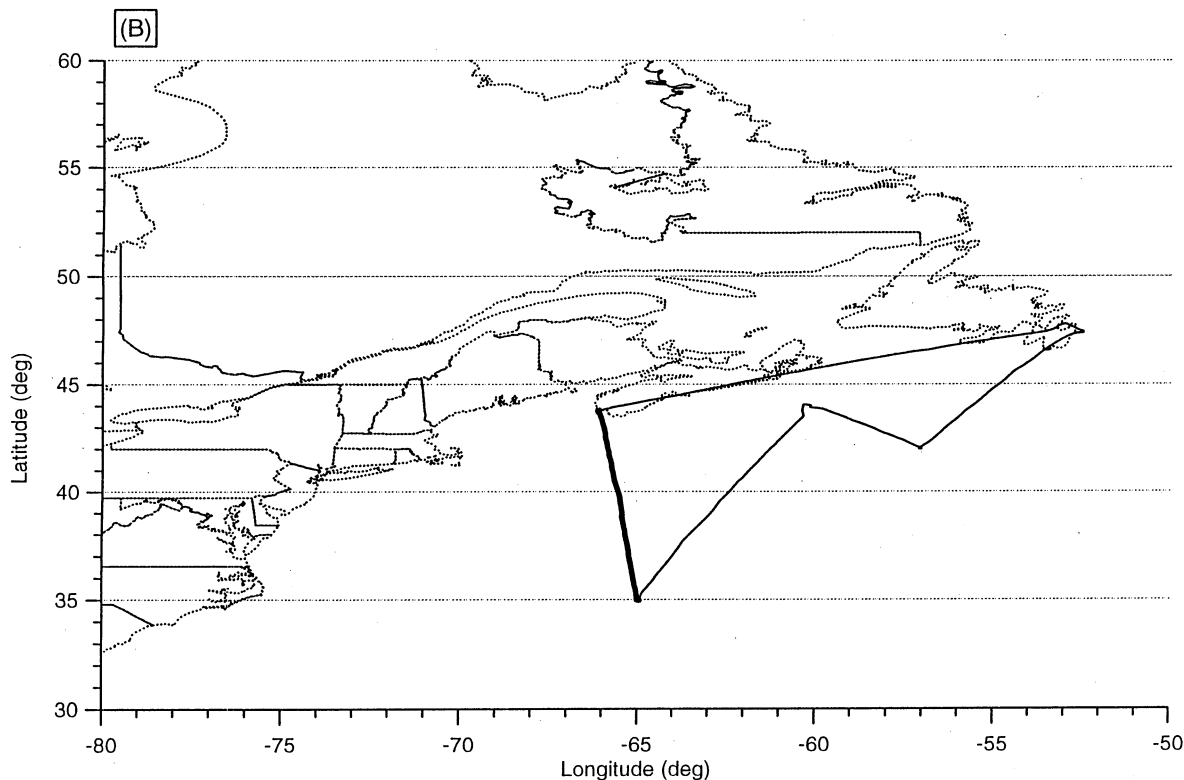


Fig. 6. (Continued)

tochemical production of CH_2O . Correlations of CH_2O with other tracers like CO will help in this regard. This information in conjunction with other measurements can then be used to assess the production of ozone in remote regions of the Northern Atlantic. In addition, we are comparing our measurements at high altitudes with models employing simplified methane chemistry, which in the absence of other hydrocarbons should be the dominant CH_2O source. Such comparisons are aimed at addressing the measurement-model discrepancies discussed in the introduction.

4. Summary and future directions

In this paper we have described an airborne tunable diode laser absorption spectrometer, which has successfully flown on three different field campaigns. We have also discussed hardware

and software features necessary for carrying out low level ambient CH_2O measurements with detection limits ($S/N = 1$) as low as 55 pptv for a 20 s average. As ambient CH_2O levels attain values around 100 pptv in clean remote regions of the mid-troposphere, such high sensitivity is critical. In fact, ambient levels in the upper troposphere attain values as low as 20–30 pptv, and hence even higher sensitivity is needed.

We have also discussed in this paper the many aspects associated with high accuracy and its verification. In particular, we have discussed issues of measurement selectivity, calibration, instrument precision, and instrument background spectra. We have also briefly discussed inlet surface effects on measurements of reactive and soluble gases like CH_2O , and we are currently in the process of conducting extensive inlet tests to quantify the exact magnitude of surface effects under a variety of sampling conditions. Finally, because of the

significance of temperature stability to instrument performance, we are in the process of re-engineering the entire temperature control scheme for the optical bench, surrounding enclosure, and laser controller. These efforts attempt to make the present airborne system more robust so that the very high sensitivities achieved in the laboratory can be routinely achieved during airborne operation. In addition, efforts are also focusing on expanding the present laser system to dual laser channel operation for simultaneous measurements of CH₂O with gases like H₂O₂.

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