A NOVEL MULTI-PASS CELL SYSTEM FOR MEASUREMENTS OF METHANE CARBON ISOTOPES USING A NEAR-INFRARED TUNABLE DIODE LASER

M. Niu [1,2*], G. Wang [1], G. Zhu [1], L. Wang [1], J. Mei [1], K. Liu [1], X. Gao [1*], W. Zhang [1]

[1] *Anhui Institute of Optics & Fine Mechanics, Chinese Academy of Sciences,
No. 350 Shushan Lake Road, Hefei, 230031, China; e-mail: niumingsheng@126.com, xmgao@aiofm.ac.cn*
[2] *Technology and Laser Institute, Qufu Normal University, Shandong Qufu, 273165, China*

A novel multi-pass cell laser absorption spectrometer to measure $\delta^{13}C$ diluted with nitrogen using a 1.658 μm near-infrared distributed-feedback laser was developed. The system temperature and pressure were measured with an accuracy of ±11 mK and ±3.2 Pa, respectively. The spectrometer is small, reliable, and compact. To minimize the temperature effect in absorbance ratio measurements, we used two appropriate absorption line pairs with nearly the same temperature dependences. The absorption spectrometer demonstrated high precision (a repetitive precision (reproducibility) of ~0.9‰ (1σ) is obtained at 300 ppmv methane concentrations). This concentration ratio is adequate for most CH_4 source characterization studies.

Keywords: isotope measurement, novel multi-pass cell, the stability of the system, measurement precise.

НОВАЯ МНОГОПРОХОДНАЯ КЮВЕТА ДЛЯ ИЗМЕРЕНИЯ ИЗОТОПОВ УГЛЕРОДА МЕТАНА С ИСПОЛЬЗОВАНИЕМ ПЕРЕСТРАИВАЕМОГО ДИОДНОГО ЛАЗЕРА, ФУНКЦИОНИРУЮЩЕГО В БЛИЖНЕЙ ИК ОБЛАСТИ СПЕКТРА

M. Niu [1,2*], G. Wang [1], G. Zhu [1], L. Wang [1], J. Mei [1], K. Liu [1], X. Gao [1*], W. Zhang [1]

[1]*Анхойский институт оптики и точной механики, Китайская академия наук,
Хэфэй, 230031, Китай; e-mail: niumingsheng@126.com, xmgao@aiofm.ac.cn*
[2] *Институт лазерных технологий, Цюйфуский педагогический университет,
Шаньдун Цюйфу, 273165, Китай*

Для измерения числа изотопов углерода, разбавленных азотом, разработан лазерный абсорбционный спектрометр с многопроходной кюветой, основанный на использовании лазера с распределенной обратной связью, излучающего в ближней ИК области спектра (λ = 1.658 мкм). С точностью ±11 мК и ±3.2 Па измерены температура и давление в системе. Спектрометр имеет малый объем, надежен и компактен. Для минимизации влияния температуры на результаты измерений предложено использовать две пары линий поглощения с подобной температурной зависимостью. Абсорбционный спектрометр продемонстрировал высокую точность (концентрации измеряемых изотопов ~0.9‰ в метане, концентрация которого 300 м.д. по объему). Данное соотношение концентраций удовлетворяет исследованию большинства источников CH_4.

Ключевые слова: измерение изотопов, многопроходная кювета, стабильность системы, точное измерение.

Introduction. Methane is a significant long-living greenhouse gas emitted from multiple natural and anthropogenic sources. It plays a central role in the chemistry of the troposphere [1, 2]. Isotopic analysis of atmospheric CH_4 provides insight into the processes producing and consuming it [3].

Measurements of ^{13}C and ^{2}H in methane by the mass spectrometry method require converting CH_4 into CO_2 and H_2O (and, consequently, into H_2) because $^{13}CH_4$ and $^{12}CH_3D$ components differ slightly in mass (below the resolution of the system) [4, 5]. So it is difficult to carry out real-time measurements of the $^{13}CH_4$

isotope. In contrast, optical techniques based on infrared absorption spectroscopy offer a useful alternative which can easily distinguish the mass of the isotopes and the configuration of the atoms in a molecule without any chemical conversion and possible interference by other hydrocarbons. Off-axis integrated cavity output spectroscopy (Off-axis ICOS), infrared cavity ring-down spectroscopy, cavity-enhanced spectroscopy [6–9], and Fourier transform infrared (FTIR) spectroscopy [10] are often used to measure methane. Among these laser-based techniques, tunable diode laser absorption spectroscopy (TDLAS) has obvious advantages for in situ isotopic composition measurements within the infrared spectral region. The distributed feedback compact laser (DFB) can be the best choice for measuring a variety of trace gases. DFB lasers have a narrower line width and better stability and discriminate closely related lines of different isotopes at specific wavelengths. Moreover, they permit realizing real-time measurements. For these reasons, we focused on the development of a near-IR multi-pass cell system able to analyze methane for slurry gas from oil wells and natural gas detection. Then we developed a method for the $\delta^{13}C$ measurement based on TDLAS, in which we determined the $^{13}CH_4/^{12}CH_4$ ratio from the intensities of infrared absorption lines of the isotope pairs. It should be noted that the latest TDLAS developments and applications have made possible fast and accurate measurements of methane and $\delta^{13}CH_4$ concentrations, for example, in anaerobic digesters [11] and deep sea seepage [12], but still at methane concentrations exceeding 500 and 1000 ppm, respectively.

We present here, as a new approach, a direct $\delta^{13}C$ measurement method based on TDLAS in which we determine the $^{13}CH_4/^{12}CH_4$ ratio from the intensities of infrared absorption lines of the corresponding isotope pairs with a 1.658-µm DFB laser using a novel multi-pass cell.

Experimental setup and methods. The setup shown here is based on the Beer–Lambert law and continuous tuning of the diode laser wavelength via modulation of the laser current. The light emitted by the laser is collimated and guided along the measurement path. After passing through the absorption cell, the light is focused on a photoelectric detector. The resulting photocurrent is directly digitalized including all offsets and disturbances. The isotope absorption coefficient ratio is defined as follows [13]:

$$R^{13CH_4} = \frac{\alpha(\nu^{13CH_4})}{\alpha(\nu^{12CH_4})} = \frac{\ln\left(I_0(\nu^{13CH_4})\big/I(^{13CH_4})\right)}{\ln\left(I_0(\nu^{12CH_4})\big/I(^{12CH_4})\right)}, \tag{1}$$

where $I_0(\nu)$ and $I(\nu)$ are the incident and transmitted intensities, respectively, $\alpha(\nu)$ is the absorption coefficient, which is proportional to the concentration of absorbing molecules, and ν^{12CH_4} and ν^{13CH_4} are the resonant transition frequencies of $^{12}CH_4$ and $^{13}CH_4$, respectively. The δ-value of the isotope absorption ratio (IAR) in ‰ is then given by

$$\delta^{13CH_4} = \left(R^{13CH_4}_{sample}\big/R^{13CH_4}_{working\ standard} - 1\right)\times 1000\%. \tag{2}$$

The selection of suitable absorption lines for methane isotopic ratio measurements is also one of the most important aspects in the setup design since the choice of absorption lines has a direct impact on the setup characteristics (namely, sensitivity, precision, and selectivity). To fall within the current-scan range of the laser, the lines must be interference-free and located close to each other (< 0.5 to 1 cm^{-1}). Additional requirements are that the lines are of nearly equal strengths and with low temperature dependences. Bearing this in mind, we selected the isotope lines of 6039.0246 and 6039.1537 cm^{-1}, whose intensities are 3.892×10^{-23} and 1.583×10^{-23} cm^{-1}/(molecule/cm^2), respectively. The application of these line pairs does not require any compensation for the isotope abundance by different optical lengths and enables us to record them quickly using a single light source. The key advantage of the single cell measurement is that the influence of the optical path difference on the delta value is almost completely eliminated.

It is important to control the precision of the experimental conditions, such as temperature and pressure, otherwise the results must be corrected. However, most authors pay little attention to the issue of control of the isotope measurement conditions with TDLAS. This report discusses in detail the temperature and pressure control of the isotope measurement system. We selected a novel compact dense-pattern multi-pass cell (DP-MPC), shown in Fig. 1. The DP-MPC consisted of two silver-coated concave spherical mirrors separated by a distance of 12.5 cm. The laser beam passed 239 times between the spherical mirrors having a reflectivity of 99.99% and the same curvature (caused by an effective absorption length of 29.8 m) [14].The selected lines in our isotope measurement had nearly equal low state energies, and for the measurement process there was no need to compensate and equalize the signal levels caused by the different natural abundance ratio of $^{13}CH_4/^{12}CH_4$. On the other hand, the weak $^{12}CH_4$ lines, generally appearing from rovibronic

transitions with much higher ground-state energies than the $^{13}CH_4$ lines, resulted in the higher temperature dependence of the $\delta^{13}C$ measurements. This temperature dependence $\Delta S/\Delta T$ is proportional to the difference of the ground state energies (E) of the corresponding transitions [15]

$$\Delta\delta/\Delta T \approx (\Delta E/kT^2)\times 1000\%,\qquad(3)$$

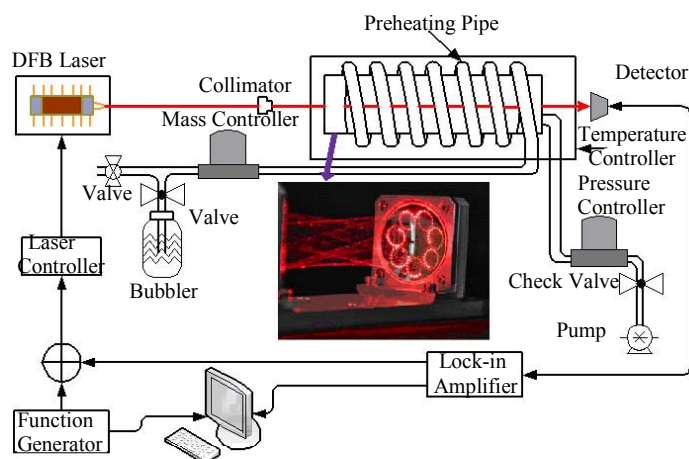where k is the Boltzmann constant and T is the absolute temperature.

Fig. 1. Scheme of the experimental setup. The embedded color picture is the photo of the multi-pass cell with the laser beam passing through it. The absorption cell is placed in an insulation box. After the absorption cell and preheated pipe were coiled with a heated belt, the insulation cotton packaged them.

In order to keep the long-term temperature of the DP-MPC steady without the temperature gradient of the measured sample gases in the absorption cell, the DP-MPC was enlaced with a heat film, and insulation cotton was wrapped around it. The sample temperatures were monitored and recorded using three calibrated platinum resistors (with an accuracy of 0.03°C and a precision of 0.01°C) attached to the outer wall of the absorption cell. The calibrated platinum resistors (Pt100) and the heat film were controlled by digital controllers (E5CN Omron Corporation). In order to avoid the temperature difference of the measured gases in the multi-pass cell, a 10-m long preheated copper tube was rolled into a spring, which was wrapped around the outside of the DP-MPC and heated by the heat film. The preheated copper tube was connected with the gas inlet of the absorption cell. The temperature of the preheated tube and the gas cell was compared with the laboratory temperature, which is monitored and controlled by the same calibrated platinum resistors and digital controllers, respectively. The whole measurement system was enclosed in a thermal insulation box with dimensions 40×40×30 cm.

In the weak absorption of isotope measurement, pressure broadening has to be considered, especially when two isotope absorption lines are close enough. The pressure broadening and shift of some lines in the $^{13}CH_4$ isotopomer were calculated and measured at room temperature by some researchers [15]. In this study, the CH_4 and N_2 gas was supplied by pressurized cylinders and metered using mass flow controllers (MFC) (D08-1G, Beijing Seven stars Electronics Co., Ltd.). All pressures of the multi-pass cell were measured and controlled using a temperature compensated capacitance type manometer manufactured by MKS (Type 247D, MKS Instruments, Inc., USA).

Before measuring the gas sample, the flowing nitrogen temperature and pressure at the arbitrary set flow velocity and the pressure in the DP-MPC were measured (Fig. 2). Through more than 4 h of the temperature and pressure measurements, it was found that the multi-pass cell could well maintain its temperature and pressure stability. The standard errors for temperature and pressure were 4.3 mK and 1.11 Pa. The fluctuation range of the temperature and pressure were 21.8 mK and 6.4 Pa.

The setup employed a fiber-coupled distributed feedback (DFB) diode laser (NLK1U5EAAA, NEL) that produced a 10 mW signal near 1.658 μm at a temperature of 40°C and with a current of 70 mA. The laser was tunable from 6037 to 6040 cm^{-1}, which is suitable for detecting $^{13}CH_4$ and $^{12}CH_4$ by probing isotope absorption lines located near 6039 cm^{-1}. The laser current and temperature were controlled with a commercial diode laser controller (ILX-Lightwave LDC-3724). Wavelength tunings were performed by
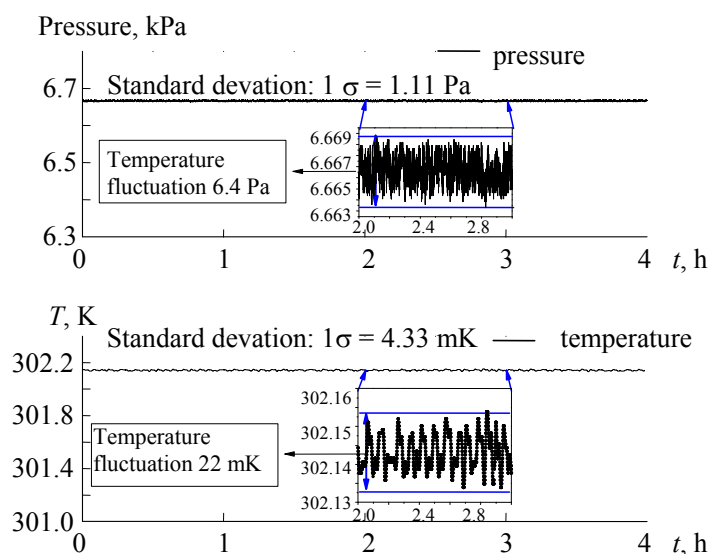
Fig. 2. The temperature and pressure of the measurement system
was kept at 302.14 K and 6.66 kPa for hours.

changing the laser temperature and current, respectively, within 0.01 mA and 0.01 K. Wavelength modulation and second harmonic detection were applied to enhance the detection sensitivity for the absorption band near the 6039 cm^{-1}. The modulation amplitude of the laser wavelength was adjusted so that the detected second harmonic signal was maximum. As in many tunable laser experiments using multi-pass cells, the precision and accuracy of the $^{13}CH_4/^{12}CH_4$ determination were limited by optical interference fringes in the absorption cell, as discussed by Sayres et al. [16]. In order to mitigate the noise appearing from optical interferences in the cavity, the laser was not aligned with the cavity axis but was displaced from this axis and, thus, was coupled to the cavity in an off-axis fashion.

The laser wavelength scan was realized by feeding an external triangular voltage ramp from a function generator (SPF05, Nanjing Sample Instrument Technologies Co., Ltd.) to the laser diode current, which swapped the laser wavelength near the absorption line at a rate of 5 Hz. The wavelength modulation was achieved by adding a 10 kHz sine wave to the DFB laser diode current. The sine wave was supplied by the sinusoidal signal output of a lock-in amplifier (Stanford Research Systems, Model SR830 DSP). The voltage ramp and the sine wave were combined with a home-made adder and then fed to the laser driver. The laser beam was collimated with a fiber-coupled collimator and subsequently injected into the compact DP-MPC. Then the output beam was focused onto a home-made photodetector. The demodulation of the detector outputs was conducted using lock-in amplifiers at the second harmonic frequency of $2f$ (f = 10 kHz is the modulation frequency of the sine wave). The parameters of the lock-in amplifier were set to be optimal. The demodulated signal was subsequently digitalized by a DAQ card (AC6115) and displayed on a laptop with LabVIEW software, and the results were stored on the PC.

In order to access the system measurement precise, the same kinds of gas were used as the sample and reference gases.

Results and discussion. Experiment data collection, background subtraction, window selection, linear regression, and data processing were integrated in the same program, which implemented the real time, continuous, and coordinated operation. The real time operation result of the program was the delta value of the isotopic abundance.

If one selects absorption transitions for the major and minor species with different line strengths, the absorption depths can be made more comparable. However, this introduces the problem of increased temperature sensitivity. Lines of different strengths generally have different ground state energies. A small thermal drift in the setup is translated into a drift of the measured δ-value [17], which leads to inaccurate measurement. Owing to this, only after the temperature and pressure of the preheat pipe and the DP-MPC, which were filled with the flowing sample gas, were steady for 30 min, were the isotope measurements started.

The pressure in the cell was kept at 1 kPa. The sample gas mass flow rate was controlled at 40 sccm by the MFCs during measurements. The gas cell temperature was set as 298 K, which was higher by 2 K than the laboratory temperature. Figure 3 shows an example set of simultaneously recorded $2f$ spectra used for measurements of the $\delta^{13}CH_4$ with a calibration gas containing 1000 parts in 10^6 by volume (ppmv) of CH_4. The time constant of the lock-in amplifier was set to 30 ms in combination with a 24 dB/octave slope and a sensitivity of 100 μV. The high signal-to-noise spectral average is shown in Fig. 3. From Fig. 3 we can get the signal to noise ratio $SNR = 1032$ for the first $^{12}CH_4$ absorption peak, and $SNR = 204$ for the $^{13}CH_4$ one. The detection sensitivity of the methane isotope was ~4.9 ppmv. Moreover, the 300 ppm methane was investigated. The delta value of $\delta^{13}CH_4$ was −7.5‰. In order to verify the accuracy and stability of the system, we collected data every 2 min, and the results are shown in Fig. 4. From these measurements we conclude that the precision of the method for the $\delta^{13}CH_4$ analysis is 9.26764×10^{-4} (0.93‰ in $\delta^{13}C$, 1σ).
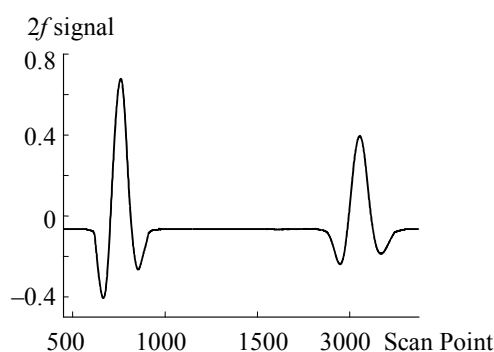

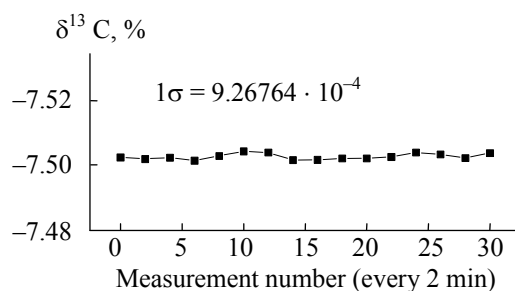Fig. 3. Simultaneously recorded $2f$ spectra of methane at 1000 ppmv.

Fig. 4. The $\delta^{13}C$‰ data every 2 min at a concentration of 300 ppmv.

We found that the methane isotope absorption line intensity at 1.658 μm was 1.583×10^{-23} cm^{-1}/ (molecule/cm^2). It was two orders of magnitude lower than for the 3 μm line. If the line intensity of $\sim 10^{-21}$ cm^{-1}/(molecule/cm^2) were selected and tens of milliwatts of output power lasers were used, the system would permit resolving uncertainties in sources such as natural wetlands, coal mining, rice paddies, etc.

Conclusion. We developed a method for determining the relative abundance of $\delta^{13}CH_4$ with a single novel DP-MPC system. This system does not need to balance the difference in path lengths for detection. The system can keep high stability and precise temperature and pressure during a long period. The ±0.93‰ (1σ) precision was obtained in the test experiment for 300 ppm sample. To our knowledge, this is the highest precision for $^{13}CH_4/^{12}CH_4$ analyses based on TDLAS with an analogous length absorption cell. In order to carry out the isotope measurement in the real atmosphere, the flow sample was measured. The whole measurement system was enclosed in a thermal insulation box of 40×40×30 cm size. Such a sensitive, low cost, long lifetime, compact and robust, handheld CH_4 sensor is very suitable for application in harsh environments and can be used for *in situ* measurements of methane anaerobic digesters and deep sea seepage. Incorporation of the presented method with such lasers beyond 3 μm will open a new era of high-sensitivity absorption spectroscopy and high-precision isotope analyses because most molecules have one to two orders of magnitude stronger absorption lines in this region than within the near-infrared region.

REFERENCE

1. C. J. Sapart, G. Monteil, M. Prokopiou, R. S. W. van de Wal, J. O. Kaplan, P. Sperlich, K. M. Krumhardt, C. van der Veen, S. Houweling, M. C. Krol, T. Blunier, T. Sowers, P. Martinerie, E.Witrant, D. Dahl-Jensen, T. Röckmann, *Nature*, **490**, 85–88 (2012).
2. G. Brasseur, S. Solomon, Aeronomy of the Middle Atmosphere, 2nd ed., Reidel, Dortrecht, The Netherlands (1986).
3. C. M. Stevens, F. E. Rust, *J. Geophys. Res.*, **87**, 4879–4882 (1982).
4. D. A. Merritt, J. M. Hayes, D. J. D. Marias, *J. Geophys. Res.*, **100**, 1317–1326 (1995).
5. M. Brass, T. Röckmann, *Atm. Meas. Technol.*, **3**, 1707–1721(2010).
6. D. S. Baer, J. B. Paul, J. B. Gupta, A. O'Keefe, *Appl. Phys. B: Laser. Opt.*, **75**, 261–265 (2002).
7. M. F. Witinski, D. S. Sayres, J. G. Anderson, *Appl. Phys. B*, **102**, 375−380 (2011).
8. Behzad Mortazavi, Benjamin J. Wilson, Feng Dong, Manish Gupta, Doug Baer, *Environ. Sci. Technol.*, **47**, 11676–11684 (2013).
9. Y. Chen, P. Mahaffy, V. Holmes, J. Burris, P. Morey, K. K. Lehmann, B. Sherwood Lollar, G. Lacrampe-Couloume, T. C. Onstott, *Planet. Space Sci.*, **105**, 117–122 (2015).
10. Hans-Martin Niederer, Xiao-Gang Wang, Tucker Carrington Jr., Sieghard Albert Sigurd Bauerecker, Vincent Boudon, Martin Quack, *J. Mol. Spectrosc.*, **291**, 33–47 (2013).
11. F. Keppler, S. Laukenmann, J. Rinne, H. Heuwinkel, M. Greule, M. Whiticar, J. Lelieveld, *Environ. Sci. Technol.*, **44**, 5067–5073 (2010).
12. S. D. Wankel, Y.-W. Huang, M. Gupta, R. Provencal, J. B. Leen, A. Fahrland, C. Vidoudez, P. R. Girguis, *Environ. Sci. Technol.*, **47**, 1478–1486 (2012).
13. Kun Liu, Lei Wang, Tu Tan, Guishi Wang, Weijun Zhang, Weidong Chen, Xiaoming Gao, *Sensors Actuators B: Chem.*, **220**, 1000–1005 (2015).
14. J. S. Margolis, *J. Quant. Spectrosc. Radiat. Transfer*, **55**, 523–836 (1996).
15. K. Anzai, H. Sasada, N. Yoshida, *Jpn. J. Appl. Phys.*, **46**, 1717–1721 (2007).
16. D. S. Sayres, E. J. Moyer, T. F. Hanisco, J. M. St. Clair, F. N. Keutsch, A. O. O'Brien, N. T. Allen, L. Lapson, J. N. Demusz, M. Rivero, T. Martin, M. Greenberg, C. Tuozzolo, G. S. Engel, J. H. Kroll, J. Paul, J. G. Anderson, *Rev. Sci. Instrum.*, **80**, 044102(1−14) (2009).
17. J. B. McManus, M. S. Zahniser, D. D. Nelson, L. R. Williams, C. E. Kolb, *Spectrochim. Acta A: Mol. Biomol. Spectrosc.*, **58**, 2465–2479 (2002).