DEVELOPMENT OF A TUNABLE DIODE LASER ABSORPTION SPECTROMETER FOR MEASUREMENTS OF THE ^{13}C/^{12}C RATIO IN METHANE

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ABSTRACT

A tunable diode laser absorption spectrometer (TDLAS) for measuring the ^{13}C/^{12}C ratio in methane has been developed. Using a triple path arrangement the spectra of the CH_4 sample, a $^{13}CH_4$/$^{12}CH_4$ isotope standard and pure $^{13}CH_4$ are recorded simultaneously and compared to evaluate the $^{13}CH_4$/$^{12}CH_4$ ratio of the sample, using a $^{13}CH_4$-$^{12}CH_4$ absorption line pair near 3007 cm^{-1}. Systematic effects due to variations in temperature, pressure, and optical density were measured for this rotational-vibrational transition pair. Optical interference effects are effectively suppressed by linearly polarizing the laser beam and using Brewster windows for gas cells and detectors. The overall δ^{13}C accuracy vs. the PDB scale is about $\pm$ 1 ‰ for a CH_4 concentration of 2.5 % (sample size: 5 μmoles = 0.11 STP cm^3 CH_4) using 36 cm long absorption cells. The future application of a multipass cell should allow measurement concentrations of CH_4 down to about 50 ppm. The main advantages of the new method are the short measurement time of 10-15 min for one sample and the direct measurement on the CH_4 molecule without the need to chemically convert it to CO_2. With the present accuracy the new method should be useful for the measurement of CH_4 sources, allowing a greater sample throughput compared to the conventional mass spectrometry technique.

1. INTRODUCTION

In recent years extensive effort has been invested in the evaluation of the global budget of atmospheric methane (e.g. Cicerone and Oremland, 1988; Ehhalt, 1988; Crutzen, 1991). In addition to direct measurements of CH_4 flux densities from various sources and extrapolation to the global scale, parallel CH_4 isotope measurements ($^{13}CH_4$, CH_3D, $^{14}CH_4$) provide important constraints on the relative contributions of the CH_4 sources since the isotopic signatures of the sources differ (Stevens and Engelkemeir, 1988; Quay et al., 1991). Also, isotopic studies are useful for understanding the processes occurring within the various sources (Levin et al., 1991). The CH_4 isotopic signatures depend, for example, on the isotopic composition of the original matter from which the methane is produced (Rust, 1981), on the CH_4 production processes (Whiticar et al., 1986), and on possible partial oxidation of the methane produced (Coleman et al., 1981). Despite our

understanding of some of the factors determining the isotopic composition of the CH_4, the global extrapolation of their effects is still very uncertain. For some entire classes of methane sources such as rice paddies or landfills no more than a few tens of individual $^{13}CH_4$ measurements are published, mainly because the measurement technique is very time consuming. However, the global isotope budgets are sensitive to the input assumptions for the mean isotope values of each source type and there is therefore a need for a greatly increased database on the source isotope signatures, especially their temporal and spatial variability.

$^{13}CH_4/^{12}CH_4$ measurements[1] have previously been performed by mass spectrometry, which requires oxidizing the CH_4 to CO_2 and measuring the $^{13}CO_2/^{12}CO_2$ ratio. In addition a separation of the methane sample from CO_2, CO, N_2O, H_2O and higher hydrocarbons is necessary (Lowe et al., 1991; Wahlen et al., 1989). We present here the development of a fundamentally different measurement method based on a tunable diode laser absorption spectrometer (TDLAS) which determines the $^{13}CH_4/^{12}CH_4$ ratio from infrared absorption lines of the two different isotopes. TDLAS has been used in recent years to measure concentrations of trace gases in the atmosphere utilizing their infrared absorptions (Schiff et al., 1987; Webster et al., 1988). The Pb-salt diode lasers operate in the 3-30 μm spectral region. The emission wavelength is coarsely determined by the exact chemical composition of the diode and is discontinuously tunable over approximately 100 cm^{-1} by varying the laser temperature ($\leq$ 100 K) and the laser current. The main advantages of TDLAS are low detection limits (in the sub-ppb region), very high specificity to the measured molecule due to the high spectral resolution, and short measurement times. A disadvantage of the presently available double heterostructure (DH) Pb-salt lasers is that they can change their mode characteristics especially after temperature cycling and that their lifetime is limited. We know of only a few efforts to apply TDLAS to measurements of naturally occuring isotope ratios: for $^{13}CO_2/^{12}CO_2$ (Wall et al.; Wong, 1985), $C^{18}O/C^{17}O/C^{16}O$ (Lee and Majkowski, 1986) and $N_2^{18}O/N_2^{16}O$ (Wahlen and Yoshinari, 1985). In this paper we report the first $^{13}CH_4/^{12}CH_4$ ratio measurements by means of TDLAS and discuss several effects which have limited the precision previously attainable for TDLAS isotope ratio measurements. The technique should also be applicable to CH_3D measurements and suitable line pairs have been identified. In both cases the measurements are performed directly on methane without chemical conversion.

2. EXPERIMENTAL

The experimental apparatus is illustrated in Fig. 1. The Pb-salt diode laser (output power: 50-150 μW in the main mode; Fraunhofer Institut für physikalische Meßtechnik, Freiburg, FRG) is mounted in a liquid

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[1]The $^{13}CH_4/^{12}CH_4$ ratios are expressed in the δ-notation:

$$\delta^{13}C = \left[\frac{R_{sample}}{R_{PDB}} - 1\right] \times 1000 [°/_{oo}]$$

where R_{sample} and R_{PDB} are the $^{13}CH_4/^{12}CH_4$ ratios of the sample and the used Pee Dee Belimnite (PDB) carbonate isotope standard (Craig, 1957).
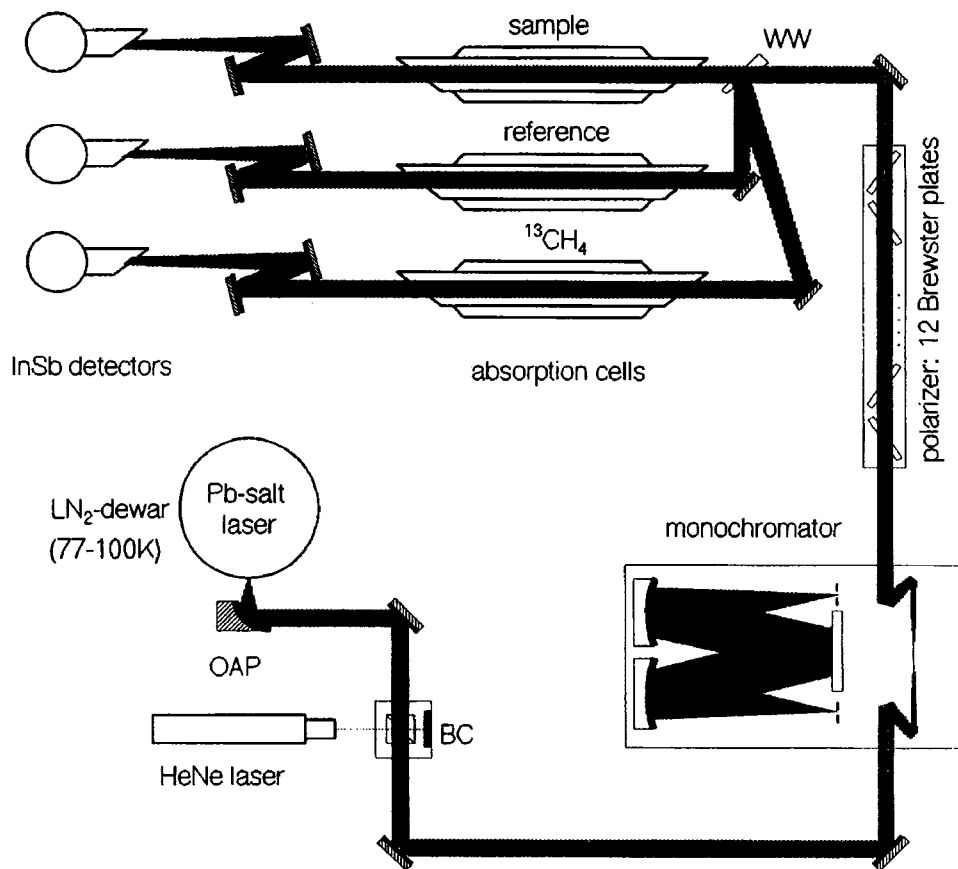
Fig. 1: Optical arrangement (abbreviations see text)

nitrogen Dewar and is temperature controlled in the range 77 to 100 K. The laser output is transmitted through a slanted CaF_2 window and collimated to a parallel beam by an off-axis-parabolic mirror (OAP) mounted outside the Dewar. A monochromator can be switched into the beam to measure the wavelength or to separate different laser modes if necessary. A set of 12 CaF_2 Brewster plates linearly polarize the laser beam before it is split into three parts using a wedged window (WW) as a beamsplitter. An absorption cell is located in each path and the laser power is focused onto three InSb detectors. The three cells contain 99.7% enriched $^{13}CH_4$, a methane isotope standard and the unknown sample, each in N_2 bath gas. The gas pressure in the cells is held at about 30 mbar to reduce pressure broadening and overlap of the spectral lines. The temperature of the gas is controlled by circulating water through a jacket around the cells. The water temperature is stabilized to $\pm$ 0.1 K by a thermostat. The bath gas is allowed into the cells via valves and the CH_4 sample introduced through septa using gas syringes. The gas contents are circulated by a pump to assure thorough mixing of the methane with the bath gas. The cell windows as well as the detector windows are mounted at the Brewster angle. For alignment purposes a HeNe laser beam can be co-aligned with the infrared beam using a beam combiner (BC).

The laser current is slowly ramped (computer generated with a scan time of 2 s) to tune the laser frequency over the absorption lines of interest. A 40 kHz sinusoidal modulation is added to the laser current. Each detector output is amplified and then demodulated at the second harmonic of the modulation frequency by a Lock-in Amplifier (LiA). The LiA outputs (time constant 10 ms) are digitized after passing two analog multiplexers. The isotope standard and the sample spectrum are sampled synchronously, while the $^{13}CH_4$ spectrum is digitized with a delay of a half sampling period (and subsequently shifted). The data are recorded with 1024 points per scan, and the analysis performed by a digital signal processor mounted inside an IBM compatible AT 80286 computer.

For calibration of the TDLAS system the isotopic composition of standard gases were measured by mass spectrometry using sample preparation as described by Bösinger (1990).

3. MEASUREMENTS

In order to cover a $^{13}CH_4$ and a $^{12}CH_4$ absorption line in one continuous scan a pair of adjacent lines was sought. Pb-salt diode lasers typically current tune 0.5-3.0 cm^{-1} within a single mode, so the line pair separation must be less than this value, and for efficient use of measurement time, preferably less than about 0.2 cm^{-1}. Also, since the natural isotopic abundance is about 1:100 and similar optical densities are advantageous, the line pair should have an approximately inverse ratio of line strengths (per molecule)[2]. Line pairs satisfying both these criteria generally arise from transitions having different ground state energies and therefore display strongly differing absorption temperature dependencies. From several candidate pairs, we chose a $^{13}CH_4$ line at 3007.15 cm^{-1} (Q branch of the ν_3 vibrational band, ground state: J=7, C=F1, N=2; E=293.2 cm^{-1}) and a neighbouring $^{12}CH_4$ line at 3007.08 cm^{-1} (Q branch of ν_3, ground state: J=16, C=F2, N=1 / C=F1, N=2 ; E=1417.1 cm^{-1} (Rothman et al., 1987)). It is important to note that the magnitude of the systematic errors discussed below, as well as the reported accuracy, refer strictly to the line pair selected. Several other suitable line pairs have also been identified.
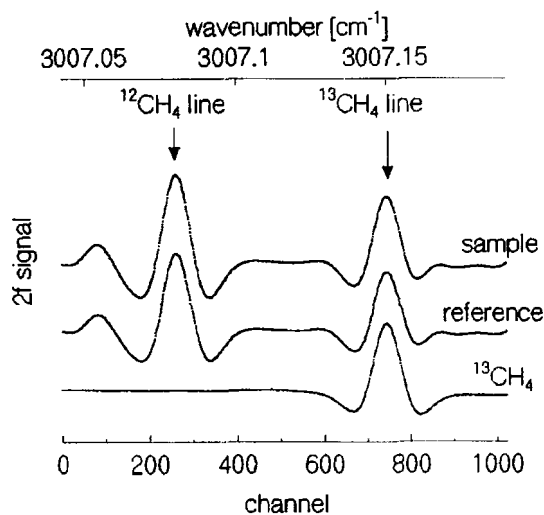

Fig. 2: Recorded 2f spectra of a CH_4 sample, a $^{13}CH_4/^{12}CH_4$ standard ($\delta^{13}C$ = -27.79 $\pm$ 0.04 ‰) and 99.7% enriched $^{13}CH_4$.

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[2]Alternatively line pairs of similar line strengths can be used with two different optical path lengths in a length ratio approximately inverse to the isotope ratio (Lee and Majkowski, 1986), however requiring a more complicated optical arrangement.

Fig. 2 shows a set of three simultaneously recorded 2f spectra for the three measurement cells. To compensate for drifts of the laser temperature and current, the position of the $^{13}CH_4$ peak is determined after each scan and the start voltage for the next ramp adjusted accordingly (line locking via laser current). The recorded spectra are treated by two multiple linear regressions. The first regression gives the proportionality constant between the $^{13}CH_4$ absorption signals in the reference cell and the $^{13}CH_4$ cell. This regression is carried out over the spectral region of the $^{13}CH_4$-line only:

$$spec._{^{13}CH_4}(i) = a_0 \, spec_{ref}(i) + polynomial \; terms \tag{1}$$

where spec(i) is the ith point of the indicated spectrum and a_0 is the regression coefficient. A second linear regression fits a linear combination of the reference spectrum, the $^{13}CH_4$ spectrum and a polynomial to the spectrum of the unknown sample over both lines:

$$spec_{sample}(i) = b_0 \, spec_{ref}(i) + b_1 \, spec._{^{13}CH_4}(i) + polynomial \; terms \tag{2}$$

The $\delta^{13}C$ value is obtained directly from the regression coefficients a_0, b_0 and b_1:

$$\delta^{13}C_{sample} = [1000 + \delta 13C_{ref}] \times \left[1 + \alpha \times \frac{a_o \times b_1}{b_0} \right] - 1000 \tag{3}$$

where α is a calibration factor discussed below. The error of the regression coefficients is evaluated as:

$$\sigma^2_{a_j} = s^2 \times \epsilon_{jj} \tag{4}$$

where ϵ_{jj} is the error matrix (inverse of the corresponding regression matrix) and s^2 the sample variance. A typical measurement consists of about 40 scans. Each scan is analyzed separately (on line) and the $\delta^{13}C$ values are subsequently averaged.

For calibration versus the PDB scale at least two standard gases are necessary, for which the isotopic compositions are determined by mass spectrometry. Currently the following two gases are used: S_0 (99.995 % pure methane, Messer Griesheim, Wiesbaden, FRG; $\delta^{13}C$ = -27.79 $\pm$ 0.04 ‰ (1σ)) and S_1 (a mixture of S_0 and 99.7 % pure $^{13}CH_4$ (l'Air Liquide, Düsseldorf, FRG), $\delta^{13}C$ = + 9.17 $\pm$ 0.06 ‰ (1σ)). S_0 is always used for the reference cell. The first step in the calibration procedure is to fill the sample and reference cell with S_0 and measure the offset (typically 2-3 ‰) produced by systematic effects which are discussed below. This offset has been found to drift only rather slowly ($\sim$ 30 min) and may be subtracted in subsequent measurements. To assure that the $\delta^{13}C$ scaling against the reference is correct, S_1 is measured against S_0 in a second step. The correction factor, α, introduced in eq.3 can be determined as:

$$\alpha = \frac{\delta^{13}C_{PDB}(S_1) - \delta^{13}C_{PDB}(S_0)}{\delta^{13}C_{TDL}(S_1) - \delta^{13}C_{TDL}(S_0)} \tag{5}$$

where the PDB subscript indicates the $\delta^{13}C$ values determined on the PDB scale by mass spectrometry and the TDL subscript the preliminary $\delta^{13}C$ values obtained by our evaluation procedure with $\alpha = 1$. Inserting α from eq.(5) into eq.(3) then yields the correctly calibrated $\delta^{13}C$ values on the PDB scale for the subsequent measurements[3]. Best results are achieved by carrying out an offset measurement after each sample measurement. The second step of the calibration procedure (i.e. determining α) need not be repeated often, because α is constant for fixed boundaries of the first regression.

4. RESULTS AND DISCUSSION

Potential Sources of Systematic Error

Constraints are put on the accuracy of the method by several systematic effects. In the pressure region near 30 mbar the resulting absorption lineshape is a Voigt profile (i.e. a convolution of a Lorentzian and a Gaussian profile) with $\gamma_L = 0.2\text{-}0.3\ \gamma_D$. The HWHM of a purely Doppler-broadened absorption line, γ_D, varies with the square root of the absolute temperature, whereas the pressure-broadened HWHM, γ_L, depends on the pressure as well as on the temperature of the gas. In addition, as mentioned above, the intensity ratio of the two lines depends strongly on temperature, since their ground state energies are different. Further, at optical densities of several percent the linear approximation of the Beer Lambert law does not hold with sufficient accuracy (10% optical density: deviation of $\sim 5\%$), thus the lineshape of the recorded 2f spectra depends on the optical density as well.
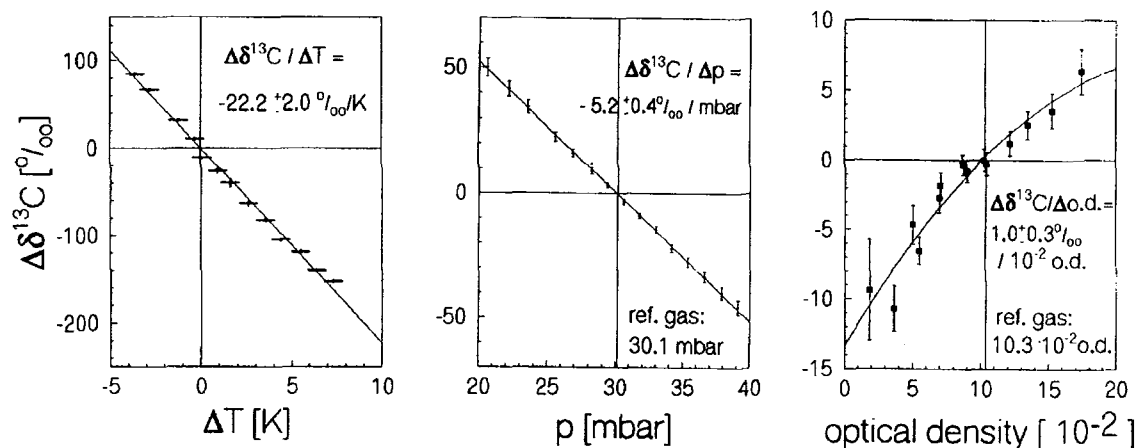

Fig. 3: Measurement of the $\delta^{13}C$ shift as a function of the difference in temperature, pressure and optical density between the sample and the reference cell.

These three parameters (temperature, pressure, and optical density) must therefore be controlled in all the three cells, especially in the sample and the reference cell. Systematic effects arising from deviations of

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[3] The calibration procedure for the applied line pair yields an α value of about 1.3 due to two weak $^{12}CH_4$ lines underlying the $^{13}CH_4$ line. However, despite the presence of these underlying features, the procedure as described leads to the correct coupling to the PDB scale.

these parameters among the different cells are investigated by varying one of these parameters in the sample cell and measuring the apparent $\delta^{13}C$ shift using the reference gas as sample. The measurements yielded a temperature coefficient of 22.2 ± 2 ‰/K, a pressure coefficient of 5.2 ± 0.4 ‰/mbar and an optical density coefficient of 1.0 ± 0.3 ‰/$(10^{-2}$ optical density) around optical densities of ~ 0.1 (cf. Fig. 3). Obviously the most critical parameter is the temperature, whereas the systematic error due to slight mismatches of pressure and optical density are well below 1 ‰. The currently used water-thermostatted cells yield an overall $\delta^{13}C$ acuracy of better than 1 ‰ (see below). The large temperature dependence is presumably one of the limiting factors for the achieved accuracy and the main cause for medium term drifts of the offset mentioned above. The rather low optical density and pressure coefficients allow correction of the $\delta^{13}C$ results, if the reference and sample cells are slightly mismatched.

Other systematic errors due to multiple beam interference (Fabry Perot Etalon fringes) can occur. In our case, the most important effect arises from multiple reflection within optical elements with two parallel surfaces, such as the windows used for gas cells and detectors, producing fringes with a free spectral range of 2-4 cm^{-1}. This interference causes the transmitted laser power to vary differently with wavelength in the different optical paths. The power variations strongly depend on laser beam alignment and its change with time due to vibrations and thermal effects (beam wander). These interferences were effectively suppressed by linearly polarizing the laser beam and mounting the windows for cells and detectors at the Brewster angle. Interference within the beamsplitter is prevented by its wedged shape.

In the application of TDLAS to methane field samples, the occurrence of neighbouring absorption lines from other gases can be of great importance. There is a weak H_2O absorption in the spectral region near the investigated $^{13}CH_4/^{12}CH_4$ pair (Rothman et al., 1987), which may interfere with the analyses, when much longer optical paths are used to decrease the concentration limit down to a few tens of ppm (see below). If unacceptable loss of accuracy were to occur for field samples, either the samples could be dried, or a new line pair could be selected.
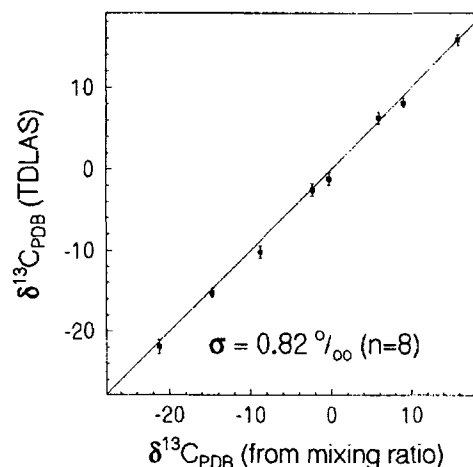

Fig. 4: $\delta^{13}C$ accuracy determined by measuring various mixtures from two gases of known isotopic composition ($\delta^{13}C = -27.79$ ‰, $+19.1$‰).

Accuracy vs. the PDB Scale

The accuracy vs. the PDB scale has been tested by mixing the reference gas ($\delta^{13}C = -27.79$ ‰) and a second gas with $\delta^{13}C = +19.1$ ‰ in various ratios at a constant optical density of 0.1 (CH_4 concentration 5 %). The mixing proportions and thus the isotopic composition were determined directly by the magnitude of the $^{12}CH_4$ absorption signals after injecting the first gas alone and after adding the second gas. The error in this evaluation of the isotopic composition is about $\Delta\delta^{13}C = 0.4$ ‰ due to the error in the mixing ratio determination. Afterwards the $\delta^{13}C$ values for the various mixtures

were measured employing the TDLAS system and compared to the evaluated values. The results are shown in Fig. 4. The standard deviation, σ, between the measured and the evaluated $\delta^{13}C$ values in this set of 8 samples is 0.8 ‰. These measurements also demonstrate the linearity of the $\delta^{13}C$ scaling against the reference. For field sample measurements further standard gases will be used to cover the typical $\delta^{13}C$ range of methane samples (-20 ‰ $\leq$ $\delta^{13}C$(atmospheric sources) $\leq$ -80 ‰).

The TDLAS isotope measurements reported by other authors cited above either employ a similar approach using adjacent absorption lines of comparable intensity (Wahlen and Yoshinari, 1985; Wong, 1985), or a dual path cell (Lee and Majkowski, 1986). The reported precision for the $^{13}CO_2/^{12}CO_2$ measurements by Wong is 2.5 ‰, for the $N_2^{18}O/N_2^{16}O$ measurements by Wahlen 0.4 ‰. In neither case, however, is there a discussion of systematic errors, in particular concerning the temperature dependence of measurements, although all the studies cited used line pairs with differing ground state energies.

5. CONCLUSIONS

We have demonstrated the feasibility of $^{13}CH_4/^{12}CH_4$ ratio measurement by means of TDLAS. At present, in order to achieve a $\delta^{13}C$ accuracy of $\Delta\delta^{13}C \leq 1$ ‰, optical densities of greater than 0.05 are necessary. This corresponds to concentrations of 2.5 vol% CH_4 in the 36 cm long absorption cells used. The planned application of a multipass reflection cell (White, 1976) with an absorption path length of approximately 200 m should decrease the concentration limit by a factor of 20000/36 to $\sim$50 ppm. This should be sufficient for most methane source measurements without sample pre-enrichment. The accuracy does not reach that obtained in mass spectrometer measurements (0.04-0.3 ‰) (Wahlen et al., 1989; Bösinger, 1990; Lowe et al., 1991; Quay et al., 1991), but is nevertheless sufficient for most investigations of methane sources since their temporal and spatial $\delta^{13}C$ variabilities are typically much greater than 1 ‰. Detailed methane source measurements have been limited by the substantial effort of sample preparation for mass spectrometer measurements. In contrast, the TDLAS measurements need only 10-15 min for one sample, including the calibration procedure.

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