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Isotopic resolution of carbon monoxide and carbon dioxide by NIR diode laser spectroscopy[1]

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Abstract

Near-infrared (NIR) absorption spectroscopy with tunable diode lasers allows the simultaneous detection of the three most important isotopologues of carbon dioxide ($^{12}CO_2$, $^{13}CO_2$, $^{12}C^{18}O^{16}O$) and carbon monoxide (^{12}CO, ^{13}CO, $^{12}C^{18}O$). The flexible and compact fiber-optic tunable diode laser absorption spectrometer (TDLAS) allows selective measurements of CO_2 and CO with high isotopic resolution without sample preparation since there is no interference with water vapour. For each species, linear calibration plots with a dynamic range of four orders of magnitude and detection limits (LOD) in the range of a few ppm were obtained utilizing wavelength modulation spectroscopy (WMS) with balanced detection in a Herriott-type multipass cell. The high performance of the apparatus is illustrated by fill-evacuation-refill cycles.

Introduction

Optical sensing by near infra-red (NIR) absorption spectroscopy offers the opportunity to detect many organic and inorganic molecules simultaneously by using a tunable diode laser. Carbon monoxide and carbon dioxide are of great interest in various environmental, medical and industrial applications, including soil gas fluxes, atmosphere gas analysis, breath gas analysis or process gas monitoring.[1-4] Isotopic signatures can provide important information about biogeochemical processes.[5]

Isotope ratios are usually expressed in the so-called δ-notation in per mille (parts per thousand, ‰) relative to a given standard material. The carbon isotopic abundance is given relative to the so called "Pee Dee Belmnite" (PDB) standard (Eq. 1) while the isotopic analysis of the oxygen isotopologues is based on the "standard mean ocean water" (SMOW) (Eq. 2).

$$\delta^{13}\mathrm{C} = \left(\frac{\left(^{13}\mathrm{C}/^{12}\mathrm{C}\right)_{\mathrm{Sample}}}{\left(^{13}\mathrm{C}/^{12}\mathrm{C}\right)_{\mathrm{PDB}}} - 1 \right) \cdot 1000 \quad \text{(Eq. 1)}$$

$$\delta^{18}\mathrm{O} = \left(\frac{\left(^{18}\mathrm{O}/^{16}\mathrm{O}\right)_{\mathrm{Sample}}}{\left(^{18}\mathrm{O}/^{16}\mathrm{O}\right)_{\mathrm{SMOV}}} - 1 \right) \cdot 1000 \quad \text{(Eq. 2)}$$

Isotope-ratio mass-spectrometry (IRMS) is the method most currently used for isotope selective gas-analysis. Unaffected by concentration effects, very high precision is maintained on a routine-level of ± 0.1 ‰ for ^{13}C and 0.3 ‰ for ^{18}O isotopologues , allowing for observation and discussion of small effects.[6] Esler et al. reached a precision of ± 0.2 ‰ for $^{13}CO_2$ using high-resolution Fourier-Transform Infrared (FTIR) spectroscopy.[7,8]

For simultaneous detection of carbon monoxide and carbon dioxide isotopes, a flexible, versatile, multi-species sensing method, with high selectivity and resolution as well as operation in an easily accessible spectral range will be presented. NIR diode laser (DL) spectrometers show a variety of advantages: low cost NIR sources and detectors, high spectral resolution and no water vapor interference in the selected spectral range. The strong power of NIR diode lasers allows isotopic resolution even if the overtone band intensities are low. The analytical scheme has been expanded towards simultaneous detection of CO and CO_2 within one measurement cycle of 15 seconds. Isotope selective measurements of carbon dioxide yield a detection limit in the low ppm range for each species and a $\delta\ ^{13}C$ resolution of ± 1.0 ‰ at 3,000 ppm CO_2.[9,10] Similar detection limits and $\delta\ ^{13}C$ resolution for the three isotopologues of carbon monoxide have been obtained.

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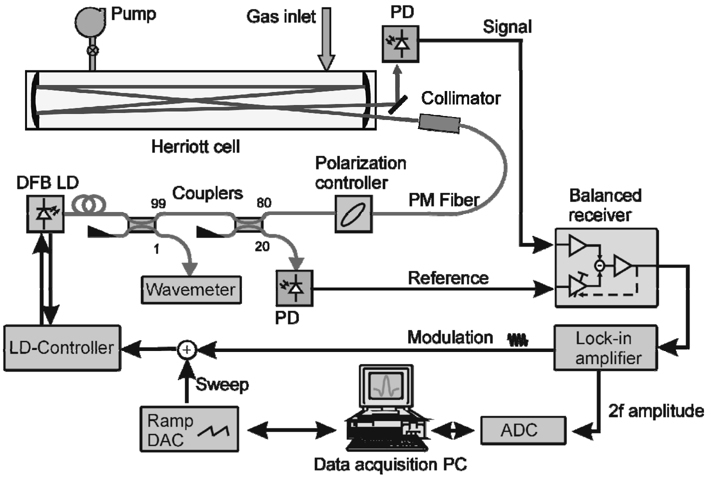
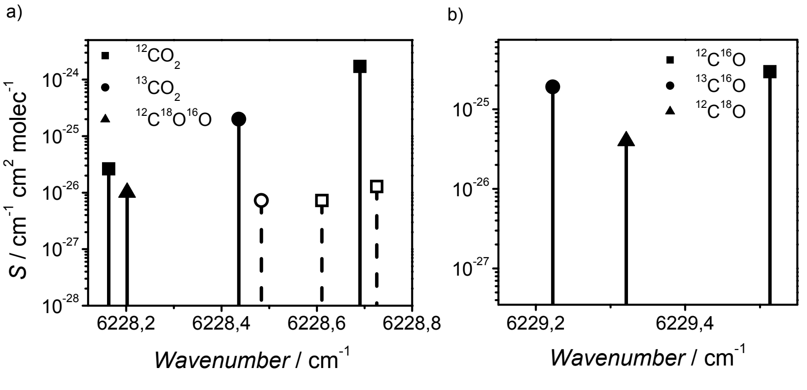
[1]

A compact and flexible fiber-optic distributed feedback (DFB) diode laser spectrometer has been developed. A fiber coupled DFB diode laser with high output power (20 mW) allows for the simultaneous detection of both species with high isotopic resolution in a Herriott-type multipass cell. Within a single frequency sweep, which is achieved by tuning the diode current, all three main isotopologues of CO_2 and CO can be measured simultaneously.[11] The overall experimental precision of the spectrometer has been evaluated by longtime measurements and fill-evacuation-refill cycles. Intensive examination of the spectral interference between the different species was carried out. The performance of the method has been validated in soil respiration experiments. Sensing for soil gas flux and breath gas analysis under real-world conditions will be feasible with a newly developed NIR-diode laser spectrometer using a shorter multipass cell (field-TDLAS) which will be suitable for field experiments.

Experimental setup and technical applications



The measurement technique is based on wavelength modulation (WM) spectroscopy for efficient noise-reduction and 2nd harmonic detection,[12,13] combined with electronically balanced signal receiving. In the domains of the $(30^01)_{III} \leftarrow (000)$ band for $^{12}CO_2$ and of $3 \leftarrow 0$ band of ^{12}CO which are located around 1605 nm, several absorption lines were analyzed (Fig. 2).[14] Based on a custom-built external cavity diode laser spectrometer with a 6000 – 6400 cm^{-1} tuning range,[9,10] a fiber-coupled DFB diode laser spectrometer (Fig. 1) allows for the isotope selective measurements of carbon monoxide (^{12}CO, ^{13}CO, $^{12}C^{18}O$) and carbon dioxide ($^{12}CO_2$, $^{13}CO_2$, $^{12}C^{18}O^{16}O$).[11] The setup is developed as a dual beam concept with electronically auto-balanced receiving. The reference path is split twice to a wavemeter (WM) (Burleigh WA-1100, Harpenden UK) for wavelength control. The signal beam is focused into a Herriott-type multi-pass cell (MPC1000S; Scienca Industira Tecnologia, Florence, Italy) with 1.12 m tube length, 8.25 l volume and a total light path of 100.9 m. Modulation and demodulation are controlled by a lock-in-amplifier (EG&G 7260 DSP Lock-In, Wokingham, UK). Gas mixtures with N_2 as inert gas and different CO and CO_2 concentrations are filled into the multipass cell at a total pressure of 60 mbar. Optical interference fringes, originating from sinusoidal background signals, were removed by background correction. Using a tunable DFB diode laser, fast switching between the two spectral ranges for isotopic resolution of CO and CO_2 is possible by varying the wavelength range of the diode laser.



Species	Wavenumber [cm^{-1}]	Linestrength S [$cm^{-1}cm^2molec^{-1}$]
$^{12}C^{16}O$	6229.513	2.978 x 10^{-25}
$^{13}C^{16}O$	6229.223	1.907 x 10^{-25}
$^{12}C^{18}O$	6229.321	4.007 x 10^{-26}
$^{12}C^{16}O_2$	6228.690	1.716 x 10^{-24}
$^{13}C^{16}O_2$	6228.436	2.002 x 10^{-25}
$^{12}C^{18}O^{16}O$	6228.202	1.007 x 10^{-26}
$^{12}C^{16}{}_2$	6228.164	2.427 x 10^{-26}

Fig. 2: Spectral range of a) CO_2 and b) CO (HITRAN data base).[14]
Tab. 1: Spectral data of CO_2 and CO (HITRAN data base).

Results and discussion

The fiber-optic setup of the newly developed TDLAS increases the mechanical stability of the spectrometer and reduces the optical fringes compared to our previous method.[9] Furthermore, the DFB diode laser has a larger output power (~ 20 mW) compared to the ECDL (~ 5 mW) and a larger mode-hopping free scan range. The use of the DFB diode laser realizes the simultaneously isotopic resolution of the main three isotopologues of carbon monoxide and carbon dioxide. To optimize all parameters extensive measurement series with constant carbon dioxide concentrations and varying measurement pressures and oscillating amplitude have been carried out. Detailed discussions and results are described in Hörner et al.[9]

Calibration plots and limits-of-detections (LOD)

To evaluate the sensitivity of the spectrometer, carbon dioxide or carbon monoxide in various concentrations (0 - 1 vol.-% of the analyte gases in nitrogen) were filled into the multipass cell and absorption spectra were measured. The resulting spectra of carbon monoxide and carbon dioxide are shown in the Figs. 3a and 4a, respectively. A plot of the line center amplitudes (A_{2F}) of the ^{12}C and ^{13}C isotopologues vs. the total gas concentration yielded excellent linearity for both gases (Figs. 3b, 4b). Detection limits of 15 ppm for ^{12}CO, 14 ppm for $^{12}C^{16}O_2$, 1 ppm for ^{13}CO, and 7 ppm for $^{13}CO_2$ were obtained, assuming a relative percentage of 1.124 for ^{13}C (PDB standard). Good linear regressions for the line center amplitudes of the ^{18}O isotopologues with detection limits of about 8 ppm for carbon monoxide and 10 ppm for carbon dioxide were acquired, according to a relative isotopic proportion of 2.005 ‰ of the ^{18}O isotopologues (SMOW standard). Obviously, the detection limits were constrained to residual baseline noise, which cannot be completely eliminated by background corrections. The given LOD are calculated according to Eq. 3 from the standard deviation of the intercept ($\sigma(A_0)$, in Volts) and the slope (m, in Volts per ppm) of the linear signal-concentration plot.

$$\mathrm{LOD} = \frac{2\sigma(\mathrm{A}_{2\mathrm{F}(0)})}{\mathrm{m}} \qquad \text{(Eq. 3)}$$

^{12}C/^{13}C and ^{16}O/^{18}O isotopic ratios of CO and CO_2

The high isotopic resolution and stability of the spectrometer were evaluated in fill-evacuation-refill cycles; iterative runs of CO or CO_2 using 0.5 vol.-% of total analyte gas concentrations were filled in the multipass cell, absorptions spectra were taken, the gas was removed and the cell was filled again. The results of 5 such cycles for a sample gas concentration of 0.5 vol.-% of both, CO and CO_2 illustrated in Figs. 5 and 6. The line center amplitudes show very low standard deviations for each species (Tab. 2). The corresponding isotope ratios ^{13}C/^{12}C and ^{18}O/^{16}O result in amplitude ratios with very small deviations (Figs. 5b, 6b). ^{13}C/^{12}C amplitude ratios with a mean value of 0.665 ± 0.009 for carbon monoxide and 0.182 ± 0.002 for carbon dioxide were obtained. The corresponding ^{18}O/^{16}O amplitude ratios result in a mean value of 0.165 ± 0.002 for CO and 0.013 ± 0.002 for CO_2. However, for quantitative isotopic analysis, calibration plots with isotopically certified samples are necessary and are one subject of future work.

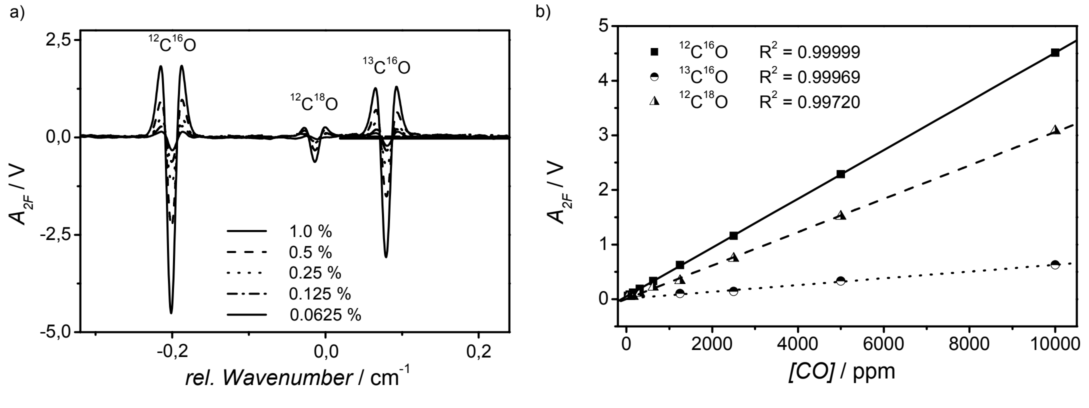


Fig. 3: a) 2nd harmonic spectra of CO in the concentration range 625 - 10,000 ppm at a total pressure of 60 mbar; b) line center amplitudes for $^{12}C^{16}O$, $^{13}C^{16}O$ and $^{12}C^{18}O$ versus the total concentration; symbols, experimental data; lines, linear fits.

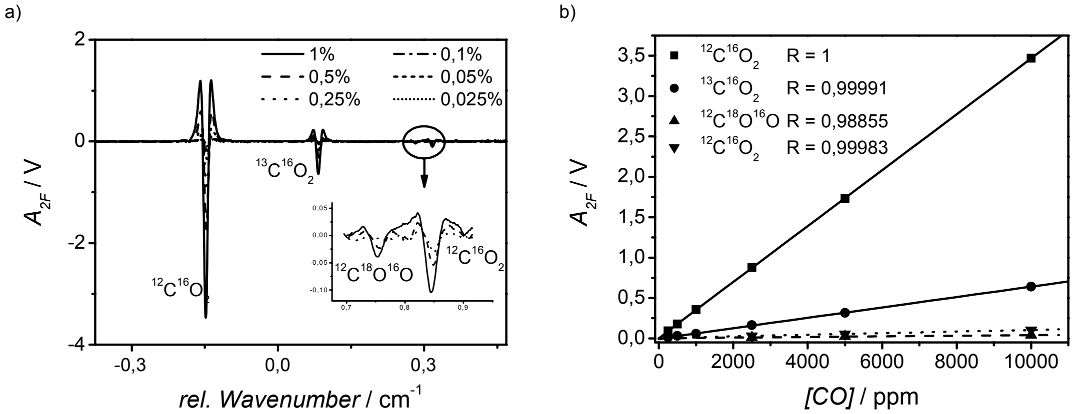


Fig.4: a) 2nd harmonic spectra of CO_2 in the concentration range 625 - 10,000 ppm at a total pressure of 60 mbar; b) line center amplitude for $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{12}C^{18}O^{16}O$ versus the total concentration; symbols, experimental data; lines, linear fits.

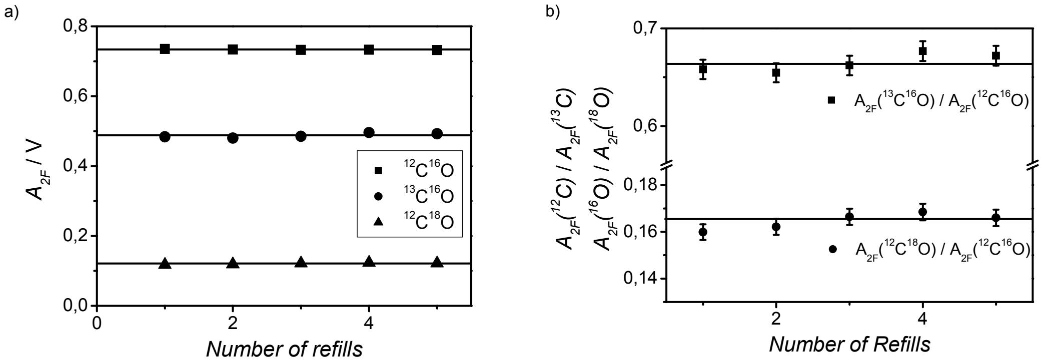


Fig. 5: Fill-evacuation-refill cycles: a) Line center amplitudes A_{2F} obtained for 5,000 ppm CO in N_2 at 60 mbar; squares: $^{12}C^{16}O$, circles: $^{13}C^{16}O$, triangles: $^{12}C^{18}O$; b) Ratio of the ^{13}C and ^{12}C amplitudes (squares) and of the ^{18}O and ^{16}O amplitudes (circles).

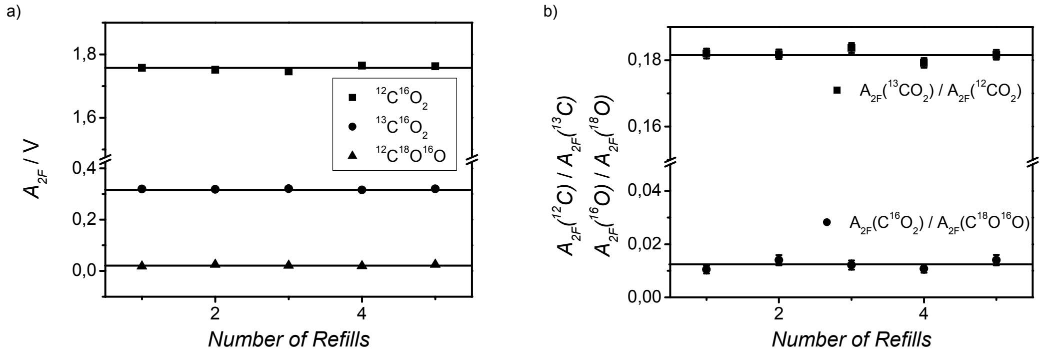


Fig. 6: Fill-evacuation-refill cycles: a) Line center amplitudes A_{2F} obtained for 5.000 ppm CO_2 in N_2 at 60 mbar; squares: $^{12}C^{16}O_2$, circles: $^{13}C^{16}O_2$, triangles: $^{12}C^{18}O^{16}O$; b) Ratio of the ^{13}C and ^{12}C amplitudes (squares) and of the ^{18}O and ^{16}O amplitudes (circles).

Species	A_{2F} / V	SD (A_{2F}) / V	$A_{2F}(^{13}C)$ / $A_{2F}(^{12}C)$	SD ($\delta^{13}C$)	$A_{2F}(^{18}O)$ / $A_{2F}(^{16}O)$	SD ($\delta^{18}O$)
$^{12}C^{16}O$	0.733	0.001	0.665	0.009		
$^{13}C^{16}O$	0.487	0.006			0.165	0.003
$^{12}C^{18}O$	0.121	0.002				
$^{12}C^{16}O_2$	1.756	0.008	0.182	0.002		
$^{13}C^{16}O_2$	0.319	0.002			0.012	0.002
$^{12}C^{18}O^{16}O$	0.022	0.003				

Tab. 2: Fill-evacuation-refill cycles: Line center amplitudes and isotopic ratios, including standard deviations.

Simultaneous isotopic analysis of CO and CO_2

Fig. 7 illustrates the spectra of a mixture of CO and CO_2 with a high isotopic resolution for all six isotopologues at a total concentration of 0.5 vol.-% for both components. The resulting spectra show no interference between the two sample gases. An uncomplicated switching between the two spectral ranges by varying the laser wavelength range still shows excellently resolved spectral lines with identical line center amplitudes and amplitude ratios, as been shown in the results above.

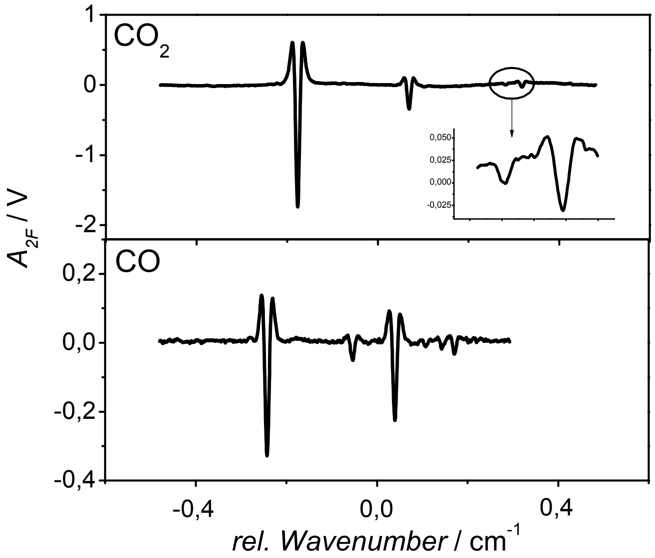


Fig. 7: Absorption spectra of a mixture of CO_2 (top) and CO (bottom) total concentration of 0.5 vol.-% for each gas without any interferences.

Conclusions

The presented TDLAS combines flexibility and versatility by allowing sensitive and isotope selective measurements of carbon monoxide and carbon dioxide. Calibration plots of the line center amplitudes dependent on the total CO or CO_2 concentrations show excellent linearity and cover a dynamic range of at least four orders of magnitude. The high precision of the instrument confirms the performance of the chosen experimental approach and offers a broad range of applications. There was no cross-sensitivity between the analyte gases or towards water vapour. Thus, the TDLAS offers the opportunity for simultaneous carbon monoxide and carbon dioxide isotopic sensing without sample preparation. With a shorter multipass cell, a mobile fiber-optic diode laser spectrometer accessible for field experiments (field-TDLAS) will soon be completed. Another emphasis of future work will be the extension of the spectrometer for a wider range of analyzable gases. The wide spectral range of available DFB diode lasers in the regime around 1600 nm offers the opportunity for isotopic analysis of further gases like methane, using the same experimental setup and switching between the different laser types.

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References

1 N. Buchmann, J.R. Ehleringer, "CO_2 concentration profiles, and carbon and oxygen isotopes in C_3 and C_4 crop canopies", *Agric. For. Meteorol.* **89**, 45-58, 1998.

2 E.R. Crosson, K.N. Ricci, B.A. Richman, F.C. Chilese, T.G. Owano, R.A. Provencal, M.W. Todd, J. Glasser, A.A. Kachanov, B.A. Paldus, T.G. Spence, R.N. Zare, "Stable isotope ratios using cavity ring-down spectroscopy: Determination of C-13/C-12 for carbon dioxide in human breath", *Anal. Chem.* **74** (9), 2003-2007, 2002.

3 U. Tsunogai, F. Nakagawa, D.D. Komatsu, T. Gamo, "Stable carbon and oxygen isotopic analysis of atmospheric carbon monoxide using continuous flow isotope ratio MS by isotope ratio monitoring of CO", *Anal. Chem.* **74** (22), 5695-5700, 2002.

4 S. Kato, H. Akimoto, T. Rockmann, M. Braunlich, C.A.M. Brenninkmeijer, "Stable isotopic compositions of carbon monoxide from biomass burning experiments", *Atmos. Environ.* **33** (27), 4357-4362, 1999.

5 G. Gagliardi, R. Restieri, G. Casa, L. Gianfrani, "Chemical and isotopic analysis using diode laser spectroscopy: applications to volcanic gas monitoring", *Opt. Lasers Eng.* **37** (2-3), 131-142, 2002.

6 I. T. Platzner, *Modern Isotope Ratio Mass Spectrometry*, Wiley & Sons, Chichester, 1997.

7 M.B. Esler, D.W.T. Griffith, S.R. Wilson, L.P. Steele, "Precision trace gas analysis by FT-IR spectroscopy. 1. Simultaneous analysis of CO_2, CH_4, N_2O, and CO in air", *Anal. Chem* **72**, 206-215, 2000.

8 M.B. Esler, D.W.T. Griffith, S.R. Wilson, L.P. Steele, "Precision trace gas analysis by FT-IR spectroscopy. 2. The $^{13}C/^{12}C$ isotope ratio of CO_2", *Anal. Chem* **72**, 216-221, 2000.

9 G. Hörner, S. Lau, Z. Kantor, H.-G. Löhmannsröben, "Isotope selective analysis of CO_2 with tunable diode laser (TDL) spectroscopy in the NIR", *Analyst* **129**, 772-778, 2004.

10 G. Hörner, S. Lau, H.-G. Löhmannsröben, "NIR-diode laser spectroscopy for isotope-selective sensing of soil-respired carbon dioxide", *Remote Sensing and Modelling of Ecosystems for Sustainability*, W. Gao, D.R. Shaw (eds.), Proc. SPIE, Vol. **5544**, 47-54, 2004.

11 R. Engelbrecht, "A compact NIR fiber-optic diode laser spectrometer for CO and CO_2: analysis of observed 2f wavelength modulation spectroscopy line shapes", *Spectrochim. Acta* **A 60**, 3291-3298, 2004.

12 P. Werle, "A review of recent advances in semiconductor laser based gas monitors", *Spectrochim. Acta* **A 54**, 197-236, 1998.

13 P. Kluczynski, J. Gustafsson, A.M. Lindberg, O. Axner, "Wavelength modulation absorption spectrometry – an extensive scrutiny of the generation of signals", *Spectrochim. Acta* **B 56**, 1277-1354, 2001.

14 L.S. Rothman, C.P. Rinsland, A. Goldman, S.T. Massie, D.P. Edwards, J.M. Flaud, A. Perrin, C. Camy-Peyret, V. Dana, J.Y. Mandin, J. Schroeder, A. McCann, R.R. Gamache, R.B. Wattson, K. Yoshino, K.V. Chance, K.W. Jucks, L.R. Brown, V. Nemtchinov, P. Varanasi, "The HITRAN molecular spectroscopic database and HAWKS (HITRAN atmospheric workstation): 1996 edition", *J. Quant. Spectrosc. Radiat. Transf.* **60** (5), 665-710, 1998.