ELSEVIER

Spectrochimica Acta Part A 58 (2002) 2389–2396

SPECTROCHIMICA
ACTA
PART A

www.elsevier.com/locate/saa

Determination of the $^2H/^1H$, $^{17}O/^{16}O$, and $^{18}O/^{16}O$ isotope ratios in water by means of tunable diode laser spectroscopy at 1.39 μm

E.R.Th. Kerstel [a,*], G. Gagliardi [b], L. Gianfrani [b], H.A.J. Meijer [a], R. van Trigt [a], R. Ramaker [a]

[a] *Department of Physics, Center for Isotope Research, University of Groningen, Groningen, The Netherlands*
[b] *Dipartimento di Scienze Ambientali della, Seconda Universita' di Napoli, and INFM-Gruppo Coordinato Napoli 2, Caserta, Italy*

Abstract

We demonstrate the feasibility of the accurate and simultaneous measurement of the $^2H/^1H$, $^{17}O/^{16}O$, and $^{18}O/^{16}O$ isotope ratios in water vapor by means of tunable diode laser spectroscopy. The absorptions are due to the $\nu_1 + \nu_3$ combination band, observed using a room temperature, distributed feedback (DFB) diode laser at 1.39 μm. The precision of the instrument is approximately 3, 1, and 0.5‰ for the ^2H, ^{17}O, and ^{18}O isotope ratios, respectively, and is at present limited by residual optical feedback to the laser. The signal-to-noise, however, is superior to that obtained in a similar experiment using a color center laser at 2.7 μm. Replacing the current laser with a better unit, we are confident that a precision well below 1‰ is attainable for all three isotope ratios. The diode laser apparatus is ideally suited for applications demanding a reliable, cheap, and/or portable instrument, such as the biomedical doubly labeled water method and atmospheric sensing. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Isotope ratios; Water; Near-infrared tunable diode laser spectroscopy

1. Introduction

Analysis of isotope ratios is a powerful tool in modern science, providing information not accessible to gas concentration measurements alone. Several of the elements that are of biological, chemical, or geological importance occur naturally with two or more isotopes. This gives rise to different isotopomers of a given molecular species. For instance, there are nine stable isotopomeric forms of the water molecule with a molecular weight ranging from 18 to 22. A large variety of physical and chemical processes, such as evaporation and oxidation, discriminate among different isotopomers This so-called fractionation is often highly characteristic of the exact processes involved and can be exploited to obtain a deeper understanding of the processes themselves or the extent at which they are operative. It is this property that makes rare isotopes ‘perfect’ natural tracers for an overwhelming number of studies in, for example, wild animal behavior, food product

---

* Corresponding author. Tel.: +31-50-3634759; fax: +31-50-3634738.
E-mail address: kerstel@phys.rug.nl (E.R.T. Kerstel).

1386-1425/02/$ - see front matter
PII: S1386-1425(02)00053-7

authenticity, paleoclimatology, and global warming (green house gas characterization). For instance, isotopes can be used as tracers to study gas exchange between different compartments (reservoirs) of the environment. The $^{13}CO_2/^{12}CO_2$ ratio is extremely useful to constrain the global atmospheric CO_2 budget [1–5], but also finds applications as a biomedical diagnostic tool, e.g. in the quantification of the amino acid metabolism by means of a ^{13}C-labeled leucine test [6–8]. The $^{13}CH_4/^{12}CH_4$ and $^{12}CH_3D/^{12}CH_4$ isotope ratios in atmospheric methane give information on source and sink processes, including its different production pathways [9–11]. Isotope studies of water, arguably the molecule of highest environmental importance of all, find application in such diverse fields as hydrology, paleoclimatology [12–14], atmospheric chemistry, and biomedicine [15,16]. It is, therefore, discouraging that the traditional analytical tools available for measuring isotope ratios in water are far more cumbersome and inaccurate than for most other molecules. This is primarily due to the incompatibility with condensable gases of the common choice of technique, isotope ratio mass spectrometry (IRMS). Nowadays commercial machines are able that achieve an extremely high precision and a high sample throughput, having benefited from over 40 years of development. In the case of water, however, these cannot be fully exploited due to the need of extensive (chemical) sample preparation. Given IRMS' inability to work directly with water, the common solution has been to resort to oxygen isotope exchange between water and CO_2 and reduction of water to H_2. Both CO_2 and H_2 are easily analyzed using IRMS, for, respectively, ^{18}O and ^{2}H. Due to the prevalence of the $^{13}CO_2$ molecule, which shows up at the same mass as ^{17}OCO, the accurate determination of the $^{17}O/^{16}O$ isotope ratio in water (expressed in terms of $\delta^{17}O$, the relative deviation of the isotope ratio with respect to the international standard material Vienna Standard Mean Ocean Water, VSMOW) is virtually impossible. The chemical preparatory steps not only severely limit the over-all throughput, but often also compromise the attainable accuracy, and sometimes precision. In particular in the case of $\delta^{2}H$, as the reduction step is accompanied by a very large fractionation. The accuracy for $\delta^{2}H$ is further reduced by the substantial correction that has to be made for H_3^+-formation in the ion source of the IRMS. At the Groningen Center for Isotope Research we, therefore, turned our attention several years ago to optical methods when looking for a replacement of our water isotope systems (off-line CO_2 equilibration and uranium reduction). Spectroscopy, in particular in the near and mid infrared (the so-called finger print region), is extremely selective of the molecular species, as well as the specific isotopomer. Infrared spectroscopy, at sufficiently high spectral resolution, can, therefore, measure isotope ratios directly in the gas phase, on very small sample sizes and often in the presence of contaminants. Moreover, whereas with IRMS one or more isotopomers may show up at the same mass, this is not an issue with isotope ratio infrared spectroscopy (IRIS). Thus, IRIS is able to measure the $^{2}H/^{1}H$ and $^{18}O/^{16}O$ isotope ratios in water, and the $^{17}O/^{16}O$ ratio as well.

Using a direct absorption spectrometer, we have already shown that IRIS can be applied successfully [17] to the measurement of isotope ratios in ice-cores (paleoclimatology) [18] and in the biomedical double-labeled water technique to quantify an organism's energy expenditure [19]. The laser source used in this case, is a commercial solid-state infrared laser (color center laser; Burleigh Inc. FCL-20). Its good single-mode performance, high output power and very broad spectral coverage from 2.4 to 3.4 μm, encompassing the usually strong fundamentals of X–H (X = C, N, O, ...) stretching vibrations in most all molecules of environmental interest, make this laser ideally suited for our laboratory-based, research set-up. However, the FCL is also poorly suited to be implemented in a portable system due to its dependence on liquid-N_2 cooling, physical size and power consumption (the latter two caused by the need of an ion pump-laser). Moreover, tuning of the laser is not straightforward: wavelength changes are effected by simultaneously adjusting the length of the resonator cavity, an intra-cavity etalon, and a grating element; partly in feed forward, partly in an electronic feedback loop [20]. Tuning of the laser thus causes amplitude and frequency noise on the output. Also, the depth of frequency modulation is limited, since a modulation modulus comparable to the FSR of the cavity (280 MHz) will cause the laser to mode-hop. This prevents an easy implementation of the very sensitive technique of wavelength modulation spectroscopy (WMS) in the gas phase, even at mbar pressures.

In this paper we demonstrate that the accurate measurement of isotope ratios in water, using a frequency modulated, single-mode, distributed feedback (DFB) diode laser operating near 1.39 μm, is feasible. Lasers of this type (III–V) were originally developed for telecommunications at 1.5 μm, but over the past couple of years they have become available at a variety of wavelengths between 1.3 and 2 μm, interesting for environmental sensing and trace gas detection purposes. Their excellent characteristics in terms of output power, single-mode performance, tunability and frequency modulation, combined with their small size and low power consumption, make them ideal candidates for the development of a cheap and reliable spectrometer that may find acceptance also outside a research laboratory. As we will show, the loss of sensitivity associated with the excitation of an overtone vibration at 1.4 μm, as opposed to a fundamental at 2.7 μm, is easily compensated for by the use of a sensitive WMS, harmonic detection technique.

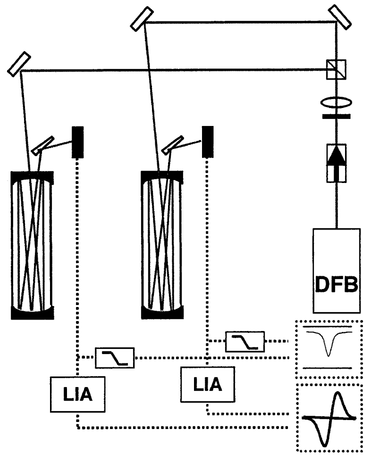

Fig. 1. Schematic representation of the experimental setup. The DFB diode laser includes optics that focus the beam through the optical isolator onto a 100 μm diameter pinhole, after which the beam is refocused onto the entrance of each gas cell by a 1 m focal length lens. Subsequently a beam splitter sends equal intensity beams to the two gas cells. The transmitted power signals are low pass filtered to obtain direct absorption profiles, and phase sensitively detected by means of lock-in amplifiers to obtain the WM spectra. The path in air is about 1 m and equal for both cells. The optical path length inside the multiple pass gas cells is 20.5 m in a 48-pass configuration.

2. Experimental details

The spectrometer is schematically shown in Fig. 1. It is based on a room-temperature InGaAsP/InP DFB diode laser, emitting about 1 mW in a single mode at a wavelength of 1392 nm. The laser's power supply and temperature controller were home-built [21], based on a modified version of the design by Libbrecht and Hall [22]. The optical path between the laser and the gas cells included a spatial filter with a 100 μm diameter pinhole to improve the spatial mode characteristics, and an optical isolator to prevent unwanted optical feedback. WMS with first harmonic detection was performed, the laser frequency being modulated at 19 kHz with a modulation index of about 2.2. The laser frequency was periodically scanned over the absorption features by means of a triangular wave, which modulated the injection current at a rate of 0.25 Hz. Frequency scans as large as 1 cm^{-1} were necessary in order to record rovibrational lines of the $H^{16}OH$, $H^{17}OH$, $H^{18}OH$, and HOD isotopomers in one scan. The absorption signals were recovered by phase sensitive detection using two digital lock-in amplifiers (Stanford Research SR830). The same signals were also low-pass filtered to obtain direct transmittance spectra. The data, sampled at a time interval of slightly less than 2 ms (1024-record length) were initially stored in the internal 16-bit wide buffers of the amplifiers, then transferred to a personal computer at the end of each scan. The lock-in time constant was 1 ms. Together with digital filtering at 24 dB per oct, this yielded an equivalent noise bandwidth of 78 Hz. Signal averaging over 20 scans was performed to further

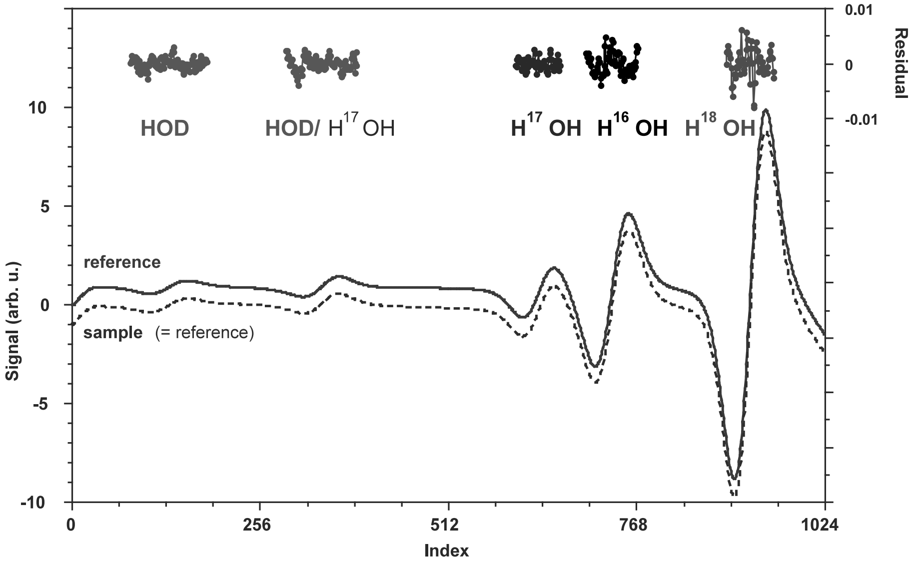

Fig. 2. Typical spectra, showing spectral features belonging to the four isotopomers of interest. The second feature from the left is due to two nearby absorptions of HOD and $H^{17}OH$ and is not used in the analysis. The spectra are not corrected for the increase in output power (from left to right) that accompanies the tuning of the laser.

improve the signal-to-noise ratio, resulting in a minimum detectable, fractional absorption of the order of 4×10^{-6} $Hz^{-1/2}$. One measurement ('delta-determination') takes 80 s, which includes the time needed to transfer the data to the PC and to wait for the next trigger at the start of a positive laser injection current slope. The S/N of the spectra shown in Fig. 2 is about 10 000 on the strongest feature (the RMS noise level amounts to 0.0009 in the units of the figure), corresponding to a S/N of 2×10^4 $Hz^{1/2}$ on a single scan. Absorption spectra were observed in two different multiple reflection gas cells simultaneously, one containing the sample, the other being filled with an isotopically well-characterized standard water (GS23: $\delta^2H = -41.0‰$, $\delta^{17}O = -3.16‰$, and $\delta^{18}O = -6.29‰$ with respect to VSMOW). The cells are passively temperature stabilized. As in the case of our color center laser apparatus, introduction of the 10 μl samples into the evacuated gas cells is done by means of syringe injection through a rubber septum, and results in a final pressure of about 13 mbar. Multiple reflection optics in both gas cells provided for an absorption path-length of 20 m, and a fractional absorption < 8%. The transmitted laser beams were focused on InGaAs photo-detectors. The remainder of the experimental set-up and the data analysis procedure are very similar or the same as for the 2.7 μm set-up. The relative deviations of the isotope ratios with respect to the reference material are determined by, for example in the case of ^{18}O:

$$\delta^{18}O = \frac{(^{18}n/^{16}n)_{\text{sample}}}{(^{18}n/^{16}n)_{\text{ref}}} - 1 = \frac{^{18}\alpha_s/^{18}\alpha_r}{^{16}\alpha_s/^{16}\alpha_r} - 1 = \frac{^{18}\varphi}{^{16}\varphi} - 1 \qquad (1)$$

Here n represents the molecular number density (in this case $H^{18}OH$ and $H^{16}OH$), α is the absorption coefficient (line intensity, equal to $-\ln[I/I_0]$), the superscripts label the isotopic species, and the subscripts refer to either the sample or reference spectrum. The intensity ratio φ is the ratio of the sample line intensity and that of the corresponding reference line. It is calculated in a least squares approximation in which the sample spectrum is fit, over a range extending one full-width-at-half-maximum, symmetric with respect to the center of the spectral feature of interest, to the sum of the corresponding region of the reference spectrum and a sloping baseline. For a more detailed discussion of the data analysis procedure we refer to the literature [17].

The spectral features selected for this study are listed in Table 1. On average their intensities are more than one order of magnitude weaker than the transitions we use for isotope ratio measurements at 2.7 μm.

3. Results and discussion

Fig. 2 shows typical spectra recorded with the 1.39 μm spectrometer. The two gas cells were filled with water of the same isotopic make-up. The upper panel shows the result of the least squares procedure in which the sample spectrum is fit in small sections around each spectral feature to the reference spectrum. The sample-to-reference line ratios determined in this manner are used to evaluate the isotope ratios of the sample (initially referenced to the GS23 local reference

Table 1
The rovibrational transitions used in this study

Isotopomer	Frequency (cm^{-1})	Intensity (10^{-24} cm mol^{-1})[a]	Temperature coeffficient (‰ K^{-1})[b]
$H^{18}OH$	7183.5864	6.2	+6.9
$H^{16}OH$	7183.6856	3.1	+5.7
$H^{17}OH$	7183.7354	1.2	−3.4
$H^{16}OD$	7183.9727	0.35	−2.5
$H^{16}OH$[c]	7184.1011	1.3	+27.0

Data were kindly provided by R.A. Toth and have partially appeared in the literature [24,25].

[a] For a natural abundance sample.

[b] Per mil relative intensity change at 296 K following a 1 K temperature increase, calculated from the ground state energies.

[c] This transition is not normally used. See the text.

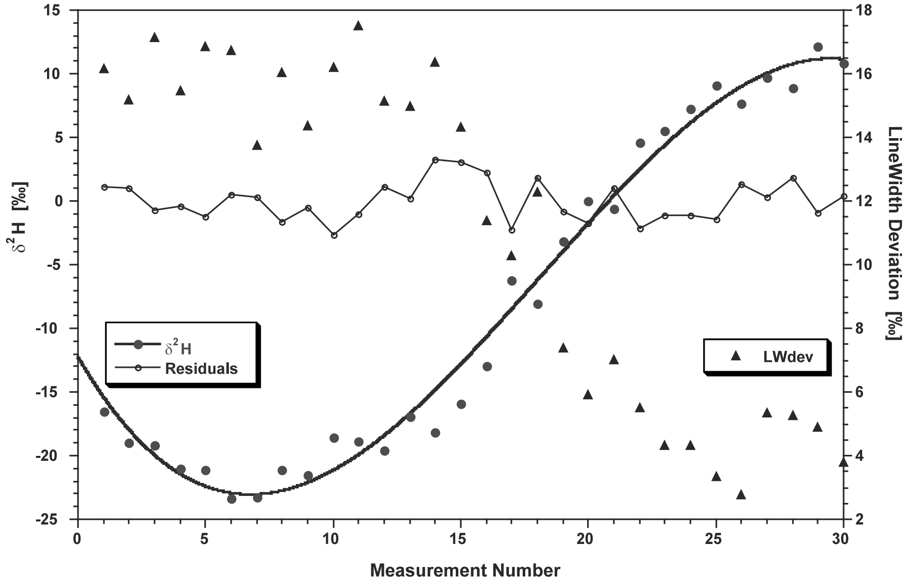

Fig. 3. The differential temperature dependence of the apparent D/H isotope ratio. The RMS deviation of the residuals (with respect to the smooth curve) amounts to 1.5‰.

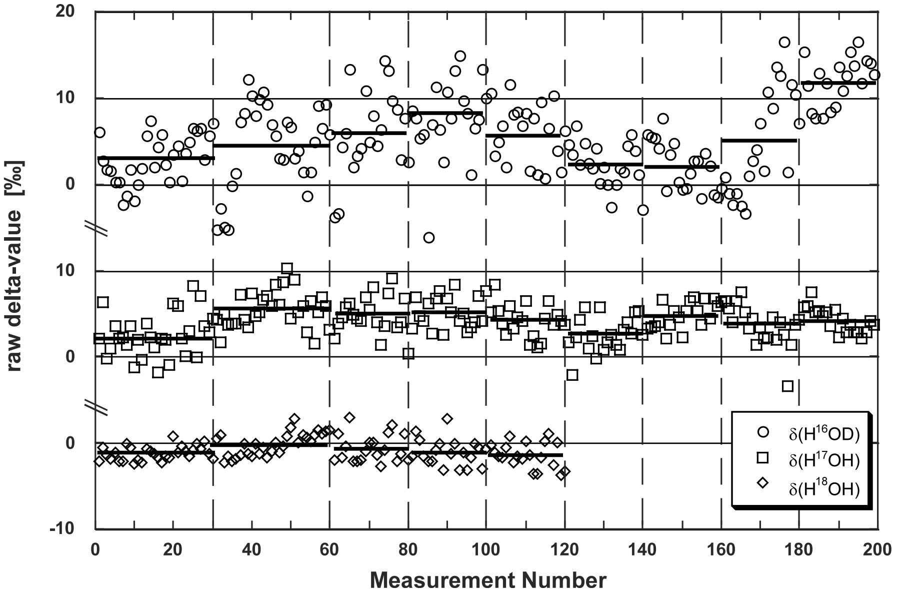

Fig. 4. Results of repeated individual measurements, including the mean values (solid horizontal lines) per series of Table 2.

material) [17]. Fig. 3 demonstrates the importance of temperature control. In this initial experiment the HOD and $H^{16}OH$ lines at 7183.9727 and 7184.1011 cm^{-1}, respectively, were used to determine the deuterium isotope ratio. The advantage of this line pair is that the laser has to be tuned over only a very small section of the spectrum. The disadvantage is the large disparity in temperature coefficients of the two lines (Table 1). At this stage of the experiment the two gas cells were placed on the optical table without any shielding from ambient (air conditioner) air flows. Both cells were filled with approximately 10 μl of the same GS23 standard water and δ-measurements were made at an approximately 3 min interval. The result is obvious: the apparent isotope ratio changes in time from about −23 to +16‰, indicating a drifting, differential temperature ($\Delta T = T_{\text{sample}} - T_{\text{ref}}$) of roughly +0.8 to −0.5 °C between the gas cells during the course of the experiment. We, therefore, brought the two gas cells together in a thermally insulating housing, using a small ventilator to circulate the air inside. No active temperature stabilization was implemented. More importantly, we were subsequently able to increase the scan width of the laser, covering the first four lines of Table 1 in one scan. In this manner we are now able to use the $H^{16}OH$ line at 7183.6856 cm^{-1}, which exhibits a much smaller temperature coefficient, as a reference line (denominator) for all three isotope ratio determinations.

In order to test our apparatus we have performed a series of measurements in which we repeatedly injected the same GS23 standard water in both gas cells. The results are presented in Fig. 4 and summarized in Table 2. In total, 200 delta-determinations were carried out for δ^2H and $\delta^{17}O$, and 120 for $\delta^{18}O$, divided over nine and five series, respectively, (unfortunately, in four series the length of the scan turned out to have been too short to completely resolve the $H^{18}OH$ feature). Each series consists of 20 or 30 delta-determinations, while each delta-determination is the average of 20 laser scans. A series of 20 delta-determinations takes 20 times 80 s, or about half an hour. Gas cell evacuation, flushing and re-filling will add another 5 min to this. The first observations is that the raw delta-values are not equal to zero. This could in principle be caused by a small, but stable temperature off-set between the two gas cells. The magnitude of the temperature coefficients (Table 1) yields temperature sensitivities for the δ^2H, δ^{17}O, and δ^{18}O measurements of -8.3, -9.1, and $+1.2$‰ K^{-1}, respectively, (ignoring the temperature dependence of the Doppler component to the line broadening). If the differential temperature is 0.53 K, one would expect to measure apparent delta-values of 4.4, 4.8, and -0.64‰, again in the same order, and in fair agreement with the measured offsets. It should be noted that also with the existing FCL-based set-up we observe gas cell dependent zero-point offsets of the same order of magnitude. In this case, however, they depend predominantly on optical alignment and do not correlate with the temperature sensitivities. In actual delta-measurements, these offsets are taken care of in a standardized calibration procedure [23]. The standard deviation of the mean of the delta-values, a measure of the precision of the measurement, is for all isotopomers larger than the corresponding mean standard error. The series-to-series variations are larger than the purely instrumental limited precision. This indicates that the measurements are limited by sample introduction errors and/or instrumental drifts. Based on our experience with the FCL-based 2.7 μm apparatus, the S/N level obtained in this experiment would suggest that a precision (much) better than 1‰ should be possible for all three isotopes, including all sample-handling errors. Indeed, the source of the current disappointing performance has been traced to background modulation due to residual feedback to the diode laser, despite of the more than 30 dB optical isolation (confirmed by measurements in our laboratory). This is also consistent with the observed correlation with line intensity. With the current set-up it proved to be impossible to reduce the amplitude of the ‘fringes’ to less than 1‰ of the strongest line in the spectrum (due to $H^{18}OH$) or to change their period such that the oscillations would be either too fast or too slow to seriously interfere with the spectral features. A new laser with pig-tailed single-mode fiber and in-fiber optical isolation is expected to eliminate these problems.

4. Conclusions

We have shown that measurement of the isotope ratios of water by means of direct absorption spectroscopy can benefit greatly from the use of a single-mode DFB laser at 1.39 μm, as opposed to the use of an FCL (color center laser) at 2.7 μm. The loss of S/N due to the more than one order of magnitude lower absorption strength of the selected transitions is easily compensated for by the use of a sensitive WMS technique not possible with the FCL. We are confident that this will also translate into a higher precision (presently about 3, 1, and 0.5‰, for δ^2H, δ^{17}O, and δ^{18}O, respectively), once the problems associated with optical

Table 2
Precision of the apparatus: raw delta values and their standard errors, all expressed in ‰

ID	δ (HOD)	SE (HOD)	δ ($H^{17}OH$)	SE ($H^{17}OH$)	δ ($H^{18}OH$)	SE ($H^{18}OH$)	n
222A	3.00	0.51	2.23	0.42	-1.22	0.15	30
222B	4.50	0.91	5.45	0.38	-0.12	0.24	30
228A	5.97	1.11	4.78	0.49	-0.87	0.31	20
228B	8.28	0.78	5.14	0.41	-1.30	0.29	20
228C	5.96	0.77	4.15	0.42	-1.44	0.33	20
301A	2.28	0.57	2.77	0.41			20
301B	2.13	0.64	4.80	0.35			20
301C	4.98	1.37	3.91	0.39			20
301D	11.87	0.61	4.03	0.28			20
Mean[a]	5.44 (3.1)	0.81	4.14 (1.1)	0.39	-0.99 (0.53)	0.26	
All[b]	5.20	0.34	4.08	0.16	-0.87	0.13	200[b]

[a] The mean delta-values include the standard deviation between brackets.

[b] The average values when all 200 (δ^2H and δ^{17}O) and 120 (δ^{18}O) measurements are analyzed together.

feedback are eliminated. However, even at the current level of precision, the instrument can already be fruitfully applied. Especially in biomedical applications of the doubly-labeled water method, since with the use of (highly) enriched water samples (and corresponding standards) the effect of residual baseline modulations becomes relatively less important. The resulting apparatus is cheaper, smaller, and easier to operate (airborne, or at a remote location, if needed) than the existing FCL-based instrument. Also not unimportant, lasers in the wavelength range used in this study are easily available.

References

[1] W.G. Mook, M. Koopmans, A.F. Carter, C.D. Keeling, J. Geophys. Res. 88 (1983) 10915–10933.

[2] C.D. Keeling, T.P. Whorf, M. Wahlen, J. van der Plicht, Nature 375 (1995) 666–670.

[3] P. Ciais, P.P. Tans, J.W.C. White, M. Trolier, R.J. Francey, J.A. Berry, D.R. Randall, P.J. Sellers, J.G. Collatz, D.S. Schimel, J. Geophys. Res. 100 (1995) 5051–5070.

[4] R.J. Francey, P.P. Tans, C.E. Allison, I.G. Enting, J.W.C. White, M. Trolier, Nature 373 (1995) 326–330.

[5] C.A.M. Brenninkmeijer, D.C. Lowe, M.R. Manning, R.J. Sparks, P.F.J. van Velthoven, J. Geophys. Res. 100 (1995) 26163–26172.

[6] D.E. Cooper, R.U. Martinelli, C.B. Carlisle, H. Riris, D.B. Bour, R.J. Menna, Appl. Opt. 32 (1993) 6727–6731.

[7] S. Koletzko, M. Haisch, I. Seeboth, B. Braden, K. Hengels, B. Koletzko, P. Hering, The Lancet 345 (1995) 961–962 and references therein.

[8] D.E. Murnick, B.J. Peer, Science 263 (1994) 945–947.

[9] S.C. Tyler, IGAC Newslett. 16 (1999) 3–7.

[10] C.M. Stevens, A.J. Engelkemeir, Geophys. Res. 93 (1988) 725–733.

[11] P. Bergamaschi, M. Schupp, G.W. Harris, Appl. Opt. 33 (1994) 7704–7716.

[12] W. Dansgaard, Tellus XVI (1964) 436–468.

[13] A.N. Salamatin, V.Y. Lipenkow, N.I. Barkov, J. Jouzel, J.R. Petit, D.J. Raynaud, Geophys. Res. 103 (1998) 8963–8977.

[14] S.J. Johnsen, D. Dahl-Jensen, W. Dansgaard, N. Gundestrup, Tellus 47B (1995) 624–630.

[15] N. Lifson, R. McClintock, J. Theor. Biol. 12 (1966) 46–74.

[16] J. Speakman, The Doubly Labeled Water Method, Chapman and Hall, 1997.

[17] E.R.Th. Kerstel, R. van Trigt, N. Dam, J. Reuss, H.A.J. Meijer, Anal. Chem. 71 (1999) 5297–5303.

[18] R. van Trigt, H.A.J. Meijer, A.E. Sveinbjornsdottir, S.J. Johnsen, E.R.Th. Kerstel, Ann. Glaciology, 35 (2001), in press.

[19] R. van Trigt, E.R.Th. Kerstel, G.H. Visser, H.A.J. Meijer, Anal. Chem. 73 (2001) 2445–2452.

[20] E.R.T. Kerstel, K.K. Lehmann, T.F. Mentel, B.H. Pate, G. Scoles, J. Phys. Chem. 95 (1991) 8282–8293.

[21] The laser power supply and TE-cooler controller were designed and built by M. Giuntini of the European Laboratory for Non-linear Spectroscopy (LENS), Firenze, Italy.

[22] K.G. Libbrecht, J.L. Hall, Rev. Sci. Instrum. 64 (1993) 2133.

[23] R. Gonfiantini, Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations; IAEA: Vienna (1984).

[24] R.A. Toth, Appl. Opt. 33 (1994) 4851–4867.

[25] R.A. Toth, Appl. Opt. 33 (1994) 4868–4879.