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9. OPTICAL ISOTOPE RATIO MEASUREMENTS IN HYDROLOGY

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1. Introduction

In this Paper we present an overview of spectroscopic methods for measuring the stable isotope ratios of water, as alternatives to isotope ratio mass spectrometry (IRMS). We do not deal with methods in which lasers are merely used to prepare the sample by means of ablation. Also, for a more detailed and wider discussion of stable isotope ratio infrared spectrometry of small molecules of environmental and biological importance, the reader is referred to a recent review (Kerstel, 2004).

IRMS is the conventional method for measuring isotope ratios and has benefited from over 40 years of research and development. Nowadays IRMS instrumentation is commercially available that reaches impressively high levels of precision, as well as throughput. Unfortunately, IRMS is incompatible with a condensable gas or a sticky molecule such as water. Therefore, in general, chemical preparation of the sample is required to transfer the water isotope ratio of interest to a molecule that is more easily analysed. For the ^{18}O isotope the method most used is the so-called Epstein-Mayeda technique: oxygen-exchange between water and carbon dioxide through the bicarbonate reaction (Epstein and Mayada, 1953). Equilibration requires several hours and an accurate temperature stabilization is needed in order to quantify the isotope fractionation associated with the reaction. The same technique also transfers the ^{17}O signature to CO_2; but the $^{17}O^{12}C^{16}O$ molecule appears in the same mass channel as the much more abundant $^{16}O^{13}C^{16}O$ molecule, making an accurate determination difficult, if not impossible. For the $^2H/^1H$ ratio, one can reduce water to hydrogen gas at an elevated temperature, using a suitable reducing agent, such as uranium (Bigelstein et al., 1952), zinc (Socki et al., 1999), or chromium (Gehre et al., 1996). (The latter two have been used in continuous flow arrangements.) Care

has to be taken that the reaction is run to completion, in order to avoid severe systematic errors. In addition, a significant correction has to be made for the formation of H^{3+} in the ion source. Competing methods are the use of platinum catalytic equilibration of a water sample and hydrogen gas (Horita and Gat, 1988; Coplen et al., 1991). But this method too has its disadvantages: the equilibrium state is accompanied by a very large isotope fractionation (about -740‰ at room temperature), which is also extremely temperature dependent (~6‰/ºC). The gas sample arriving at the IRMS contains approximately one-quarter the original amount of deuterium, considerably decreasing the (already low) mass-3 signal, with obvious consequences for errors due to background correction, amplifier offset, and, above all, the H^{3+}-correction. Furthermore, the amount of water required is rather large (typically 4-5 mL), prohibiting the use of this method in quite a number of possible applications. The same is true for electrolysis (Meijer and Li, 1998). In fact, the only realistic alternative appears to be on-line pyrolysis of water in combination with a continuous-flow IRMS (Begley and Scrimgeour, 1997; Phillips et al., 2000). The latter method is able to deal with very small sample sizes (of the order of 1 µL), provides a high throughput, and is able to achieve good precision.

It may be clear that for the larger part these chemical conversion steps are time-consuming, sometimes hazardous (in the case of uranium reduction) and often compromise the overall accuracy and throughput (Brand et al., 1996; Meijer, 2001). Moreover, the two distinct sample preparations for δ^2H and $\delta^{18}O$ determinations potentially lead to uncorrelated (systematic) errors that do not (partially) cancel in the difference of the two measurements. As we will see later, this is of importance in biomedical doubly labelled water studies, and in the determination of the so-called deuterium excess parameter used in ice-core research. Apart from these drawbacks specific to water, IRMS instrumentation is expensive, voluminous and heavy, confined to a laboratory setting, and usually requires a skilled operator. All or most of these issues may be addressed by optical measurement techniques, although for the ^{18}O isotope one may have to accept a reduced level of precision in most, but not all, cases.

2. Infrared spectrometry

The near and mid-infrared absorption spectrum of gas phase water shows a large number of highly characteristic rotational-vibrational transitions (so called because they can be associated with rotational and vibrational stretching and bending motions of the molecule) that are very sensitive to isotopic substitution (in fact, such is the case for most small molecules). Figure 1 shows the spectrum of water over a wide range in the infrared. At sufficiently low vapour pressure and high instrumental resolution the individual ro-vibrational transitions are easily resolved, and can be uniquely assigned to a water molecule of particular isotopic composition (isotopologue). Even at higher pressure, or in the liquid phase, the unresolved vibrational bands of the deuterium isotopologue may be sufficiently displaced to be useful for a quantitative determination of the deuterium to hydrogen isotope ratio. Since the intensity of the experimentally recorded spectral features (whether individually resolved ro-vibrational transitions, or an unresolved vibrational band)

may be directly related to the abundance of the absorbing species, recording the spectrum containing abundant and rare isotopologue features, in both an unknown sample and an isotopically well-known reference material, enables one to relate the isotopic composition of the sample to that of the reference material.

3. Direct absorption spectroscopy

In direct absorption spectroscopy, the attenuation of infrared light of frequency ν and intensity I_0, when traversing an optical path of length l through a gas cell filled with the material of interest, is given by Beer's law of linear absorption (see, for example, Demtröder, 1982.

$$\frac{I_t}{I_0} = e^{-\alpha(\nu)} = e^{-S \cdot f(\nu - \nu_0) \cdot n \cdot l} \quad or: \quad \alpha(\nu) = -\ln\left(\frac{I_t}{I_0}\right) \tag{1}$$
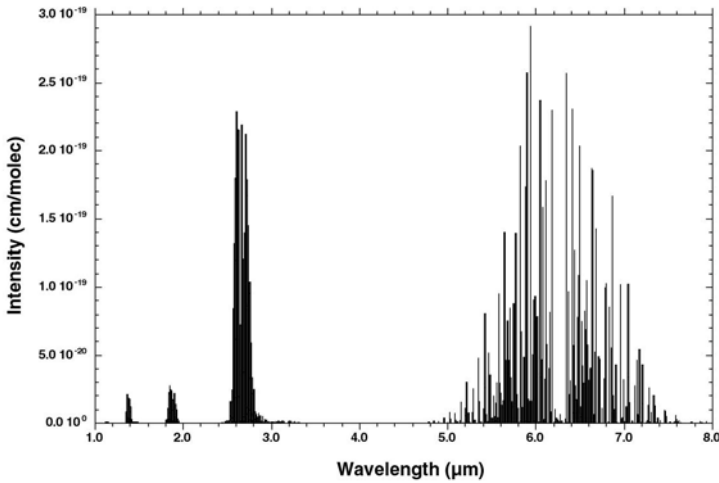
Here, I_t is the transmitted intensity and α the dimensionless absorbance. The latter is proportional to the line strength S, which depends on the transition dipole matrix element connecting the lower and upper states of the transition, as well as on the number of molecules in the lower state.

FIG. 1. Simulated (near) infrared spectrum of water based on the HITRAN 1996 database. The individual ro-vibrational transitions are assumed to be infinitesimally small.

The absorbance is also proportional to the normalized line shape function $f(\nu - \nu_0)$, where ν is the frequency of the light and ν_0 the frequency for which f is maximum. Finally, the absorbance is proportional to the number density n of the absorbing molecules, and the optical path length l.

Typically, the signal-to-noise ratio (SNR) of a direct absorption measurement reaches a maximum for an absorbance α not too far from unity. If α approaches zero, the ratio of two almost equal quantities (I_0 and I_t) will have a large uncertainty, whereas for very large α the measurement of a very small transmitted intensity I_t will carry a large relative error. In practice, it is most often the path length l that is adjusted such that α is between roughly 0.3 and 3 for the majority of the samples to be analysed. Of course, for weak molecular absorptions, or in the case of very small sample sizes, this may simply mean maximizing the optical path length.

4. The Groningen colour centre laser setup

In Figs 2 and 3 we illustrate the principal of an isotope ratio measurement by means of infrared spectroscopy, using our own colour centre based experiments as an example (Kerstel et al., 1999).
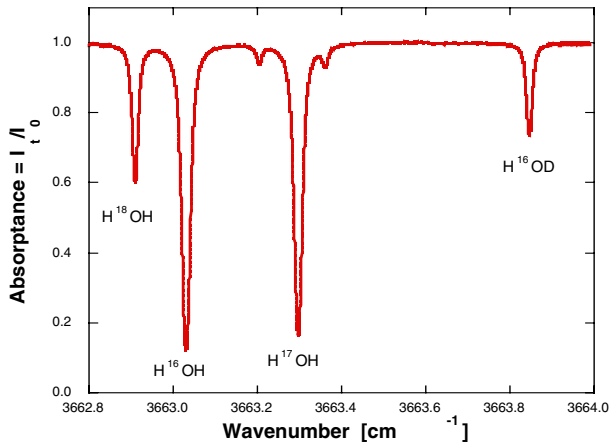

FIG. 2. Experimental registration of the absorption spectrum of a natural water sample. The four major isotopologues have absorptions of the same order of magnitude in a small spectral range around 3663 cm^{-1} (2.73 μm). The small absorptions on the shoulders of the H^{17}OH line are due to H^{16}OD.
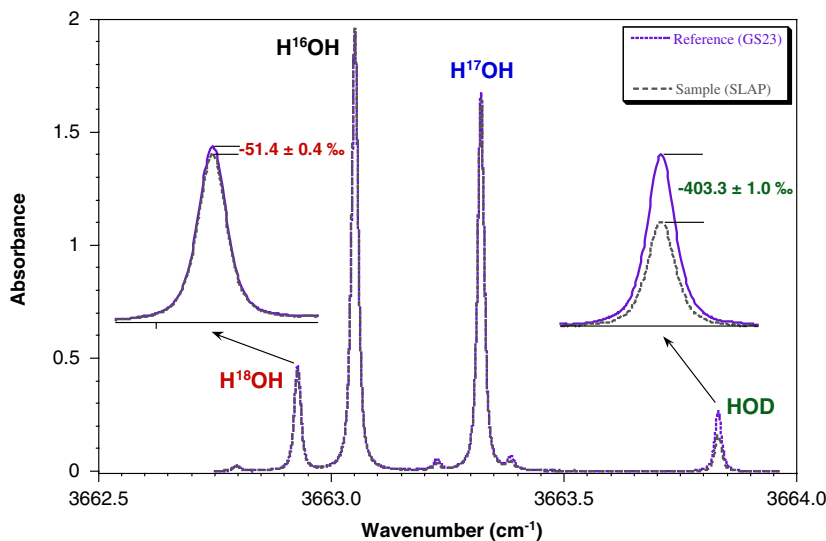
FIG. 3. Principle of the isotope ratio determination. In this figure, the absorbance spectra of sample and reference have been scaled to give equal $H^{16}OH$ absorbances. The isotope ratio may then be "read" directly from the ratio of the corresponding line intensities. In this case, the reference material was a local (Groningen) standard ($^2\delta=-41.0‰$, $^{17}\delta=-3.36‰$, and $^{18}\delta=-6.29‰$) and Standard Light Antarctic Precipitation was used as "unknown" sample ($^2\delta=-428.0‰$, $^{17}\delta\approx-29.7‰$, and $^{18}\delta=-55.5‰$).

Figure 2 shows an experimental registration of absorption by a vapour-phase, natural water sample as a function of the light frequency ν in a small spectral region near 2.73 μm (3664 cm^{-1}). The absorption features correspond to ro-vibrational transitions in the most abundant isotopologue, $H^{16}OH$, and the rare isotopologues $H^{17}OH$, $H^{18}OH$, and $H^{16}OD$. The absorption spectrum can be converted to an absorbance spectrum, as shown in Fig. 3, using the Beer law of Eq. (1).

Figure 3, in fact, shows two spectra recorded in the same region, one belonging to the "unknown" sample, the other to a reference material (back-traceable to an international standard material such as Vienna Standard Mean Ocean Water, VSMOW). The relative deviation $^x\delta_r(s)$ of the isotopic ratio of the sample (xRs), with respect to that of the reference (^xR_r) is given by:

$$^{x}\delta_{r}(s) \equiv \frac{^{x}R_{s}}{^{x}R_{r}} - 1 = \frac{\left(^{x}n/^{a}n\right)_{s}}{\left(^{x}n/^{a}n\right)_{r}} - 1 \qquad (2)$$

The subscript s refers to the sample, r to the reference material. The superscripts a and x refer to the most abundant ($H^{16}OH$) and the rare isotopologue species ($H^{17}OH$, $H^{18}OH$, or $H^{16}OD$), respectively. With a proper choice of experimental conditions, the δ-value follows directly from the intensities in the spectra:

$$^{x}\delta_{r}(s) = \frac{\left(^{x}\alpha/^{a}\alpha\right)_{s}}{\left(^{x}\alpha/^{a}\alpha\right)_{r}} - 1 \qquad (3)$$

Here, $\alpha = \alpha(\nu_{0})$ represents the experimentally determined (maximum) absorbance at centre-line frequency, provided that the exact same line shape applies for all transitions. Alternatively, one may use the integrated line intensity. In Eq. (3) the assumption has been made that the optical path length l is the same for each isotopic species, or for the sample and reference spectra, or for both.

Since the line strength S depends on the number of molecules in the lower level of the transition, it is in general temperature-dependent: a change in temperature will redistribute the population over the rotational levels of the ground vibrational state (see, for example, Kerstel, 2004). Sample and reference spectra should therefore be measured at exactly the same temperature, and/or the isotopologue lines should be chosen such that their temperature coefficients are nearly equal. In general, this implies that the transitions should originate from ground state rotational levels with very nearly the same energy.

Table 1 lists the relevant parameters for the transitions used in our study. It may be seen that the most unfavourable situation occurs for the deuterium measurement: for a measurement taken at room temperature, the $^{2}\delta$-value would change by $-7.8‰$ for each degree of temperature difference between sample and reference cells. However, since to good approximation the measurement does not depend on the absolute temperature, but rather the difference between the sample and reference gas cells, passive stabilization with a good thermal contact between both gas cells is sufficient to make the temperature induced error negligible (i.e. $< 0.1‰$).

It should be noted that the isotope ratios thus determined are molecular isotope ratios. However, it can be shown that for all practical purposes these are equal to the more commonly used atomic isotope ratios (Kerstel, 2004).

The experimental layout is shown in Fig. 4. The laser is tuned in frequency under computer control. A fraction ($\sim$2%) of the output of the laser is directed to each gas cell (four in total, to allow for the simultaneous measurement of one reference material and three samples – this in order to increase the throughput of the apparatus), of which again a fraction (10%) is used to measure the power entering each gas cell, while the remainder makes multiple passes through the cell between specially designed reflective optics for a total path length of 20 m. Before a

measurement, the gas cells are flushed with dry nitrogen, evacuated, and then filled with 10 µL of liquid water.

Table 1. The ro-vibrational transitions used in this study [a]

Frequency [cm^{-1}]	Intensity [b] [cm·molecule^{-1}]	Temp. coeff. [c] at 300 K [K^{-1}]	Isotope
3662.920	$1.8 \cdot 10^{-23}$	$1.3 \cdot 10^{-3}$	$^1H^{18}O^1H$
3663.045	$7.5 \cdot 10^{-23}$	$4.4 \cdot 10^{-3}$	$^1H^{16}O^1H$
3663.321	$6.4 \cdot 10^{-23}$	$-1.5 \cdot 10^{-3}$	$^1H^{17}O^1H$
3663.842	$1.2 \cdot 10^{-23}$	$-3.4 \cdot 10^{-3}$	$^1H^{16}O^2H$

a) All values are taken from the HITRAN 1996 spectroscopic database (http://www.hitran.com).

b) The intensities are for a natural water sample with abundances: 0.998, 0.00199, 0.00038, and 0.0003 for $^1H16O^1H$, $^1H^{18}O^1H$, $^1H^{17}O^1H$, and $^1H^{16}O^2H$, respectively.

c) The temperature coefficients give the relative change with temperature in absorption intensity of the selected transitions. They are calculated using the HITRAN 1996 database.

The power and signal beams are amplitude modulated at incommensurate frequencies around 1 kHz and detected by the same detector. A phase-sensitive detector (lock-in amplifier) recovers both signal and power measurements. The use of one optical detector and one lock-in amplifier (Perkin-Elmer 7265) per gas cell ensures that these devices contribute the same coherent noise and drifts to both the signal and power measurement, such that these cancel out in the ratio of signal to power. In this manner we are able to measure the $^2\delta$, $^{17}\delta$, and $^{18}\delta$ values of naturally occurring water samples with an accuracy of better than 1‰, 0.5‰, and 0.5‰, respectively, and a throughput of about 4 to 5 samples per hour (including gas cell evacuation and sample injection). The accuracy for $^2\delta$ is comparable to that which can be obtained by IRMS. As mentioned above, $^{17}\delta$ is difficult to determine by

means of IRMS, making the laser determination quite unique. The $^{18}\delta$ accuracy is about one order of magnitude lower than possible with IRMS, but at higher enriched ^{18}O concentrations, the accuracy of IRMS and our laser instrument become comparable (see Table 2).

Table 2. Comparison of calibrated accuracy routinely obtained with the Groningen colour centre laser (FCL) setup and IRMS instrumentation.

Isotope ratio	δ-range [‰]	1σ-accuracy [‰]	
		FCL	IRMS
$^{2}H/^{1}H$	-500 – 15,000	0.6 – 55	1 – 100
$^{17}O/^{16}O$	-100 – 300	0.4 – 2	
$^{18}O/^{16}O$	-250 – 1,200	0.5 – 3.5	0.05 – 3

We have successfully used the colour centre laser based isotope spectrometer in applications in biomedicine (energy expenditure measurements by means of the so-called doubly labelled water method) (Trigt et al., 2001; Trigt et al., 2002a) and in ice-core studies to reconstruct the Earth's past climate and (Trigt et al., 2002b). The biomedical studies determine the CO_2 production as a direct measure of energy expenditure (Speakman, 1997). This is done by injecting a small amount of water, highly enriched in both ^{2}H and ^{18}O and following the decay of their concentrations. The ^{18}O concentration diminishes as ^{18}O leaves the body in the form of CO_2 (through the bicarbonate O-exchange reaction, which is accelerated by the anhydrase enzyme) or H_2O, whereas ^{2}H can leave the body only in the form of H_2O. Therefore the area between the ^{18}O and ^{2}H decay curves gives the CO_2 production over a certain period in time. The energy expenditure calculation thus involves the differences of $^{2}\delta$- and $^{18}\delta$-determinations. The overall error benefits in particular from the fact that both isotope ratio measurements take place simultaneously on the same sample, without requiring different chemical pretreatments for each measurement. Moreover, since these studies use highly enriched samples, the accuracy of laser and IRMS instrumentation is comparable and the laser technique can compete effectively with IRMS, also in this respect.

The ice-core studies measured the $^{2}\delta$-value (versus depth) as a proxy for the local (palaeo-) temperature, but also the so-called deuterium excess value, which can be shown to depend on other important climate variables (such as the temperature and relative humidity in the source region of the precipitation). The deuterium excess is defined as $^{2}\Delta = ^{2}\delta - 8 \cdot ^{18}\delta$. A precise determination of $^{2}\Delta$ thus requires a precise determination of $^{2}\delta$, and in particular $^{18}\delta$. Here, the laser setup cannot (yet) compete with IRMS. Still, the laser measurements proved rather useful as a check on the absolute accuracy (a possible shift of the δ scale), as they are much less sensitive to sample contamination, in this case by residual drilling fluid.

The colour centre laser is an excellent laboratory research instrument, mainly because of its very wide spectral coverage. Almost all infrared active small molecules have one or more strong absorption bands within its tuning range from 2.4 µm to 3.4 µm. Unfortunately, it is also a rather complicated, expensive, and large laser system, making it much less well suited for portable applications, and it is unlikely that the spectrometer will be copied by other isotope laboratories. For these reasons we have started using high quality diode lasers of designs originally developed for telecommunications (Kerstel et al,. 2002). These are not (yet) available in the same favourable spectral region of the colour centre laser, but operate near 1.4 µm in the region of water overtone and combination band vibrations. As can be seen in Fig. 1, the transitions in this region are at least one order of magnitude weaker than in the 2.7 µm region. Still, the low-noise properties of the diode laser in combination with the sensitive detection technique of wavelength modulation, has enabled us to obtain very favorable preliminary results with precision (i.e., not calibrated to an international standard) levels of 0.2‰ for $^{18}\delta$ and 0.5‰ for $^{2}\delta$ and $^{17}\delta$ (Gianfrani et al., 2003).

5. Other direct absorption techniques

In the above-mentioned spectrometers, wavelength selection is obtained by the use of a very narrow bandwidth laser. On the time scale of a typical isotope ratio measurement (from seconds to several minutes) our lasers exhibit line widths of several MHz, or typically at least two orders of magnitude smaller than the molecular absorption width (~0.01 cm-1). Such a high resolution is difficult to obtain by dispersive elements like prisms or gratings, but may not always be required.

6. Grating spectrometer

In fact, in one of the earliest infrared isotope ratio studies, Gaunt used a broad band light source in combination with a grating spectrometer near 4 µm to measure $^{2}H/^{1}H$ ratios between 0.015% and 0.08% with a relative error of 2% in liquid water samples from integrated vibrational band intensities (Gaunt, 1956). Much later, Fusch used the same experimental technique, but improved the measurement precision to <30‰, while at the same time reducing the sample requirement by a factor of 10, down to about 0.1 mL (Fusch, 1985).

7. Fourier transform spectrometry

An alternative detection technique is Fourier transform infrared (FTIR) spectrometry, in which a broadband light source illuminates the sample held in a gas cell inside the stationary arm of a Michelson interferometer. As the length of the second arm is changed in a periodic manner, an interferogram is recorded that is the Fourier transform of the sample gas absorption spectrum. The resolution of the instrument is proportional to the path length difference travelled by the mirror in the second arm. In practice this limits the resolution of an FTIR instrument to about 0.01 cm^{-1}. At this level of resolution the instrumentation quickly becomes rather

expensive and bulky. Although most small molecules of environmental interest have an average rotational line spacing of the order of 1 cm^{-1}, allowing for a relatively compact FTIR apparatus, this is not true for water. Using a high-resolution FTIR spectrometer, Griffith and co-workers have been able to measure carbon and oxygen isotope ratios in natural air CO_2 and oxygen and nitrogen isotope ratios in pure N_2O with excellent precision (0.1‰ for $\delta^{13}C$, 1-2‰ for $\delta^{15}N$, and ~4‰ for $\delta(N_2^{18}O)$ and $\delta(N_2^{17}O)$) (Esler et al., 2000a,b; Turatti et al., 2000). However, we are aware of only one, low-resolution (8 cm^{-1}), FTIR study on water: Fusch et al. determined δ^2H over a very wide range of enrichments (–500‰ to 16,000‰) in 60 µL liquid water samples with an accuracy ranging from 3‰ to about 45‰ (Fusch et al., 1993).

8. Non-dispersive infrared spectrometry

Finally, we would like to mention the technique of non-dispersive infrared (NDIR) spectrometry, which has been applied with quite some success to the measurement of $\delta^{13}C$ in exhaled breath analyses. In its most common form NDIR uses an amplitude modulated broad band light source (lamp) and gas-specific detector units. Gas- and isotopologue specificity of the detectors is achieved by filling a small chamber with the pure isotopologue gas. Heating of the gas is detected with a microphone (photoacoustic detection), or alternatively, the transmission through the chamber is measured with an infrared detector. NDIR is by definition a spectrally low-resolution technique yielding a signal that is the integrated absorption over a relatively large fraction of the absorption spectrum of the molecule of interest (in practice limited by a narrow band-pass filter). As described here, it requires that at least part of the isotopologue absorption is well separated from that of the most abundant molecule. The selectivity can be high for ^{13}C-analysis in CO_2, as the asymmetric stretching band used in this scheme is shifted considerably (66 cm^{-1}) upon ^{13}C substitution. An entirely different implementation of NDIR is possible that actually depends on the overlap of the isotopologue bands. In this heterodyne scheme, the signal is derived from the absorption of amplitude modulated infrared radiation by a pressure-modulated gas (Dimeff, 1972; Irving et al., 1986). The latter technique in particular may be applicable to water isotope ratio measurements, but we have not encountered such an implementation in the literature.

9. Indirect techniques

In indirect detection techniques, the absorption of infrared radiation is not detected directly, but rather by its influence on other properties of the gas, such as heat dissipation (photoacoustic spectroscopy) or the electrical response of a gas discharge (opto-galvanic effect). The detection signal therefore depends in general on other parameters in addition to those seen in Eq. (1), most notably the laser power. As the signal now depends directly on the number of absorbing molecules, indirect absorption techniques are characterized by a zero background and thus potentially very sensitive. This is not necessarily an advantage for isotope ratio measurements, where SNR and signal linearity are often more important.

10. Photoacoustic detection

The technique of laser photoacoustic detection was used by Matsumi et al. to determine the $^{18}O/^{16}O$ isotope ratio in small (5 μL) gas phase water samples (Matsume et al., 1998). They used a pulsed dye laser in the visible region of the spectrum (720 nm) to excite a weak third overtone OH stretching vibration. The sound wave generated in the gas cell containing the sample was detected with a sensitive microphone. The measurement precision was disappointing (~16‰), mainly because of the weakness of the third overtone transition, but perhaps also because of the poor noise characteristics of the pulsed laser source.

11. Opto-galvanic detection

The opto-galvanic effect has been used for isotope ratio measurements ($\delta^{13}C$ and $\delta^{18}O$) in exhaled breath CO_2 analyses, using a powerful CO_2 laser to boost the weak opto-galvanic signals in a CO_2 RF discharge (Murnick et al., 1998). As far as we know, the technique has not been used with water.

12. Discussion

Optical isotope ratio measurements of the $^2H/^1H$ ratio in water have proved competitive with IRMS in terms of accuracy. In this respect, fractionation effects during sample handling constitute the dominant source of analytical errors. It appears unlikely that an optical method will be able to reach the very high accuracy possible with IRMS for $\delta^{18}O$ determinations on natural samples. However, for highly enriched samples laser spectrometry may already be a viable alternative to IRMS. The possibility of using laser spectrometry to measure $\delta^{17}O$ easily may be used for independent verification of $\delta^{18}O$ measurements on the same sample (Trigt et al., 2000b), or in exotic applications. For example, we have determined the ^{17}O concentration in the heavy water used in a solar neutrino experiment (Kerstel, 2001) and, in collaboration with the group of D. Romanini in Grenoble, we have recently built a very low water-concentration isotope spectrometer to measure the isotopic composition (and in particular $\delta^{17}O$) of stratospheric water. The latter instrument is based on the extremely sensitive detection technique of cavity ring-down spectroscopy, which is essentially a clever way to increase the effective optical path length in direct absorption spectroscopy by determining the life-time of a photon inside a high finesse (high reflectivity) optical cavity (see, for example the review in Berden et al., 2000).

Of course, accuracy is not the only factor to be considered when comparing laser spectrometry to IRMS. There are certainly applications for which other aspects are more important. One could think of industrial plant or volcanic emission monitoring, requiring, for example, robustness, portability, remote operation in a hostile environment, compactness, and real-time measurements. Other advantages of optical methods that may be considered are the high selectivity, thus avoiding the need of chemical sample pretreatment, the non-destructive nature of the measurement, making it possible to recover the sample if needed, and low cost. Last but not least,

methods based on direct absorption are conceptually simple, which helps reduce the required scale correction and normalization with respect to IRMS.

Finally, we would like to quote one of the recommendations made by the IAEA Advisory Group meeting on new approaches for stable isotope ratio measurements (IAEA, 2001):

> During the past few years a variety of new techniques have appeared. Here we discuss in particular clinical applications of isotope measurements and laser spectrometry techniques. The requirements for clinical use are similar to those required for field deployment – easy of use, self diagnostic, robust, and moderate cost.

[…]

> For such new techniques to be accepted by the isotope community they should be adequately compared with existing state-of-the art equipment and checked against isotope reference materials that are back-traceable to (IAEA) primary standards. Publications should distinguish between precision, accuracy, as well as instrument stability. In addition they should clearly state the procedure followed for calibration (defining the scale zero) and normalization (scale multiplication factor). In practice this means, e.g. for the case of water, that VSMOW, SLAP, GISP and a number of local standards should be measured.

Unfortunately, the terms precision (a measure of the reproducibility of the result) and accuracy (a measure of the deviation from the true value) are sometimes used too loosely in the literature. Moreover, since measurements should be made with respect to a local reference material, instead of the international standard material (which is simply too expensive and rare to be used on a daily basis), the total variance can be decomposed into at least two components: the variance of the local reference material with respect to the international standard, and that of the sample with respect to the local reference (Jasper, 2001). Both should be reported. Conformity with the procedures outlined above is essential if optical isotope ratio instrumentation is to move from the physics laboratory to the isotope ratio work floor.

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