Measurement of Trace Gas Fluxes Using Tunable Diode Laser Spectroscopy [and Discussion]

Mark S. Zahniser, David D. Nelson, J. Barry McManus, Paul L. Kebabian and D. Lloyd

Phil. Trans. R. Soc. Lond. A 1995 **351**, 371-382
doi: 10.1098/rsta.1995.0040

Measurement of trace gas fluxes using tunable diode laser spectroscopy

By Mark S. Zahniser, David D. Nelson, J. Barry McManus and Paul L. Kebabian
Aerodyne Research, Inc., 45 Manning Road, Billerica, Massachusetts 01821-3976, U.S.A.

A fast-response, high precision, tunable diode laser spectrometer has been developed for field measurements of methane and nitrous oxide fluxes using the eddy correlation method. The instrument uses a novel multiple-pass absorption cell with astigmatic mirrors to provide a long absorption path length (36 m) in a small volume (0.3 l). The combination permits rapid response with sufficient sensitivity for eddy correlation flux measurements over a wide range of meteorological conditions. Signal processing uses a least-squares fitting algorithm to determine absolute trace gas concentrations directly from the absorption spectra using spectral line parameters at data rates up to 20 Hz. The precision for methane and nitrous oxide is 0.1% of ambient levels with a 1 s averaging time. Extensions of the method to measurements of surface-reactive gases such as nitric acid and ammonia are possible using rapid sampling techniques to minimize surface interactions.

1. Introduction

Infrared absorption spectroscopy using tunable diode lasers (TDLs) has received wide usage for sensitive measurements of atmospheric trace gases over the past ten years (Schiff *et al.* 1983, 1994; Kolb 1991). Due to the difficulties of using these cryogenically cooled laser diodes and to the operator expertise required to build, align and maintain such systems, TDLs have only recently been used for trace gas flux measurements in the field (Wienhold *et al.* 1994; Edwards *et al.* 1994; Verma *et al.* 1992; Hovde *et al.* 1995; Anderson & Zahniser 1992). These measurements have been limited mainly to stable gases, particularly methane and nitrous oxide which have minimal surface interactions with enclosed sampling systems. Trace gases such as nitric acid and ammonia present difficulties for fast-response sampling due to memory effects on the inlet tubing and sampling cell walls. In addition, atmospheric concentrations of these gases are two to three orders of magnitude lower than for methane and nitrous oxide, which makes their detection more difficult.

We have developed a rugged and robust TDL system suitable for field measurements of trace gases using eddy correlation. A major emphasis in the design of this system was placed on rapid response. The multipass absorption cell, which is designed to maximize the path length in a minimal volume, allows rapid gas flushing times with a moderately sized vacuum pump. Coupled with unique data-

Phil. Trans. R. Soc. Lond. A (1995) **351**, 371–382

Printed in Great Britain

TEX Paper

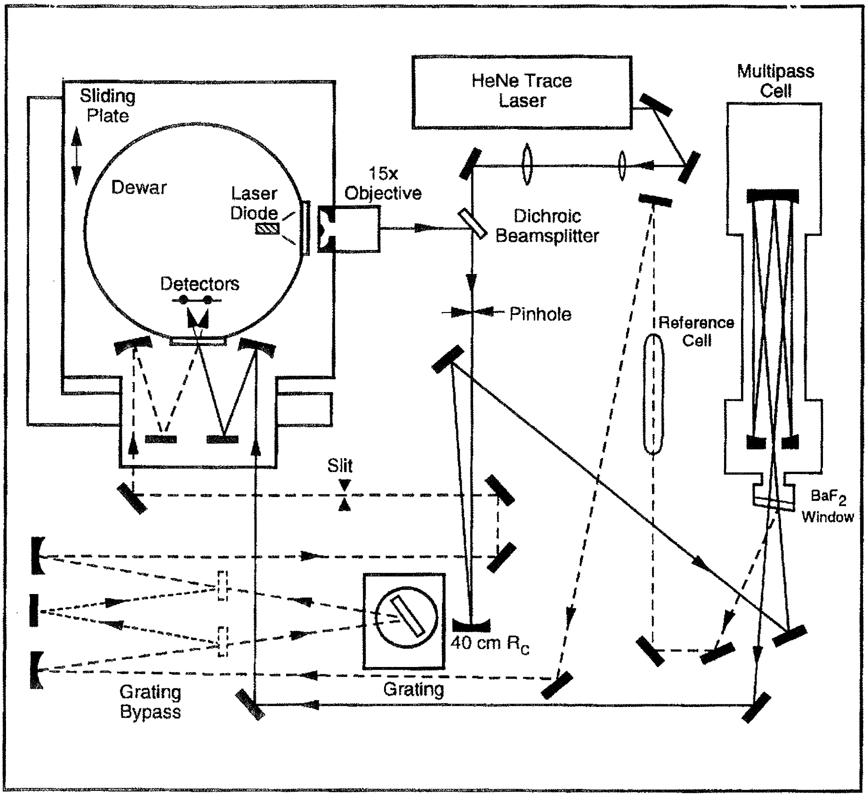

Figure 1. Design outline for the optical module.

processing, the overall system can achieve a true 3 Hz bandwidth. The compact absorption cell design also permits a relatively small optical bench to be used and yet maintains sufficient sensitivity for measuring changes in methane and nitrous oxide approaching one part per thousand of their ambient levels with a 1 s averaging time. The capabilities of the system are being extended to provide fast response sampling of surface reactive species such as ammonia and nitric acid.

2. Instrument description

The instrument consists of a nitrogen Dewar for temperature control of the TDL, an optical module for laser beam collection and transport, a multiple-pass absorption cell, and computer-controlled electronics for laser frequency control and data acquisition.

(a) Design of the optical module

The optical module (figure 1) fits on a 60 × 70 cm^2 table. This compact design is facilitated by the small optical absorption cell and by the liquid nitrogen Dewar that contains both the laser diode and two detector diodes. An automatic fill system with a 50 l capacity storage Dewar can provide unattended operation for up to 7 days.

The optical train of the module is as follows. Infrared light from the laser diode in the Dewar is collected by a reflective microscope objective (15×) and focused on a 0.2 mm pinhole, which defines the input aperture. This pinhole is used mainly during alignment, so it is mounted on a removable kinematically indexed base. The microscope objective is mounted on an X–Y–Z translator to allow accurate focusing on the fixed aperture. Past the input aperture, the infrared light is focused in a narrow beam into the optical absorption cell. The beam returns from the cell nearly collimated and with an angle of 0.1 rad (6°) from the input beam. The exit beam is steered back to the Dewar and is focused on a detector. Light reflecting from the cell input window is used as a wavelength reference beam. The reference beam passes through a gas calibration cell and a grating monochromator and is focused on a second detector. The calibration cell contains a low pressure mixture of methane and/or nitrous oxide. Light passing through this cell has strong absorption features used to identify spectral line positions. It may also be used to lock the laser diode wavelength. The monochromator provides identification of the wavelength of the diode when setting up the instrument and during the characterization of a new diode.

There is a parallel visible optical system for alignment and setup. A red HeNe ‘trace’ laser beam passes through a dichroic beamsplitter and is coaligned with the infrared beam. Coalignment is guaranteed by focusing the beam through the input aperture. The trace beam is an indispensable aid for alignment of the optical system. In addition, the trace beam is used to calibrate the monochromator accurately, by higher order diffraction. The fourth port of the dichroic beamsplitter can be used to observe the laser diode. An eyepiece mounted at the position conjugate to the pinhole forms an effective (150×) microscope for viewing the laser diode and for initially positioning the collecting objective after changing diode positions.

(*b*) *Multipass mirror system*

Multipass absorption cells are a widely used means of providing long optical pathlengths in a compact volume. Of several factors to be considered in the evaluation of a multipass cell design, the first is the total available pathlength. The signal-to-noise ratio (SNR) in an absorption measurement increases with the pathlength, up to a limit where loss from the many reflections becomes important (Werle & Slemr 1991). Another, and often the most important, factor limiting the effective SNR at long pathlengths is the appearance of optical interference fringes. These fringes, which are due to scattering in the cell, can have a free spectral range close to the frequency width of molecular absorption lines and thus tend to obscure the spectral features of interest. Finally, the volume of an absorption cell for a given pathlength is a limiting factor in the measurement response time.

Off-axis resonator Herriott cells (Herriott *et al.* 1964; Herriott & Schulte 1965) are easy to align and have a relatively low level of interference fringes. The simplest Herriott cell consists of two spherical mirrors separated almost by their radius of curvature. An optical beam injected through a hole in one mirror in an off-axis direction recirculates several times before exiting through the coupling hole. The beam spots fall on elliptical patterns on the mirrors, and within the cell the beams fill a volume describable as a flattened hollow hyperboloid. The number of passes is adjustable with changes in the mirror separation.

In a variation on the traditional Herriott cell, used in this instrument, astigmatic mirrors (Herriott & Schulte 1965) minimize the cell volume for a given

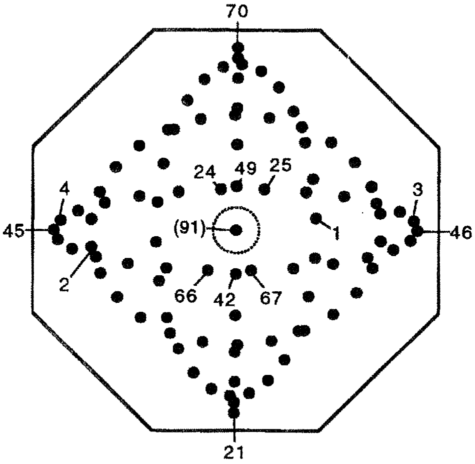

Figure 2. Spot pattern on astigmatic mirrors for the 182 pass design. Spot numbers are shown for the entrance mirror with centre coupling hole.

pathlength. The different horizontal and vertical radii of curvature produce beam spots on the mirrors which form a Lissajous pattern, as shown in figure 2, rather than the elliptical paths found in the conventional Herriott cell. The optical path therefore fills the optical absorption volume better, resulting in a smaller volume for a given pathlength.

We have designed and constructed such a cell based on a particularly favourable combination of curvatures to produce 182 passes before exiting (Kebabian 1992; McManus *et al.* 1995). The cell has a 20 cm base length which gives a path length of 36 m. With 3.8 cm diameter mirrors, the enclosed volume is 0.3 l. The mirrors have a reflectivity of 99.2% from 3 to 10 μm, resulting in 20% transmission of light through the cell. The dimensions of the mirror mounts and cell are shown in figure 3.

(*c*) *Data acquisition system*

The data acquisition method is based on rapid sweep integration over the full infrared transition line shape. This is accomplished by scanning the laser frequency under computer control and synchronously measuring the transmitted infrared light intensity. This spectral information is analysed in real time with a nonlinear least-squares fitting routine which returns both the spectral line profile and laser intensity spectrum (baseline). The area between the absorption line and the baseline, together with the known absorption coefficient for the line is used to calculate the column density of the species being observed.

The laser temperature and current are controlled by Laser Photonics controllers. In a typical experiment, the laser temperature is held constant while the current through the laser is modulated with a computer-generated sawtooth to sweep the output frequency across the infrared line. The ramp is generated in *ca.* 100 discrete steps at a rate of 300 kHz with a digital-to-analogue converter board. Thus the 100 point spectrum (figure 4) containing the infrared line is taken at a rate of 3 kHz. During approximately one-tenth of the duty cycle the laser

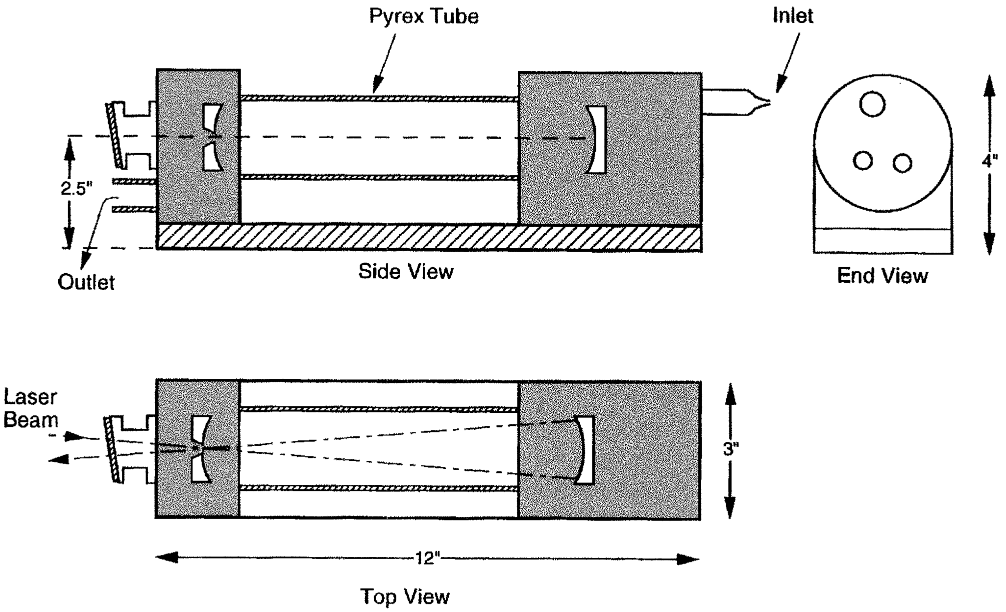

Figure 3. Schematic of 0.3 l volume 36 m astigmatic absorption sampling cell.

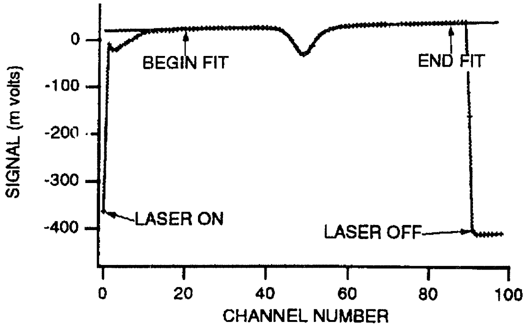

Figure 4. TDL spectrum of ambient methane line at 1327 cm^{-1} and Voigt profile fit. The trace is an average of 150 scans in a total time of 0.05 s.

current is dropped below the lasing threshold to provide a precise measurement of the zero light-detector voltage.

The infrared detectors are photoconductive HgCdTe (bandwidth of 300 kHz). This voltage change is amplified by a low noise preamplifier and sampled by a 12 bit analogue-to-digital converter (ADC). The conversion time for the ADC is 3 μs. The result of each conversion is transferred to the extended memory of a 80486 based computer using direct memory access. This process is fast enough to maintain a continuous 300 kHz data stream with 100% duty cycle.

The computer program which controls the data acquisition process monitors the data being written to the circular buffer in extended memory and grabs a block of it for processing whenever one half of the buffer is ready. Since this process uses only about 7% of the available CPU time, the program is able to perform several other tasks in real time without losing data. The most important of these tasks is to average signals from absorption spectra with a high speed assembly language subroutine. Two channels of data may be sampled with the data points alternating between channels so that the two absorption spectra are interleaved and are therefore effectively measured simultaneously.

The program also executes a nonlinear least-squares fitting routine to determine the integrated absorption intensity for the absorption spectrum from each channel. The diode laser power spectrum is represented as a slowly varying polynomial of adjustable order; typically a quadratic or cubic polynomial is used. The absorption lineshape is fit to either a Gaussian, pressure-broadened Lorentzian or Voigt profile. The position, width and height of the line are simultaneously fit together with the diode laser polynomial baseline. The result of the fitting routine is displayed on the computer screen as a function of time so that trends in the trace gas column densities are immediately apparent. For continuous fast response measurements as used in eddy correlation flux methods, a data stream rate of up to 20 Hz is achievable.

The absolute trace gas mixing ratio is calculated from tabulated line strength, pressure broadening coefficients and lower state energies from the HITRAN database (Rothman *et al.* 1992) and the measured temperature and pressure of the absorption cell. A calibration gas may also be automatically switched into the cell at predetermined intervals. The absolute accuracy of the spectral fit is typically a few percent for methane and nitrous oxide. The ability to convert the absorption signal directly to trace gas concentration is most important for surface active or reactive trace gases such as nitric acid where it is difficult to obtain accurate calibration sources.

(*d*) *Determination of sampling pressure*

The optimum sampling pressure is determined by a compromise between maximizing the line-centre absorption cross section and minimizing interferences from other species. In the high pressure limit, the maximum line-centre absorbance for a Lorentz line profile is independent of sampling pressure since any change in trace gas density due to pressure is compensated by an inverse change in the line width. As the pressure in the sampling cell is reduced, both the number density and the line broadening decrease so that there is no change in line-centre absorbance until the Lorentz linewidth approaches the Doppler width. Since the Doppler width is pressure independent, at low pressure the line-centre absorbance is proportional to pressure. The optimum pressure is generally in the range where the pressure broadened linewidth equals the Doppler width. For methane at $3058\ \mathrm{cm}^{-1}$ and $T = 300$ K the optimum is in the range of 30–50 Torr†.

3. System performance examples

The instrument response time was determined in the laboratory by rapidly switching between ‘zero’ air and room air containing ambient methane (*ca.* 1.9 ppm). This was accomplished using an automatic valve with a switching time on the order of a few milliseconds just upstream of the needle valve which regulated the cell pressure at 38 Torr. The data rate, set at 21 Hz for these measurements, is typical of that used in eddy correlation mode. As figure 5 shows, the

---

† 1 Torr ≈ 133 Pa.

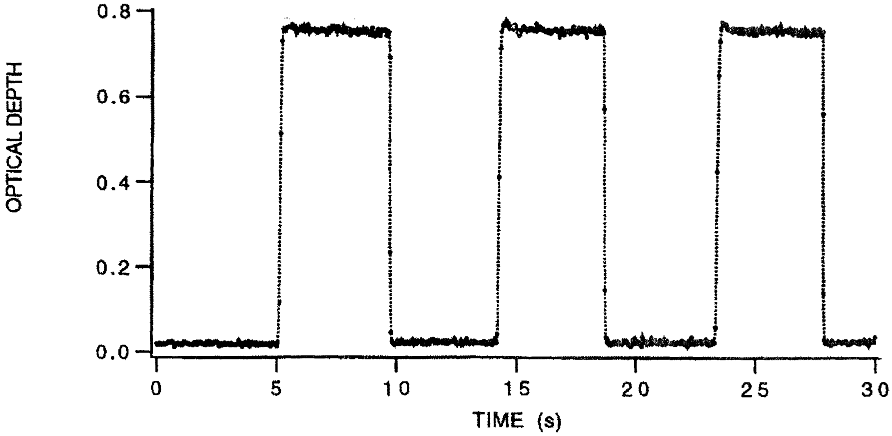

Figure 5. Response time of 36 m absorption cell. Pumping speed, $5\ \mathrm{l\,s^{-1}}$; data rate, 0.046 s per point (22 Hz); response time, $(1/e) = 0.05$ s; bandwidth, $1/(2\pi\tau) = 3$ Hz.

cell time constant $(1/e)$ of $\tau = 0.05$ s agrees closely with the value expected from the volume of the cell, 0.27 l, divided by the pumping speed of $5\ \mathrm{l\,s^{-1}}$. There is no apparent tailing or smearing of the response from the expected single exponential decay. The bandwidth of the instrument at $1/(2\pi\tau) = 3$ Hz is limited by the pumping speed.

The measurement precision in the fast response eddy correlation mode is typically about 0.6% (r.m.s.) of ambient methane with a signal averaging time of 0.05 s (20 Hz). The precision improves as expected with the square root of the measurement time. For measurements of gradients or of previously collected bag samples where time response is not as important, the precision with a 1 s averaging time is typically *ca.* 0.15% of ambient, or 3 ppb for methane.

As an example of data collected in this mode, figure 6 shows methane concentrations from samples collected in Tedlar bags from an aircraft flight over northern Scotland. The bags were taken to the field site later in the day and analysed with the TDL instrument. Each bag was sampled for 40 s followed by addition of calibration gas with 1990 ppb methane. The flow rate through the system was decreased to *ca.* $0.5\ \mathrm{l\,s^{-1}}$ for a flow response time of about 1 s.

The instrument performance for N_2O is similar to that for methane. Although ambient levels are lower by a factor of 5 for N_2O, the line strengths in the $2200\ \mathrm{cm^{-1}}$ region are stronger than those for methane at $3017\ \mathrm{cm^{-1}}$ so that the fractional absorptions in a 36 m path are both in the range of 5–10%. A representative trace for nitrous oxide taken in the high precision mode is shown in figure 7. With an averaging time of 10 s the precision is on the order of 0.2 ppb or slightly less than 0.1% of ambient.

4. Rapid sampling of surface-active gases

Other trace gases of interest for atmospheric–terrestrial exchange are detectable by TDL absorption but most present greater experimental difficulty than methane and nitrous oxide. Surface-active species such as nitric acid and ammonia are notoriously ‘sticky’ on sampling lines and inlets. The associated sampling losses or long equilibration times have precluded eddy correlation flux measurements

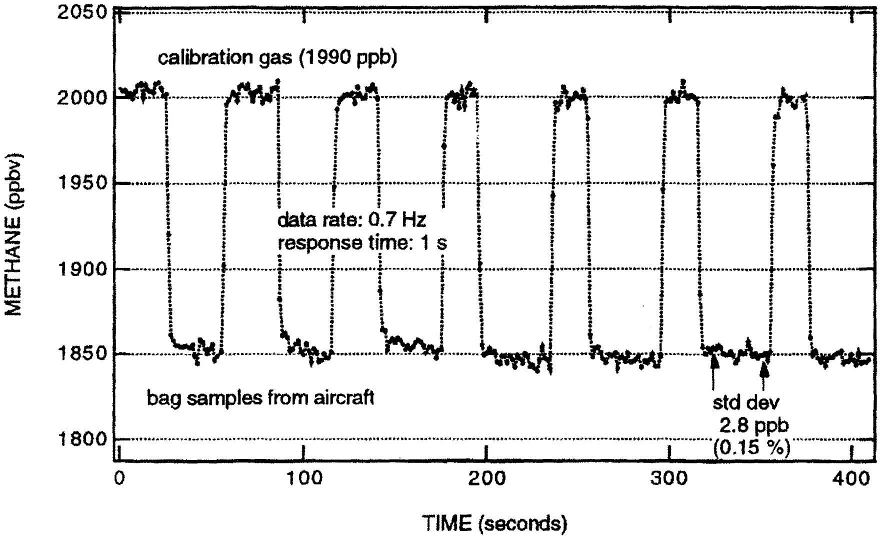

Figure 6. Methane data from aircraft bag samples taken in high precision mode.

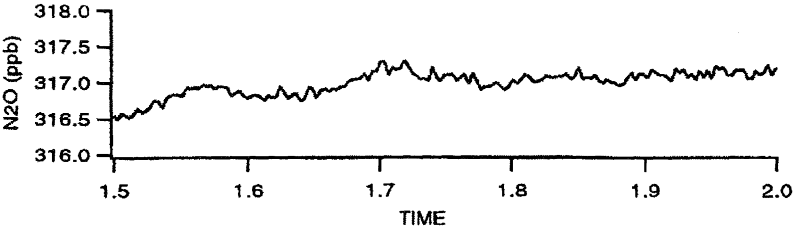

Figure 7. Longer term instrument precision for N_2O monitoring calibration gas for one half-hour period.

for these species. In addition, the low ambient concentrations of these gases make their detection even by TDL absorption difficult.

In an attempt to overcome some of these difficulties, we have designed a sampling cell with an aerodynamic inlet that minimizes the effects of surface absorption and desorption on the walls of the cell and the inlet. The larger volume of this cell, 3 l, provides a smaller surface-to-volume ratio, allows a longer pathlength to increase the detection sensitivity, and yet is small enough for subsecond time response using a modest vacuum pump. Our present system has a nominal pathlength of 100 m which may be extended to 200 m by a slight change in mirror spacing (McManus *et al.* 1995).

Air enters the sampling cell (figure 8) through a sonic orifice at the entrance of a 1.9 cm diameter stainless steel tube, which then directs the gas flow over the back mirror into the main cell volume. The entrance block is contoured to provide a smooth transition region for flow expansion to minimize eddy recirculation regions in the cell. The flow exits around the periphery of the front mirror into an exhaust plenum leading to the vacuum pump.

The time response for this system to methane and for nitric acid are compared in figure 9. For methane, cylinder air with 2 ppm CH_4 was alternated with dry

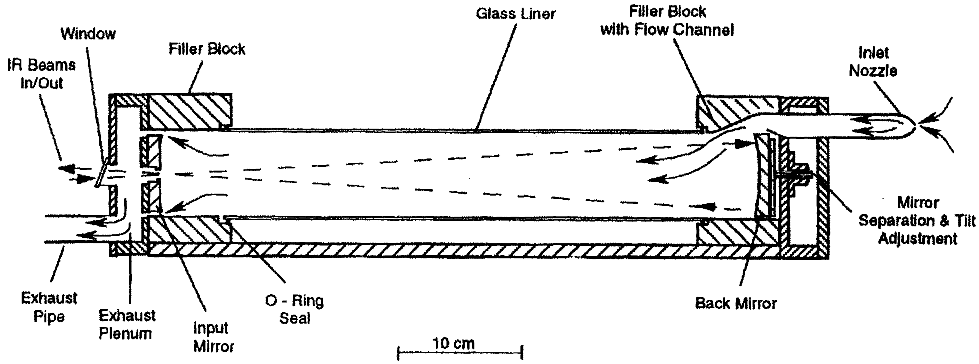

Figure 8. Fast response multiple pass absorption cell.

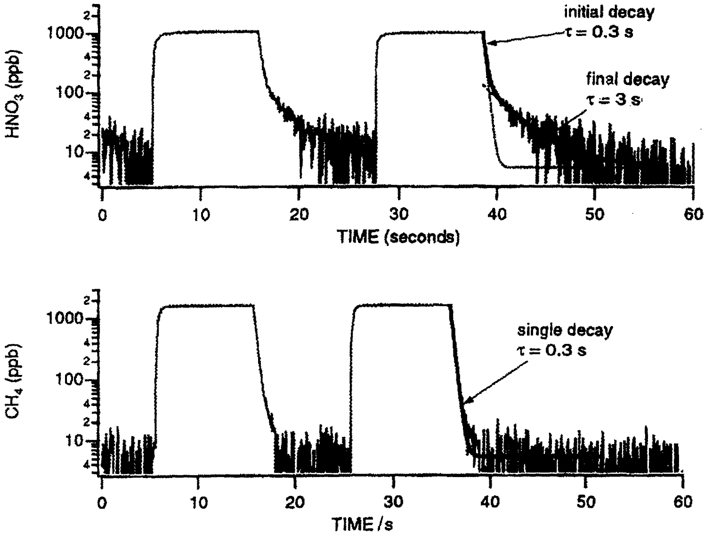

Figure 9. Response time comparison for methane and nitric acid.

nitrogen using a fast-response solenoid valve attached to the inlet orifice. A single exponential decay over two orders of magnitude is observed as the methane level approaches the 20 Hz noise level of about 5 ppb. The time constant for the decay of 0.3 s is equal to the 3 l volume of the cell divided by the measured pumping speed of 10 l s^{-1}. The single exponential nature of the decay indicates that the amount of gas trapped in recirculation zones or dead volumes within the cell is less than 1% of the total throughput.

Nitric acid vapour for these response time tests was generated by bubbling a small flow of nitrogen, less than 1% of the main cell flow, through a dilute nitric acid solution. A square-wave addition of HNO_3 was obtained by manually inserting and removing the bubbler exit tube into the main flow just in front of the sampling orifice. The observed decay plot was bi-exponential with an initial time constant of 0.3 s (identical to that for methane), but with a second decay time constant of 3 s due to absorption and desorption from the walls of the cell. The much shorter initial decay means that *ca.* 90% of the nitric acid vapour passes

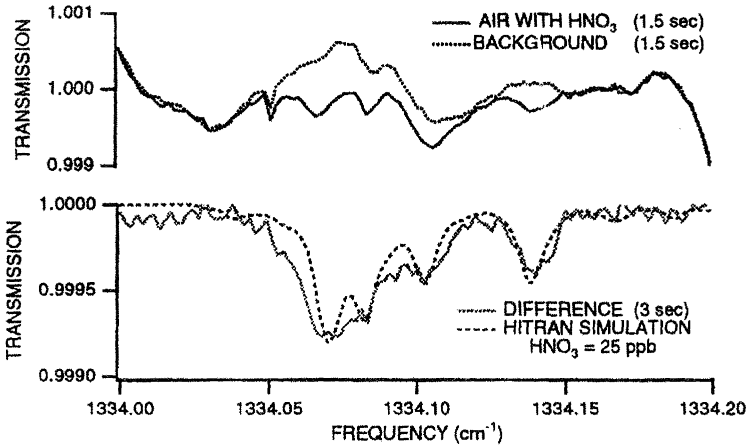

Figure 10. Nitric acid spectrum with fast response background subtraction.

through the cell without interacting with the walls under these flow conditions. Rapid response sampling even of sticky gases such as nitric acid may therefore be accomplished with proper design of the sampling cell and a sufficiently large pumping speed. Using this arrangement, eddy correlation measurements of nitric acid fluxes are feasible in principal.

Rapid-response sampling is also crucial to detect concentrations of gases such as HNO_3 at less than 1 ppb. With a pathlength of 100 m, 1 ppb of HNO_3 results in a fractional absorption of only 3×10^{-5} for the strongest lines in the 1330 cm^{-1} vibrational band. The main limitation in detecting fractional absorptions less than 10^{-4} with TDL spectroscopy is structure in the background spectrum caused either by optical interference fringes or by weak absorptions from other atmospheric species overlapping the spectral region of interest. Background subtraction can greatly enhance the detection sensitivity if the modulation of sample and background can occur on a time scale which is shorter than the variability of the background.

The effectiveness of background subtraction is shown in figure 10. The top two traces, with and without nitric acid, are displayed as transmission spectra by taking the difference between the transmitted intensity and a third order polynomial fitted to the background trace. Structure on the background trace due to interference fringes and absorption from other unidentified molecular species is apparent. The lower panel shows the direct difference between the two transmitted intensities. The difference spectra corresponds to 25 ppb of nitric acid as determined by comparison to the simulated calculation using spectral line parameters in the HITRAN database (Rothman *et al.* 1992). The signal-to-noise ratio is greater than 10 to 1, giving a detection limit of about 1 ppb in a signal-plus-background data collection time of only 3 s. Longer averaging times can be used to lower the detection limit as long as the switching time interval is sufficiently short (a few seconds) for the background to remain constant.

This method is applicable to other surface active trace gases including NH_3, O_3, SO_2, NO_2, HOCl and even to highly reactive species such as the HO_2 radical. We are presently developing modulation techniques, such as photolysis and chemical reaction at the sampling cell inlet, which could be selected to eliminate the trace gas but preserve the background gas mixture. Development of these techniques will greatly extend the applicability of TDL absorption for atmospheric-terrestrial exchange processes.

References

Anderson, S. M. & Zahniser, M. S. 1992 Open-path tunable diode laser absorption for eddy correlation flux measurements of atmospheric trace gases. *SPIE* **1433**, 167–178.

Edwards, G. E., Neumann, H. H., den Hartog, G., Thurtell, G. W. & Kidd, G. 1994 Eddy correlation measurements of methane fluxes using a tunable diode laser at the Kinosheo Lake Tower Site during the Northern Wetlands Study (NOWES). *J. geophys. Res.* **99**, 1511–1517.

Herriott, D. R., Kogelnik, H. & Kompfner, R. 1964 Off-axis paths in spherical mirror interferometers. *Appl. Opt.* **3**, 523–526.

Herriott, D. R. & Schulte, H. J. 1965 Folded optical delay lines. *Appl. Opt.* **4**, 883–889.

Hovde, C. D., Stanton, A. C., Meyers, T. P. & Matt, D. R. 1995 Methane emissions from a landfill measured by eddy correlation using a fast response diode laser sensor. *J. atmos. Chem.* (In the press.)

Kebabian, P. L. 1994 Off-axis cavity absorption cell with improved tolerance of fabrication errors. US Patent no. 5 291 265.

Kolb, C. E. 1991 Instrumentation for chemical species measurements in the troposphere and stratosphere. *Rev. Geophys. Suppl.*, pp. 25–36.

McManus, J. B., Kebabian, P. L. & Zahniser, M. S. 1995 Astigmatic mirror multiple pass absorption cells for long pathlength spectroscopy. *Appl. Opt.* (In the press.)

Rothman, L. S., *et al.* 1992 The HITRAN molecular database: editions of 1991 and 1992. *J. Quant. Spectros. Rad. Transfer* **48**, 469–507.

Schiff, H. I., Hastie, G. W., Mackay, G. I., Iguchi, T. & Ridley, B. A. 1983 Tunable diode laser systems for measuring trace gases in tropospheric air. *Environ. Sci. Technol.* **17**, 352A–364A.

Schiff, H. I., Mackay, G. I. & Bechara, J. 1994 The use of tunable diode laser absorption spectroscopy for atmospheric measurements. *Res. Chem. Intermed.* **20**, 525–556.

Verma, S. B., Ullman, F. G., Billesbach, D. B., Clement, R. J., Kim, J. & Verry, E. S. 1992 Eddy correlation measurements of methane flux in a northern peatland ecosystem. *Boundary-Layer Meteorol.* **58**(3), 289–304.

Werle, P. & Slemr, R. 1991 Signal-to-noise ratio analysis in laser absorption spectrometers using optical multipass cells. *Appl. Opt.* **30**, 430–434.

Wienhold, F. G., Frahm, H. & Harris, G. W. 1994 Measurements of N_2O fluxes from fertilized grassland using a fast response tunable diode laser spectrometer. *J. geophys. Res.* **99**, 16 557–16 567.

Discussion

D. Lloyd (*Microbiology Group, UWCC, Cardiff, U.K.*). Are the 'tails' of the response curves for difficult 'sticky' species temperature dependent? Could the surfaces be heated to diminish chemi- and physi-absorption processes?

M. S. Zahniser. I should think so, but we haven't tried that yet.

D. Lloyd. Does the sticky siloxyl coating work on steel as well as on glass?

M. S. Zahniser. No, the siloxyl coating works by chemically bonding to the silicon in the glass so that the hydroxyl end of the molecule is exposed to the gas phase.

D. Lloyd. Dr Zahniser rather glossed over ‘the grain of sand at the heart of the machine’. How does the diode work?

M. S. Zahniser. The tunable diode is of the Pb-salt type. Its temperature-dependent band gap allows rapid scanning through a frequency range appropriate to the near infrared absorption band of the gas by varying the electrical current applied to the diode.