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Measurement of Gas Phase Hydrogen Peroxide in Air by Tunable Diode Laser Absorption Spectroscopy

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Tunable diode laser absorption spectroscopy has been applied to the determination of gas phase hydrogen peroxide in ambient air with sub-ppbv (parts per billion by volume) detection limits for measurement times of the order of minutes. The methods for calibrating the instrument and for assuring the absence of spectroscopic and sampling interferences at the level of our present detection limits are described. Ambient air monitoring with our system indicates that the hydrogen peroxide mixing ratio is often < 0.3 ppbv. Five-minute average mixing ratios of up to 2.9 ppbv have been measured at sites in southwestern Ontario, Canada, during the summer months of 1984 and 1985, while the highest 1-hour average value observed was 2.1 ppbv.

INTRODUCTION

Hydrogen peroxide is believed to be the most important oxidant in the aqueous phase conversion of S(IV) to S(VI) [*Penkett et al.*, 1979; *Middleton et al.*, 1980] and is therefore directly involved in the chemical transformations leading to the acidification of precipitation. Although formed mainly in the gas phase, H_2O_2 is highly soluble. Reliable measurements of H_2O_2 in both the gas and the aqueous phases in the troposphere are therefore essential for the understanding of the processes involved in acid deposition.

Atmospheric hydrogen peroxide is mostly formed by the recombination of hydroperoxy, HO_2, radicals. During the daytime, photolysis of H_2O_2 produces the HO radical, which is recognized to be a key species in atmospheric chemistry. Measurements of H_2O_2 mixing ratios in tropospheric air are therefore also important for understanding the behavior of the odd hydrogen radicals [*Logan et al.*, 1980].

Despite its importance, relatively few measurements of this species in the gas phase have been reported. *Bufalini et al.* [1972] report 40–180 ppbv (parts per billion by volume) H_2O_2 during moderate and severe smog episodes at Riverside, California. *Kok et al* [1978*a*, *b*] found midafternoon values of 10–30 ppbv at two locations in the south coast air basin of southern California and mixing ratios of 100 ppbv in the plume of wildfires. *Kelly et al.* [1979] report much lower mixing ratios of 0.3–3 ppbv at a rural site near Boulder, Colorado. Their values are close to the 0.2- to 2-ppbv levels predicted by models for summer mid-latitudes [*Logan et al.*, 1980].

These previous studies have relied on bubbling ambient air through an aqueous solution containing some trapping agent, with subsequent analysis of the resulting solution. The formation of H_2O_2 as an artifact of this sampling procedure, most probably by reactions of ozone and its decomposition products with water, has now been demonstrated [*Zika and Saltzman*, 1982; *Heikes et al.*, 1982; *Heikes*, 1984]. In addition, the aqueous trap methods may suffer from SO_2 interferences [*Heikes et al.*, 1982] and from interference by organic peroxides, which are also expected to be present in tropospheric air [*Logan et al.*, 1980]. Although progress has been made in overcoming these artifacts (A. L. Lazrus, private communication, 1985), the results of earlier studies must be treated with caution.

Direct measurement of H_2O_2 in the gas phase avoids these artifacts effects. *Kley and Stone* [1978] proposed a method based on the VUV photolysis of H_2O_2 to yield excited OH radicals which could be sensitively detected by their fluorescence, but so far this method has not been implemented. The feasibility of H_2O_2 measurements by kilometer path length Fourier transform infrared spectroscopy was assessed by *Tuazon et al.* [1980] and by *Hanst et al.* [1982], with resulting estimates of detection limits between 40 and 100 ppbv.

The tunable diode laser absorption spectrometer (TDLAS) method fulfils the requirement of detecting H_2O_2 directly in the gas phase, removing the possibility of such artifacts as may occur in the aqueous trapping methods. In addition, the method has other advantages for monitoring atmospheric in H_2O_2; this paper shows that it can provide sensitive measurements (sub-ppbv detection limits) with averaging times of a few minutes, and a further advantage is its very high specificity towards the target molecule by virtue of the high spectral resolution employed. Unlike methods which depend on the chemical properties of the molecule, no special procedures are required to avoid interferences from, for example, organic peroxides.

EXPERIMENTAL

The TDLAS method takes advantage of the high monochromaticity and rapid tunability of Pb salt diode lasers to measure absorptions arising from single rotational-vibrational lines in the mid infrared spectrum of a molecule. In order to facilitate the measurement of very low optical densities ($<10^{-5}$) at line center and to reduce the chances of overlap between absorption lines, reduced pressures ($\sim$25 torr) are used to minimize pressure broadening of the rotational lines. The atmospheric sample is pumped rapidly at the reduced pressure through a White cell, which also provides the necessary long optical path lengths (about 40 m in our present instrument). A description of our original system has been published previously [*Hastie et al.*, 1983], and details of our improved TDLAS systems for trace atmospheric gas monitoring will be provided elsewhere (G. W. Harris et al., unpublished manuscript, 1986).

Application of the TDLAS method to the quantitative measurement of a particular species requires effort in three areas: (1) the selection and characterization of a suitable diode laser and of laser operating conditions; (2) the development and validation of a calibration method, and (3) the establishment of sampling procedures.

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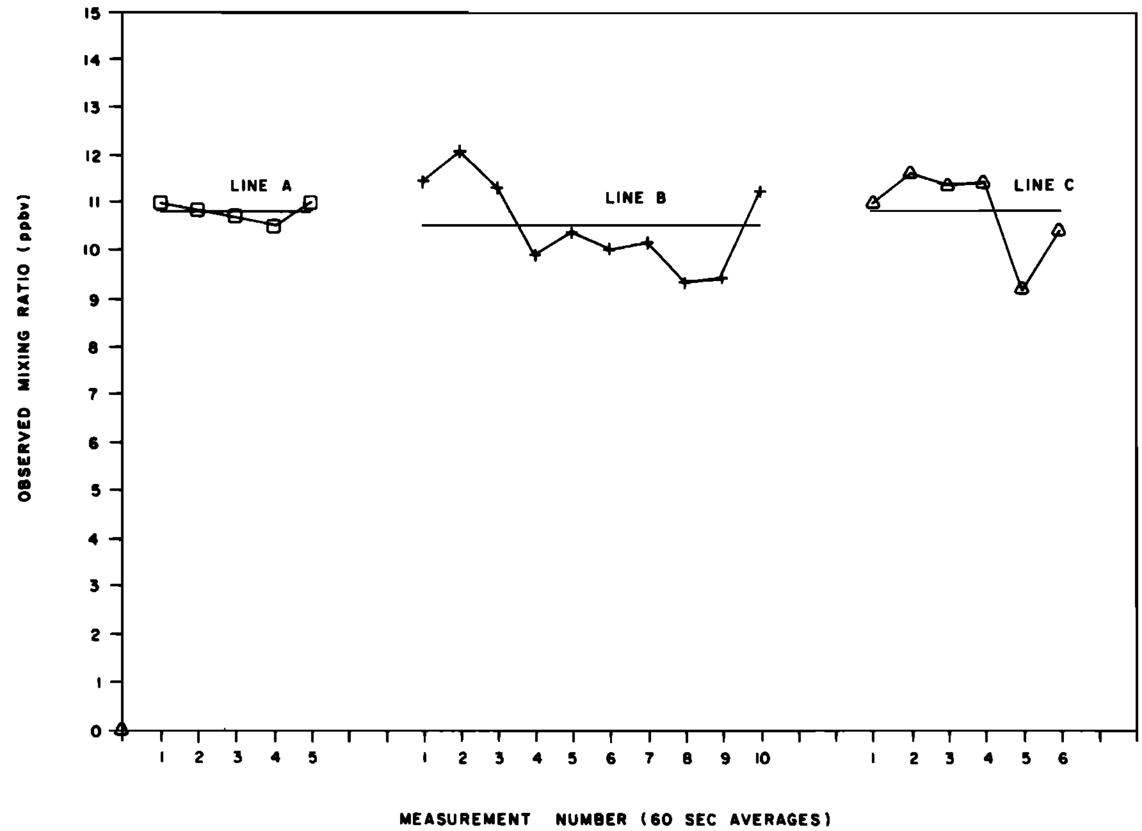

Fig. 1. Measurements of an estimated 11 ppbv H_2O_2 added to scrubbed ambient air using three different H_2O_2 absorption lines. Each data point is obtained from a 60-s average spectrum. The horizontal lines show the mean of each data set. Line A was used for ambient air monitoring.

Selection of Laser Diode and Operating Conditions

The most prominent vibrational absorption band of H_2O_2 is the v_6 band centered near 1260 cm^{-1}. According to the Air Force Geophysics Laboratory (AFGL) absorption line compilation [*Rothman et al.* 1983*a*, *b*], the strongest group of rotational lines in the band are near the center of the *R* branch around 1285 cm^{-1}. The selection of an individual line for air-monitoring purposes involves a number of compromises between the properties of the available lasers, the strengths of the absorption lines of the target molecule, and the avoidance of absorption lines from other atmospheric species which may interfere spectroscopically. The important laser characteristics for this application relate to output wavelength range, output mode structure, frequency and amplitude stability, and beam profile intensity distribution.

Five lasers were obtained from two manufacturers for evaluation in this work, and two lasers were judged suitable for complete characterization. The lasers which were rejected either provided insufficient output power, did not operate in a single-frequency mode near the target region, were inherently noisy (poor power-to-noise ratio), or had a poor (severely non-Gaussian) beam intensity profile.

Of the two lasers selected for further work, one was supplied by Laser Analytics (Bedford, Massachusetts) and after detailed evaluation was operated on the H_2O_2 lines at 1264.590 cm^{-1} and 1264.622 cm^{-1}. These lines have integrated line strengths of 0.4 and 1.6 × 10^{-20} cm^2 $molecule^{-1}$ cm^{-1}, respectively. To assign these and other lines in the H_2O_2 band, a grating spectrometer, calibrated by superimposing a helium-neon laser beam and the tunable diode laser (TDL) beam, was used to ascertain the TDL output wavelength to an accuracy of about ±0.5 cm^{-1}. The lines are then assigned by comparison of the recorded spectrum of H_2O_2 in this region with the line listings in the AFGL compilation [*Rothman et al.*, 1982*a*, *b*]. Simultaneously recorded spectra of N_2O and H_2O aid in the assignment process. The grating spectrometer is used simply to identify the spectral region of the absorption band under study. When actual measurements are made, the grating spectrometer is removed, and the highly monochromatic laser beam is tuned over a region corresponding to a few absorption line widths (about 10^{-2} cm^{-1}) centered at the target absorption line.

Most of the work reported here was done with a second laser supplied by the Fraunhofer Institute for Physical Measurement Techniques (Freiburg, Federal Republic of Germany), operated at the H_2O_2 line at 1284.2044 cm^{-1}, which has a line strength of 3.6 × 10^{-20} cm^2 $molecule^{-1}$ cm^{-1}. Only the line at 1283.740 cm^{-1}, of the several hundred lines in the v_6 band of H_2O_2, has a significantly greater intensity ($s = 5.04 \times 10^{-20}$ cm^2 $molecule^{-1}$ cm^{-1}). That line is, however, overlaid by an interfering absorption in ambient air and therefore cannot be used for air monitoring.

It should be noted that neither the assignment of a selected line to a particular transition in the molecule nor knowledge of its integrated line strength is strictly necessary for the present purposes. However, if the selected line can be identified and if its integrated line strength is known, it is possible to ascertain whether other lines which are significantly stronger than the one selected exist elsewhere in the spectrum of the molecule and hence whether further work on laser and absorption line selection procedures are warranted.

Investigation of Possible Spectroscopic Interferences

Line assignment and line compilations are not used for screening the selected region for spectroscopic interferences. The absence of interferences in the vicinity of the wavelength of the selected line is checked experimentally. The investigation of interferences, the selection of suitable laser operating conditions, and the determination of system detection limits are not independent tasks but are carried out iteratively. Depending on the molecule and on the laser or lasers available, several to several hundred separate rotational-vibrational lines may be candidates for use in a measurement system aimed at that molecule.

During an atmospheric measurement the laser frequency is swept across a narrow (about 10^{-2} cm^{-1}) region centered on the target absorption line. Absorption features lying outside of this narrow window do not interfere with the measurement. One possible exception is the case of very intense lines arising from species which have large and variable mixing ratios (such as water vapor) which may cause a degradation in detection limit even if the interfering line is centered outside the window. This is because the Lorentzian "tail" of the intense line may have significant optical density in the window and as the mixing ratio of the interfering species varies the shape of the background spectrum will alter. If this occurs, the precision of background subtraction will be degraded and will result in poorer detection limits. This effect will not, however, lead to a false identification of the target molecule.

Chance interferences are readily identified. Since the laser is scanned across a wavelength region contained the target absorption line, line shape information, and the exact line center position are determined. Interference resulting from partial overlap of an absorption line with the target line is immediately apparent from the line shape. Such interferences, and even the rare cases of exact overlap (line centers identical to $\pm 10^{-3}$ cm^{-1}), can be studied by changing the concentration of the target gas in the sampled air as well as by inspection of spectra arising from ambient air from which the target molecule has been removed ("scrubbed"). Any interferences will be reflected in a lack of linearity of the instrument response toward added H_2O_2. If, in any of these procedures, interfering absorption lines are detected, that particular absorption line is abandoned and another absorption line is selected.

An unequivocal test for the absence of interferences is afforded by comparison of the mixing ratios calculated from several separate absorption lines. There is a vanishingly small probability that any interfering gas (or gases) could have exact overlap and identical ratios of line strengths as the target gas at each wavelength. In the case of H_2O_2 we have identified five different lines which pass all the above tests for freedom from interference. As pointed out above, it was not necessary to spectroscopically assign each of these lines for this test, nor to determine their exact wavelengths.

Figure 1 shows mixing ratios measured on three lines, labeled A, B, and C, which lie close to each other in the H_2O_2 spectrum and which were judged to be interference free to the level of the detection limits on the basis of the above tests. The instrument was calibrated on each line by addition of a 35-ppbv spike to scrubbed ambient air, and then a second lower spike of ~11 ppbv added to ambient air was measured on each line.

Lines B and C gave poorer detection limits than line A, as can be judged from the scatter in the data in Figure 1, and were not used for ambient monitoring. However, the means of the three measurement sets are identical within one standard deviation. These data were obtained using background subtraction, as described below, and 1-min signal averaging. The means and standard deviations are 10.82 ± 0.18 (line A), 10.54 ± 0.89 (line B) and 10.86 ± 0.84 (line C), further confirming the absence of interferences on the lines.

Calibration Procedures

The procedure for calibrating the TDLAS for ambient H_2O_2 measurements is addition of a known flow of the target gas to a known flow of air at the ambient air-sampling inlet. In this way the sensitivity of the complete system is calibrated directly in terms of ambient H_2O_2 mixing ratio and exact knowledge of instrumental factors, such as the relationships between the magnitude of the $2f$ signal (signal detected at twice the modulation frequency, f) and optical density in the White cell or of the factors governing the line width of the absorption line and of the $2f$ line, is not required so long as such factors are held constant.

The calibration method will also compensate for any first-order surface processes affecting the throughput efficiency of the sampling system. Higher-order effects (if present) would be best accounted for when the mixing ratio of the added calibration "spike" is comparable to the mixing ratio of the target gas in ambient air. For H_2O_2 the ambient mixing ratio is low, and this requirement must be compromised by the need to maintain calibration precision. Calibration is performed on mixtures containing 5–30 ppbv H_2O_2.

The calibration gas is added at controlled flow rates in the range 10–50 standard mL min^{-1} to an airstream flowing at about 5 standard L min^{-1}. Calibration in the low-ppbv range therefore requires a stable source of H_2O_2 with mixing ratios of a few ppmv (parts per million by volume). The source developed for this work consists of a 4-m-long coil of low-density polyethylene tubing, 0.32-mm OD and 0.16-mm ID (Imperial Eastman type P-22-1/8) which is immersed in either 30 or 50% stabilized solutions of H_2O_2 thermostated to ±0.2 K in the range 300–320 K. The H_2O_2 permeating into the tube is carried away by the dry nitrogen carrier gas.

All parts of the device in contact with H_2O_2 solution were pretreated with a 50/50 mixture of H_2O_2 (90%) and concentrated H_2SO_4. The parts were immersed in this mixture, which was then cautiously warmed (inside a fume hood) until steady gas evolution was observed. This procedure appeared to prevent subsequent decomposition of H_2O_2 by impurities on the surfaces. By suitable choice of coil length, solution concentration, and bath temperature, permeation rates in the range 5–500 ng min^{-1} which provide the desired mixing ratios of calibrating gas may be obtained with these devices.

The permeation rate of the calibration source was determined by the colorimetric $TiCl_4$ method of *Pilz and Johann* [1974]. A stock solution is prepared by dissolving 11.6 mL of $TiCl_4$ (Alfa Products, Danvers, Massachusetts) in 50 mL of concentrated HCl (37%. 12 *M*). This solution is bright yellow and keeps indefinitely. Prior to use the stock solution is diluted tenfold with distilled water to produce a colorless solution which is somewhat unstable and must be discarded after 2–3 days. One mL of this working solution and 10 mL of 1.2 *M* HCl are placed in an impinger, and the calibration gas stream is bubbled through the impinger until a slight yellow coloration is observed (1–10 hours depending on the permeation rate). The solution is then brought up to 50 mL total volume by addition of distilled water, and its absorbance at 415 nm is compared to that of a blank solution which has not been exposed to H_2O_2. Matched 10-cm-long cuvettes are used. The yellow coloration is due to a Ti-H_2O_2 complex of 1:1 stoichiometry [*Pilz and Johann*, 1974] with an absorption

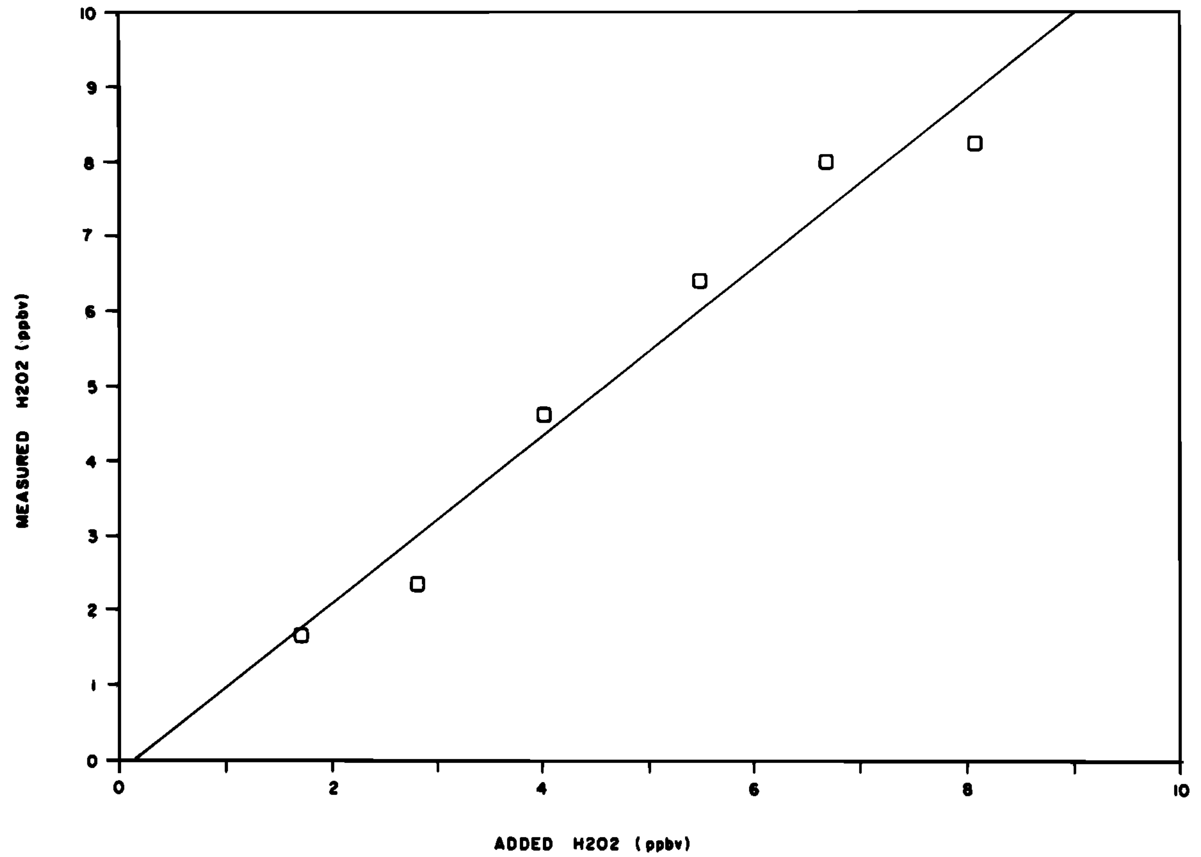

Fig. 2. Response linearity towards 1.7–8.3 ppbv H_2O_2 added to scrubbed ambient air. The least squares line has slope 1.12 and intercept −0.15 ppbv.

coefficient at 415 nm equal to 735 M^{-1} cm^{-1} [*Pilz and Johann*, 1974; *Kok et al.*, 1978*b*]. No change in absorbance at 415 nm was observed when the nitrogen carrier gas alone was passed through the impinger. The artifact H_2O_2 production which has caused problems with impinger methods for ambient air-monitoring purposes does not occur when pure nitrogen is used as carrier gas [*Heikes*, 1984]. The H_2O_2 permeation rate may be calculated from the absorbance measurement and the collection time.

Repeated measurements of the permeation rate from individual permeation sources over a period of several months showed a decrease of 10-20% per month. The devices were recalibrated at least weekly during measurement periods and were refilled with fresh solution if the permeation rate fell below the desired range.

Materials Tests and Sampling Procedures

Since H_2O_2 may readily decompose on reactive surfaces, all materials to be used in the parts of the instrument contacted by the gas flow were tested for inertness toward H_2O_2. Preliminary screening was performed by inserting the material in the gas stream between the permeation device and the $TiCl_4$ impinger and noting any changes in the concentration. The H_2O_2 mixing ratios were in the low-ppmv range for these tests and the gas flow rates were 10–50 standard mL min^{-1}. Pyrex glass, perfluoroalkoxy (PFA) Teflon, and CaF_2 (used for IR windows) did not affect the H_2O_2 mixing ratio measured at the impinger. One and a half meters of 6.4-mm OD polytetrafluoroethylene (PTFE) Teflon tubing initially removed 24% of the incoming H_2O_2, but after overnight conditioning in the gas stream, no further H_2O_2 removal occurred. Conditioning also prevented destruction of H_2O_2 on a PFA Teflon needle valve (Galtek Corporation, Chaska, Minnesota) and a three-way all-PTFE Teflon solenoid valve (Nacom Industries, Tustin, California). Stainless steel tubing, metal needle valves, and aluminum tubing destroyed H_2O_2 almost completely, as did several epoxy-based glues (commonly used for affixing IR windows to Pyrex). Cells with Pyrex glass bodies and CaF_2 windows sealed with PTFE gaskets passed 95–100% of the incoming H_2O_2, and these cells were used for containing high concentrations of H_2O_2 for frequency calibration (line locking) purposes.

Material testing in the 2–50 ppbv range was carried out by inserting samples of the material between the ambient air inlet and the white cell. No H_2O_2 losses were observed on 30 m of 6.35-mm OD PTFE inlet tubing or on the Teflon solenoid and needle valves when the airflow was at its usual value of 5 standard L min^{-1}.

Both the high- and low-concentration material tests showed that $FeSO_4$ and Hopcalite catalyst remove H_2O_2 quantitively from the gas stream. These materials were therefore used to scrub ambient air H_2O_2 for acquiring background spectra. The scrubbers were glass tubes, 3.0-cm OD, packed with either 27 g of ferrous sulphate or with 35 g of 8–10 mesh Hopcalite (Mine Safety Appliances Company, Evans City, Pennsylvania). The $FeSO_4$ scrubber was preferred because it is probably less perturbing toward other trace constituents of ambient air (and the ideal is to use ambient air with only H_2O_2 removed for our background spectra). $FeSO_4$ reduces NO_x in air, but interferences from NO_2 and HNO_3 were explicitly ruled out.

RESULTS

Linearity and Response Time Tests

The linearity of the instrument response was ascertained by adding H_2O_2 in the mixing ratio range from 1.7 to 50 ppbv to

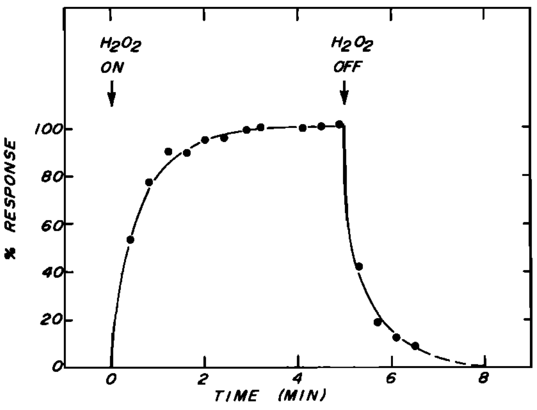

Fig. 3. Instrument response to the sudden addition and subsequent removal of a spike of 50 ppbv H_2O_2 at the ambient air inlet.

scrubbed ambient air and measuring the signal amplitude. Figure 2 shows the results of the linearity checks at the lower part of this range, 1.7–8 ppbv. The slope of the least squares line in Figure 2 is unity within 12% and the intercept of 0.15 ppbv is less than the detection limit, while the r value for the linear regression is 0.988.

To investigate whether the interior surfaces of the multiple-reflection cell affect the H_2O_2 mixing ratio, the signals observed when mixtures in the ppmv range flowed through a 9.5-cm-long cell were compared with those measured in the 40-m path length White cell when the same H_2O_2 flow was diluted with known flows of scrubbed air to yield ppbv mixtures in the White cell. The ratios of the measured optical densities in the White cell to that calculated from the path length ratio and the optical densities in the short cell were unity within one standard deviation (relative standard deviation 12%). This result shows that H_2O_2 is not lost on the internal (Teflon coated) surface of the multiple-reflection cell and that the calibration system operates linearly over the flow ranges used.

The response time of the instrument towards changes in the incoming H_2O_2 mixing ratio was investigated by suddenly introducing or removing flows of calibration gas. The response time constant was approximately 0.6 min. Figure 3 shows the time response of the signal to a pulse of 50 ppbv H_2O_2.

This response time is about 6 times longer than the residence time of the gas in the multiple-reflection cell and is intermediate between values found for gases such as NO_2, which appear not to interact with surfaces in the sampling train, and for strongly interacting gases such as HNO_3 [*Hastie et al.*, 1983]. H_2O_2 therefore appears to require some time to come to steady state with the surfaces of the instrument. The response time is, however, considerably shorter than the averaging time required to obtain sub-ppbv detection limits and so does not represent a constraint on instrument performance. Moreover, the fact that the response time was found to be independent of the mixing ratio over the range investigated, coupled with the response linearity down to at least 1.7 ppbv, suggests that after the brief stabilization period the gas inlet and white cell surfaces to not cause perturbations in the H_2O_2 mixing ratios.

Instrument Detection Limits

The detection limits are estimated by either of two methods. The first is based on the reproducibility at the 95% confidence level of low-ppbv level measurements of calibration gas mixtures [*Parris et al.*, 1977]. Figure 4 shows the response repro-

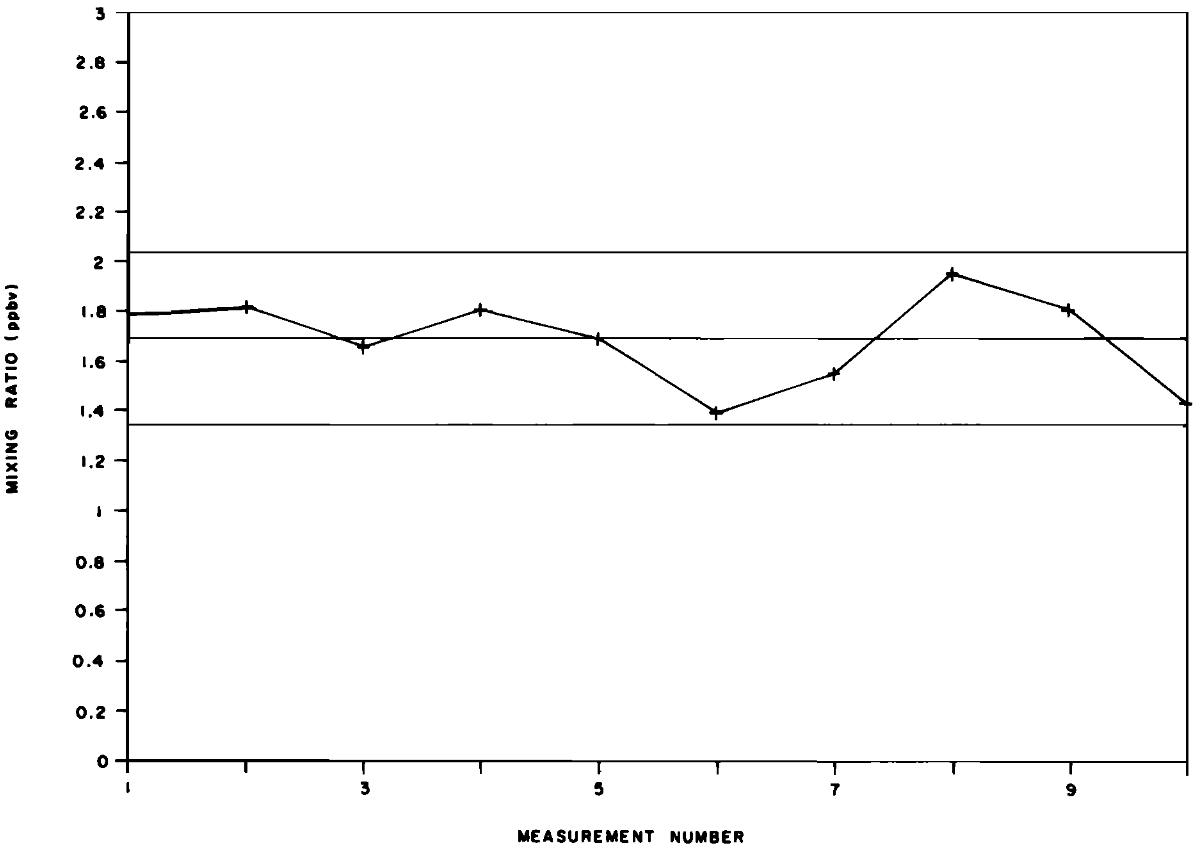

Fig. 4. Response reproducibility towards ~1.7 ppbv H_2O_2. Each measurement is a 120-s average. The horizontal lines show the mean and ±2 times the standard deviation of the data set.

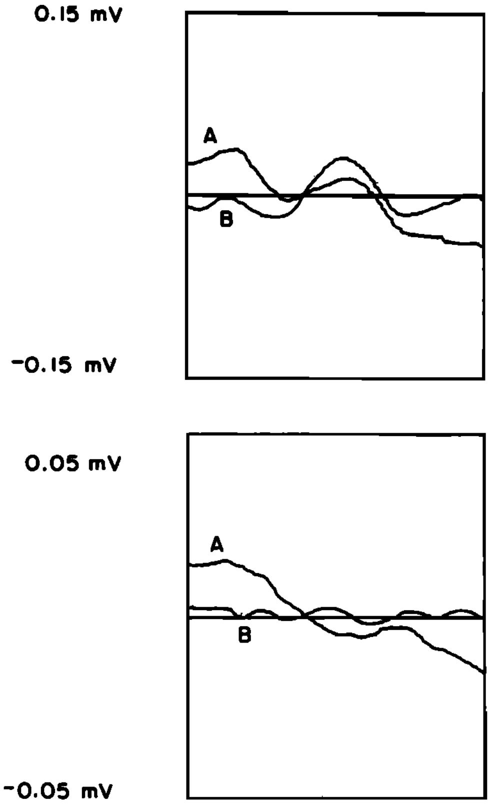

Fig. 5. (top) Calibration spectrum from 8.0 ppbv H_2O_2 (*a*) before and (*b*) after subtraction of a scrubbed ambient air background spectrum. (Bottom) (*a*) Scrubbed ambient air background spectrum and (*b*) the residual resulting from subtraction of two such background spectra. The detection limit estimated by least squares fitting the calibration spectrum to the residual is 0.56 ppbv. Each spectrum was obtained with a 180-s averaging time. The spectra are centered at 1284.2044 cm^{-1} and the scan range is about 10^{-2} cm^{-1}.

ducibility towards ~1.7 ppbv H_2O_2 added to scrubbed ambient air. Twice the standard deviation corresponds to ~0.3 ppbv.

The second method uses a computer-automated procedure. Two successive background spectra of scrubbed ambient air are acquired, and one is subtracted from the other. The detection limit is then determined by the results of the least squares fit of a calibration spectrum to the residual. This procedure is illustrated in Figure 5. The top plot shows a calibration spectrum due to 8.0 ppbv H_2O_2 both before and after background subtraction. The bottom plot shows a background spectrum and the result of subtracting two such background spectra acquired sequentially. The fitting procedure yields an estimate of the detection limit of 0.56 ppbv for the data shown in Figure 5. The estimates of the detection limits obtained by the automatic method and by considering the reproducibility of the signal from known, constant calibration mixtures were very similar. The automatic estimation method was used most frequently. The detection limits obtained in this work for H_2O_2 in ambient air are <0.6 ppbv for signal-averaging, times of 3–5 min and can be reduced further, usually to approximately 0.3 ppbv, by more extended signal averaging.

Measurements of Ambient Air

Ambient air was sampled from an inlet located 2 m above the roof of our laboratory building and about 20 m above ground. The building is situated near the northern edge of metropolitan Toronto, and winds reach the site from the northwest to northeast quadrant without encountering large local sources of pollution and without crossing the city. Suitable wind conditions obtained on 5 sunny days between February 29 and June 3, 1984, and H_2O_2 measurements were carried out on each of these days.

Each ambient air measurement was accompanied by a detection limit determination, similar to that shown in Figure 5. In the measuring sequence a background spectrum (ambient air through the H_2O_2 scrubber) was first determined. An ambient spectrum was then accumulated, followed by a second background measurement. With an averaging time of 180 s for each spectrum (corresponding to about 2000 individual scans) and a short waiting period after switching valves to eliminate response time effects, four ambient air measurements were made each hour accompanied by four detection limit determinations.

H_2O_2 was deemed detected only if the hourly averages of the ambient air measurement were significantly (95% confidence level) higher than the hourly averages of the absolute values of the detection limits and if the ambient spectra were signficantly correlated, (again at the 95% confidence level) with the line shape information obtained from the calibration

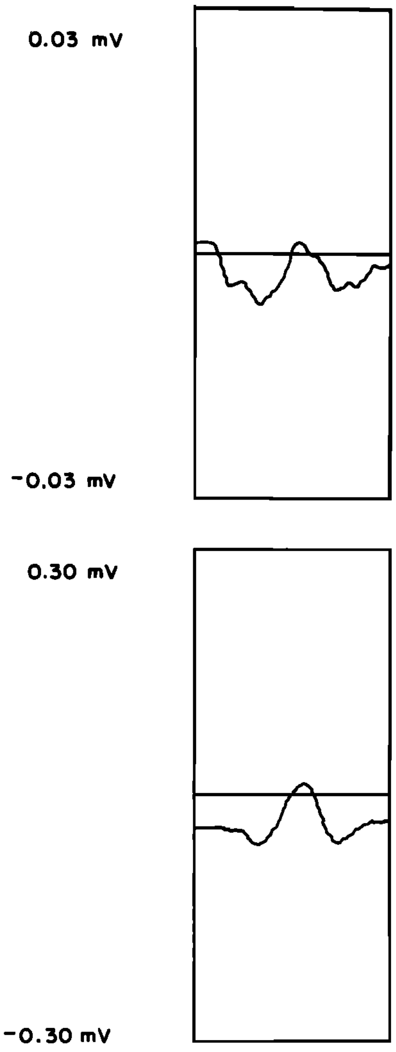

Fig. 6. (Top) Average ambient air spectrum centered at 1284.2044 cm^{-1} measured at Sarnia, Ontario, between 2019 and 2102 EDT on July 3, 1984. The laser scan is about 10^{-2} cm^{-1} in width. (Bottom) The 2f absorption signal obtained from a 23.8-ppbv H_2O_2 calibration mixture in the same wavelength region.

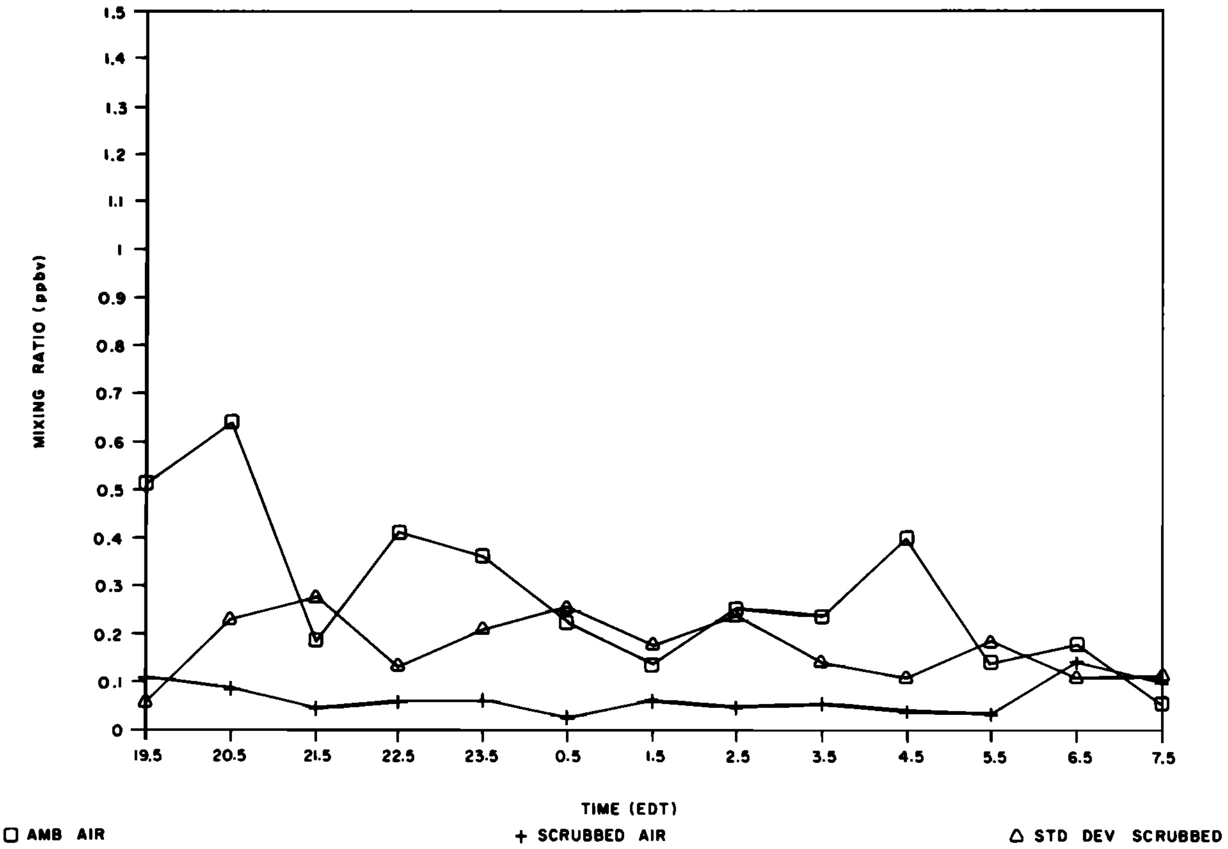

Fig. 7. Ambient H_2O_2 monitoring data. Air sampled from outside our laboratory building in Toronto, Ontario, on June 4–5, 1985. The squares indicate the 1-hour average ambient air signal. The crosses show the absolute values of the 1-hour averages of the detection limit determinations, while the diamonds indicate the standard deviations of these 1-hour average detection limit determinations.

spectra. No H_2O_2 could be detected during these measurements, even with hourly detection limit averages as low as 0.3 ppbv. This implies that the H_2O_2 mixing ratios were below this level on the measurement days.

Positive identification and measurements of H_2O_2 were made in southwestern Ontario during the period June 26 and July 8, 1984. These measurements were part of a mission conducted by the Ontario Ministry of the Environment to study air in the vicinity of the petrochemical plants at Sarnia, Ontario. Our TDLAS system made measurements of a number of components during this period, and the H_2O_2 mixing ratios were above our detection limits during 7 of the 11 measurement days. Figure 6 shows the averaged ambient air spectrum in a wavelength interval of approximately 10^{-2} cm^{-1} centered at the H_2O_2 absorption line at 1284.2044 cm^{-1} and obtained over a 43-min monitoring period on July 3, 1984. The ambient H_2O_2 mixing ratio giving rise to this spectrum is 2.09 ± 0.24 ppbv. Such data represent the first unambiguous spectroscopic measurements of atmospheric H_2O_2 in the gas phase.

The averages of the observed H_2O_2 mixing ratios obtained in each 24-hour period of the study period ranged from <0.3 to 1.5 ppbv. It should be noted that these values are not actual 24-hour averages, since our monitoring was neither continuous nor carried out on a consistent schedule each day. While the TDLAS normally operates quite reliably in the field, giving data coverage of 80–90%, our data coverage on H_2O_2 during this study was much lower, since a considerable amount of time was spent in investigating and improving instrument performance during this exploratory program. A full report on the results of this mission including our H_2O_2 measurements will be the subject of a future publication.

Additional monitoring was carried out at the laboratory site during the spring and early summer of 1985. Although the H_2O_2 mixing ratios were at or below our detection limits much of the time, measurements which met our detection criteria were made on several days between late April and early June. The mixing ratios ranged from <0.3 to ~ 1.5 ppbv during this period.

Figure 7 shows ambient air H_2O_2-monitoring data obtained during the evening and nighttime hours of June 4–5, 1985. The detection limit of the instrument during these measurements is also indicated in Figure 7. We show the absolute values of the hourly means of the detection limit determinations (based on the reproducibility of consecutive scrubbed air spectra as described above) and the standard deviations of the hourly mean of the detection limit determinations. The hourly means of the detection limit determinations were usually below 0.1 ppbv and always below 0.2 ppbv, while the standard deviations of these hourly means were less than 0.3 ppbv. The largest absolute value for a single detection limit determination (based on 5-min signal averaging) during these measurements was 0.7 ppbv. The hourly average ambient air signals were always positive and exceeded the standard deviation of the scrubbed air measurements in most cases. This data is representative of the performance of our instrument at its present stage of development. The mean values of the ambient air measurements declined during the night from 0.6 ppbv to about 0.2 ppbv.

CONCLUSIONS

A tunable diode laser absorption spectrometer system has been developed for measuring H_2O_2 in ambient air. The system has been shown to provide unambiguous identification of this species with no interferences from other atmospheric gases (at least to the level of our present detection limits). Calibration techniques have been developed and tests have been conducted to demonstrate the integrity of the sampling procedures. The response of the signals are linear with H_2O_2 mixing ratios, and the response time to perturbations in mixing ratios was determined to be 0.6 min.

H_2O_2 has been positively identified in suburban air and measured at mixing ratios of up to 2.9 ppbv. We used extended signal averaging (of the order of 1 hour) to consistently achieve detection limits as low as 0.3 ppbv. Measurements of suburban air indicate that the H_2O_2 mixing ratios are below this limit for much of the time, in contrast to earlier reports. Better performance must therefore be achieved if this system is to obtain measurements over the full range of ambient H_2O_2 mixing ratios with good time resolution. An upgraded TDLAS system capable of these tasks has been designed and constructed and is at present undergoing evaluation.

The H_2O_2 mixing ratios which we have measured to date are much lower than the 40–180 and 10–30 ppbv reported by *Bufalini et al.* [1972] and by *Kok et al.* [1978*a*] for polluted sites. Generally, they are also lower than the 1.2–2.6 ppbv reported by *Kok* [1980] and are comparable with the range of 0.3–3.0 ppbv measured by *Kelly et al.* [1979] in rural air. Model calculations [*Logan et al.*, 1980] predict clean air H_2O_2 mixing ratios from 0.2 ppbv to 2 ppbv in summer at mid-latitudes, which is consistent with our findings and detection limits in clean and suburban air.

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