5

Unusual samples

5. Certification of an unusual water sample

The first two major applications of the Laser Spectrometer (LS) have been described in Chapter 3 and 4. In this chapter, a more exotic application of the laser spectrometric technique is described. This specific application can serve as an example of the more general application of the LS method in certifying isotopically labelled species as sold by many suppliers. The stated enrichments can then be checked.

5.1 Analysis of ^{17}O content in Ontario Hydro heavy water

In this section, an experiment will be described in which the ^{17}O content is measured on a water sample with an extremely high deuterium content. The LS provides a manner to measure the ^{17}O abundance, after some modifications have taken place in the measurement procedure and the data analysis, compared to the previously discussed settings. The text is based on the measurement report on this experiment (Kerstel 2001a).

5.1.1 Introduction

The deuterated heavy water analysed here (99.92% D_2O) is used as the detection medium in a Canadian experiment designed to detect solar neutrinos (Waltham 1992). Because of the large neutron capture cross–section of ^{17}O, there is interest in knowing its abundance to a reasonable level of accuracy. Previous measurements of the ^{17}O abundance have resulted in two rather different values: $5.5 \cdot 10^{-4}$ (already long ago determined by Atomic Energy Agency of Canada), and a more recent value of $17 \cdot 10^{-4}$ measured with the advanced electron cyclotron resonance ionisation source on the 88" cyclotron at Berkeley (Simpson 2001). The natural abundance of ^{17}O (see Chapter 1) equals $3.8 \cdot 10^{-4}$.

Here we report on the measurement of the ^{17}O abundance by means of the Stable Isotope Laser Spectrometer (LS) at the Groningen Centre for Isotope Research. The spectrometer is based on direct absorption of infrared radiation passing about 20 m through the gas phase water sample. The intensities of selected isotopomer lines in the sample spectrum are compared to the corresponding intensities in the spectrum of a reference material in order to calculate the isotope ratios of interest. For each heavy isotopomer we scale the intensities of spectral features belonging to this isotopomer using the intensity of an abundant $H^{16}OH$ spectral feature. Principally due to the very low abundance of the rare isotope, the so–determined *molecular* isotope ratio $[H^{17}OH]/[H^{16}OH]$ is for all practical purposes equal to the *atomic* isotope ratio $[^{17}O]/[^{16}O]$.

5.1.2 Constants and definition of symbols

In Table 5.1 the constants are listed which are used in the calculations for the isotope abundances.

Table 5.1: Constants used to calculate the isotope abundances.

parameter	value	uncertainty	description	Ref
m_H	1.0078825 amu		atomic mass ^1H	Verkerk (1986)
m_D	2.014102 amu		atomic mass ^2H	Verkerk (1986)
m_{16}	15.99492 amu		atomic mass ^{16}O	Verkerk (1986)
m_{17}	16.99913 amu		atomic mass ^{17}O	Verkerk (1986)
m_{18}	17.99916 amu		atomic mass ^{18}O	Verkerk (1986)
$^{17}R_0$ [1])	$3.8 \cdot 10^{-4}$	$0.2 \cdot 10^{-4}$?	^{17}O isotope ratio of VSMOW $(=[^{17}O]/[^{16}O])$	Li (1988)
$^{18}R_0$	$2.0052 \cdot 10^{-3}$	$5 \cdot 10^{-7}$	^{18}O isotope ratio of VSMOW $(=[^{18}O]/[^{16}O])$	Baertschi (1976)
$\delta^{17}O(GS-23)$	-3.33‰	0.3‰ [2])	$^{17}R_{GS-23}/^{17}R_{VSMOW}-1$	
$\delta^{18}O(GS-23)$	-6.29‰	0.05‰	$^{18}R_{GS-23}/^{18}R_{VSMOW}-1$	

1) Li (1988) gives $^{17}R_0$ as $(3.799 \pm 0.009) \cdot 10^{-4}$, (corresponding to 0.03790 atom%). Considering the difficulties associated with its determination and the controversy in the literature concerning the best value, we will base our error analysis on an assumed uncertainty of $0.2 \cdot 10^{-4}$, more than one order of magnitude larger than the one–sigma error in $^{18}R_0$ as claimed by Baertschi (1976). As we will see, in this case the error in $^{17}R_0$ and our measurement error contribute about equally to the final error in the ^{17}O abundance of the heavy water sample.

2) Error based on laser–spectrometric measurement. Almost one order of a magnitude smaller when calculated from $\delta^{18}O$ in combination with the mass–dependent fractionation formula of Meijer and Li (1998).

5.1.3 Procedure

The procedure for measuring this sample is different than for natural or DLW samples: Since it is basically D_2O (instead of H_2O), all of our regular spectral features (Chapter 2) disappear. There are no working standards available to compare the sample spectrum to, so we need to dilute the sample first with water of known isotopic make-up and a natural ^2HOH level.

5.1.3.1 Dilution

The original sample was diluted with an isotopically well–characterised local standard, known as GS–23 ($\delta^2H = -41.0‰$, $\delta^{17}O = -3.36‰$, and $\delta^{18}O = -6.29‰$ on the VSMOW-SLAP scale). As mentioned before, dilution is required to increase the initially extremely weak signal on the spectral features of interest: $H^{16}OH$ and $H^{17}OH$ (and $H^{18}OH$). In addition, the dilution factor should be high enough to bring the intensities of nearby spectral features belonging to ^2HOH down to a level where they no longer interfere unacceptably with the spectral features belonging to $H^{16}OH$ and $H^{17}OH$ (and $H^{18}OH$). But the mixing ratio may not be so large as to wash out the $H^{17}OH$ signal. A compromise in these demands was found using mixing ratios of sample : local standard water (GS-23) of about 1:30 and 1:75. The exact mixture rates (A and B) can be found in Table 5.2. The resulting ^2HOH concentrations thus become about 3% and 1.3%, respectively.

Table 5.2: Mixing parameters for the two diluted heavy water mixtures.

	Mixture A (1:75)	Mixture B (1:30)
M_s (mass D_2O sample) (g)	1.0996	3.1751
M_b (mass GS–23 buffer) (g)	74.2682	93.9224
$f := M_s/(M_s+M_b)$	0.013151	0.029531
$\Delta f/f$ (relative weighing error)	0.0005	0.0002

5.1.3.2 Isotope ratio measurement

The measurements were basically carried out as described in Chapter 2. However, the ^{17}O line present in the standard spectral region of our spectrometer (3662.7 cm^{-1} to 3664.0 cm^{-1}) has weak ^2HOH absorptions present on each of its shoulders. This is not a major problem for natural abundance water samples or enriched samples as encountered in biomedical applications. The highest enriched samples we have measured so far ($\delta^2H = 15000‰$) contain about 0.2% of ^2HOH. In the present case, the ^2HOH concentration is at least 6 times higher, and the resulting absorptions give rise to ^2HOH lines that are more intense than the ^{17}O line itself. This feature is illustrated in Figure 5.1. In the case of Mixture B, the intensity of the ^2H lines ("162") accompanying ^{17}O ("171") even saturate. These strong neighbouring lines influence the ^{17}O line in an unacceptable manner. We therefore located a nearby spectral region with a more favourable set of lines for this specific goal. This region is from 3660.1 cm^{-1} to 3661.6 cm^{-1}

and encompasses the lines given in Table 5.3. Figure 5.2 presents typical spectra obtained in this region for both the reference water (GS–23) and the 75–fold diluted D_2O sample. Here, the only ^2HOH line present is much weaker than in the previous section (and not even visible for the natural abundance spectrum of GS-23), while the $H^{17}OH$ and the $H^{18}OH$ have sufficient intensity for accurate determinations.

Table 5.3: The transitions used in the determination of the ^{17}O and ^{18}O abundances."161" is used to indicate $H^{16}OH$, "181" for $H^{18}OH$, "171" for $H^{17}OH$, and 162 for ^2HOH.

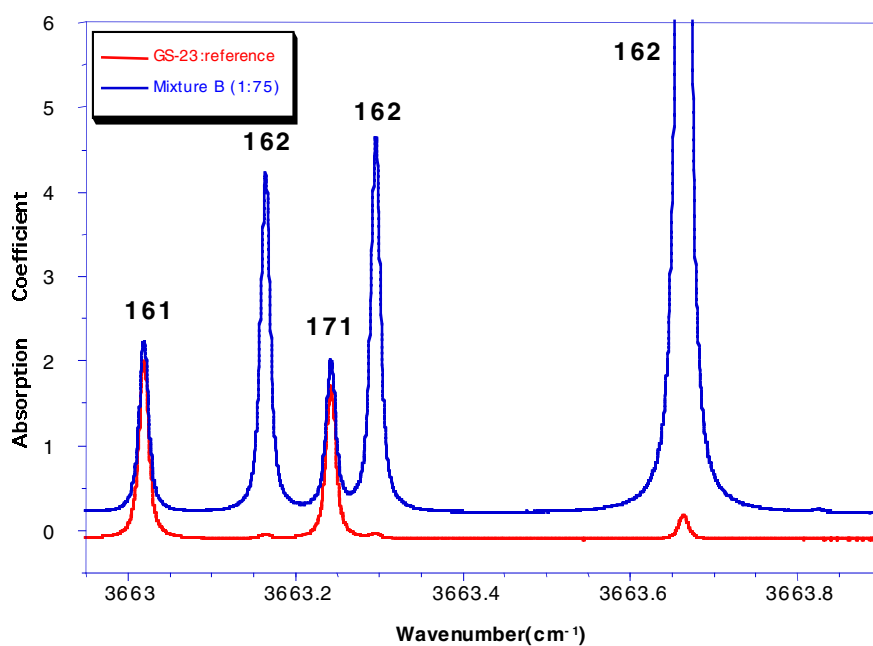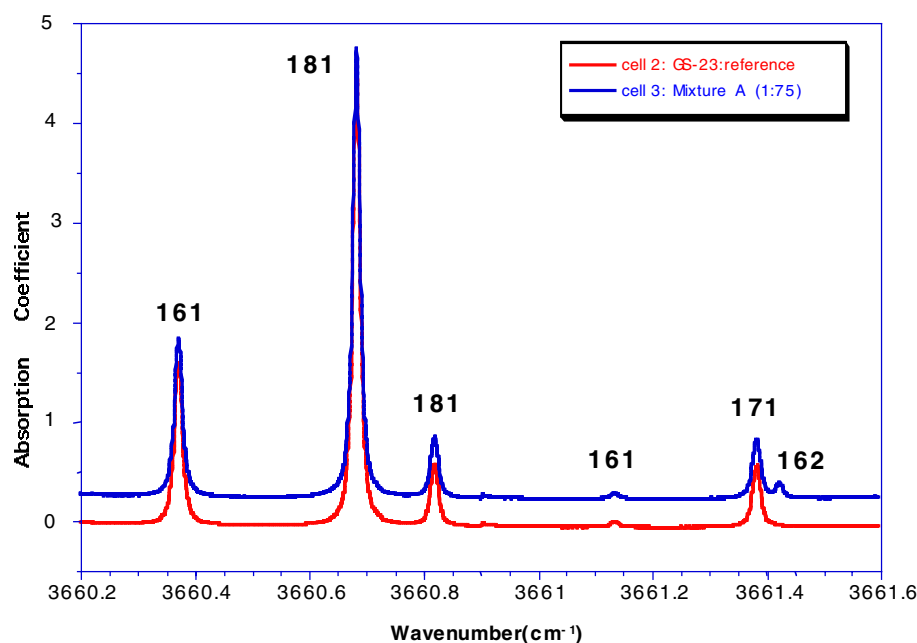| isotope	frequency (cm^{-1})	intensity (cm/molec)	temp. coeff (‰/K)
161	3660.376	$6.1 \cdot 10^{-23}$	-2.8
181	3660.844	$2.3 \cdot 10^{-23}$	-0.24
171	3661.373	$2.2 \cdot 10^{-23}$	-1.5

Figure 5.1: "Traditional" spectral region

Figure 5.2: New region for ^{17}O and ^{18}O.

Since no working standard of isotopic make-up comparable to the samples is available, we used the local GS–23 as the working standard. The $\delta^{17}O$ and $\delta^{18}O$ values of GS-23 are close enough to the expected sample values, but the δ^2H value is very much different between sample and working standard.

A number of independent δ–measurements were carried out, each consisting of 10 or 20 individual laser scans with in one gas cell the measurement reference material and in the other gas cell the diluted heavy water sample. The measurements are summarised in Table 5.4. Even after changing the spectral region, the procedure used by Kerstel (1999) to calculate the δ–values proved too sensitive for the overlap of the $H^{17}OH$ line at 3661.373 cm^{-1} with the (very) weak ^2HOH absorption on its shoulder (see Figure 5.2). It was therefore deemed necessary to write a new analysis routine that fits a superposition of Voigt profiles with variable position, height and width to the experimental spectra. The new procedure proofed slightly inferior to the old procedure when tested on "normal" water samples and routine measurements, but far superior in the present case where the deuterium concentration differs so dramatically between the working standard and sample water mixtures A and B.

The measured ^{17}O and ^{18}O δ–values show a strong positive correlation (see Figure 5.3). This suggests that measurement–to–measurement variations are related to sample–handling problems, e.g., fractionation processes inside or outside the gas cell occurring during or after sample injection.
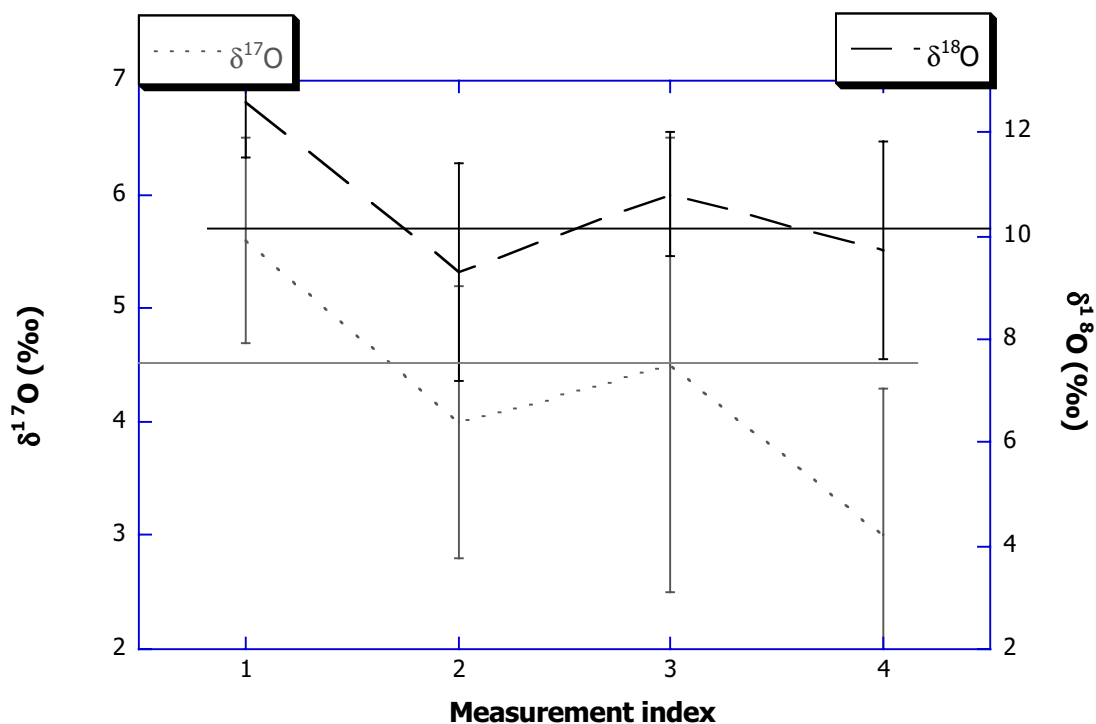

Figure 5.3: Corrected results for Mixture A (1:75) showing the correlation between the ^{17}O and ^{18}O measurements. The horizontal lines represent the weighted means.

5.1.3.3 Analysis

Mixture A (1:75)

The four measurements (#1 to #4 in Table 5.4) on Mixture A (1:75) yield weighted averages of:

$$\delta^{17}O_{GS-23} = (4.6 \pm 0.6)‰ \qquad \text{and}: \qquad \delta^{18}O_{GS-23} = (11.3 \pm 0.7)‰$$

and referencing with respect to VSMOW:

$$\delta^{17}O_{VSMOW}^{corr} = (1+\delta^{17}O_{GS-23}^{corr})\cdot(1+\delta^{17}O_{VSMOW}^{GS-23})-1$$

$$= (1.16 \pm 1.0)‰$$

and:

$$\delta^{18}O^{corr}_{VSMOW} = (1 + \delta^{18}O^{corr}_{GS-23}) \cdot (1 + \delta^{18}O^{GS-23}_{VSMOW}) - 1$$
$$= (3.85 \pm 1.1)\%o$$

The above two final values for $\delta^{17}O$ and $\delta^{18}O$ are consistent with atomic fractional abundance of the heavy water sample of:

$^{17}f_s = (5.08 \pm 0.63) \cdot 10^{-4}$ and: $\quad ^{18}f_s = 3.53 \cdot 10^{-3}$

The error in $^{17}f_s$ was calculated assuming an error $\Delta(\delta^{17}O) = 1\%o$ for the measurement of $\delta^{17}O$ and a relative weighing error $\Delta f/f = 0.000\ 5$ for the measurement of the mixing ratio (relative concentration) of sample and GS–23 buffer solution. The error in $^{17}f_s$ also includes a contribution from the <u>estimated</u> uncertainty in the isotope ratio of VSMOW: $^{17}R_0 = 3.8 \cdot 10^{-4} \pm 0.2 \cdot 10^{-4}$. If we assume that $^{17}R_0$ is known with zero uncertainty, the error in $^{17}f_s$ reduces to $0.29 \cdot 10^{-4}$. In other words: the uncertainty in the absolute ^{17}O isotope concentration of the international calibration material VSMOW contributes for more than 50% to the uncertainty in the ^{17}O concentration of the heavy water sample.

(Note: ^{17}f refers to the concentration $[^{17}O]/([^{16}O]+[^{17}O]+[^{18}O])$, while ^{17}R refers to the isotope ratio $[^{17}O]/[^{16}O]$. Thus $^{17}f = {}^{17}R/(1+{}^{17}R+{}^{18}R)$ and $^{17}R = {}^{17}f/{}^{16}f$).

Table 5.4: Overview of the measurements. The δ–values are expressed with respect to GS–23 and have been corrected for the zero–offset. The errors presents one standard deviation.

#	date	Serie #	# scans	sample	quantity (µl)	$(\delta^{17}O)^{raw}$ (‰)	$(\delta^{18}O)^{raw}$ (‰)
1	20010320	*3	10	Mixture A 1:75	10	5.6 ± 0.9	12.6 ± 1.1
2	20010321	*1	20	Mixture A 1:75	10	4.0 ± 1.2	9.3 ± 2.1
3	20010321	*2	20	Mixture A 1:75	5	4.5 ± 2.0	10.8 ± 1.2
4	20010323	*1-4	40	Mixture A 1:75	10	3.0 ± 1.3	9.7 ± 2.1
5	20010323	*5-8	40	Mixture B 1:30	10	8.0 ± 1.2	18.3 ± 1.3

Mixture B (1:30)

Similarly, we obtain the following result for measurement #5 on Mixture B (1:30):

$$\delta^{17}O^{corr}_{VSMOW} = (4.6 \pm 1.6)‰ \qquad \text{and:} \qquad \delta^{18}O^{corr}_{VSMOW} = (11.9 \pm 1.7)‰$$

These values for $\delta^{17}O$ and $\delta^{18}O$ are consistent with atomic fractional abundance of the heavy water sample of:

$$^{17}f_s = (4.80 \pm 0.46) \cdot 10^{-4} \qquad \text{and:} \qquad ^{18}f_s = 3.22 \cdot 10^{-3}$$

In this case, the error in $^{17}f_s$ was calculated assuming an error $\Delta(\delta^{17}O) = 1.6‰$ for the measurement of $\delta^{17}O$ (more overlap with ^2HOH line and thus greater uncertainty than when measuring Mixture A and a relative weighing error $\Delta f/f = 0.000\ 2$ for the measurement of the mixing process. As before, it includes a contribution from the very conservatively <u>estimated</u> uncertainty in the isotope ratio of VSMOW: $^{17}R_0 = 3.8 \cdot 10^{-4} \pm 0.2 \cdot 10^{-4}$. If we assume that $^{17}R_0$ is known with zero uncertainty, the error in $^{17}f_s$ reduces to: $0.21 \cdot 10^{-4}$. And again the uncertainty in the absolute ^{17}O concentration of the international calibration material VSMOW contributes for more than 50% to the uncertainty in the ^{17}O concentration of the heavy water sample.

5.1.4 Concluding remarks

The values of the mixture A and B agree very well(with their errors excluding the contribution of the uncertainty in $^{17}R_0$): 5.08 ± 0.29 and 4.80 ± 0.21, respectively. The weighted average is 4.90 ± 0.16. However, if the uncertainty in $^{17}R_0$ is taken into account, the measurements on the two diluted mixtures may be combined into the final values:

$$^{17}f_s = (4.9 \pm 0.5) \cdot 10^{-4} \qquad \text{and:} \qquad ^{18}f_s = 3.4 \cdot 10^{-3}$$

The error given is an estimated value based on the two measurements presented above and taking into account that these may be correlated through the determination of the zero offset.