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### Water enriched in the rare stable isotopes

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## Summary

This thesis deals with various aspects of the stable isotopes of H and O in water, and more specifically in water, in which the abundances of the rare isotopes  $^2\text{H}$  and  $^{18}\text{O}$  (and to some extent also  $^{17}\text{O}$ ) have been increased. Subjects of the thesis are measurement of the isotope abundances of such artificially enriched waters, production and calculation of enriched reference waters, and application in the field of thermometry.

The field where such artificially enriched (or "labelled") waters are used the most is in biology and medicine. The singly labelled water (SLW) method, in which only one stable isotope is enriched (usually  $^2\text{H}$ ) is used for establishing the total amount of body water of humans and animals. The doubly labelled water (DLW) technique (with both  $^2\text{H}$  and  $^{18}\text{O}$  enriched) is used for measuring their energy expenditure. .

The way in which the SLW method establishes the total amount of body water (and thus produces valuable information about body composition) is based on the dilution of the originally administered isotope label by the total body water. Provided the labeled water has been fully equilibrated through the body, only one sample of one of the possible body fluids (saliva, blood, urine) suffices to establish the total body water. The way in which the DLW method, that uses both the isotopes  $^2\text{H}$  and  $^{18}\text{O}$ , establishes the total energy expenditure is more complicated. If water enriched, or "labeled" in  $^2\text{H}$  is introduced into the body, the label is diluted by intake water (in food, drink) and washed out through water leaving the body (as urine, sweat and water vapour in breath). If  $^{18}\text{O}$ -labeled water is introduced, the label is washed out by the same routes as the  $^2\text{H}$  label, but also by carbon dioxide. Thus the slope of oxygen label decline is steeper than that for hydrogen, and the difference is proportional to the amount of carbon dioxide produced, which is again directly related to energy expenditure. The decay rate difference between  $^2\text{H}$  and  $^{18}\text{O}$  is mostly relatively small (10-15 % of the decay rates themselves). The individual rates must therefore be established accurately, which implies accurate and precise instrumentation for the measurements of  $^2\text{H}$  and  $^{18}\text{O}$  content as well as reliable reference waters in order to calibrate the isotope measurements (chapter 2-5).

For DLW applications, dual-inlet Isotope Ratio Mass Spectrometry (IRMS) has been traditionally used. However, as IRMS cannot measure condensable gases such as water directly, on top of the micro-distillation of blood or urine to pure water, conversion of the body water

sample to small molecules such as H<sub>2</sub> and CO<sub>2</sub> is required. This sample preparation is not without problems, and in addition is quite costly and time consuming. In our group, the feasibility of laser spectrometry technique in biomedical DLW method has already been demonstrated [1]. This has a number of advantages over the IRMS; among these are better precision for  $\delta^2\text{H}$ , higher sample throughput and the absence of chemical sample pretreatments (although micro-distillation remains a necessity).

In chapter 2 and 3 of this thesis, we report our development and characterization of a prototype gas analyzer based on Optical Feedback Cavity Enhanced Absorption Spectroscopy (OF-CEAS) for more sensitive and precise measurement of the  $^2\text{H}/^1\text{H}$ ,  $^{17}\text{O}/^{16}\text{O}$ , and  $^{18}\text{O}/^{16}\text{O}$  isotope ratios in liquid water at high levels of  $^2\text{H}$  and/or  $^{18}\text{O}$  enrichment. An evaporator unit was built to instantly vaporize the liquid water samples and to subsequently transport the vapour to the gas analyzer. This analyzer incorporates a flash evaporator that has been developed to instantly vaporize liquid water. The performance of the instrument was assessed in a wide range from natural to highly enriched water samples. The accuracy was verified using waters with well-known isotopic abundances. The instrument was shown to be linear over a wide range of water isotopes ( $\delta^2\text{H} = -424$  to  $+16000$  ‰,  $\delta^{18}\text{O} = -54$  to  $+2300$ ‰, and  $\delta^{17}\text{O} = -29$  to  $+870$  ‰). The accuracy and precision of isotope ratio determinations for enriched waters match or exceed those of our pyrolysis-IRMS laboratory. Moreover, its ability to measure  $^{17}\text{O}$  with good accuracy and precision would make triply labelled water (TLW) analyses possible. The present set-up allows analysis of 4 water samples per hour; the entire measuring process is fully automatic and requires no user intervention. Although the performance of the instrument is satisfactory for our needs, it is surpassed by the newest commercial products on the market, in particular that of Los Gatos Research Inc.(using Off-Axis Intracavity optical spectroscopy), and of Picarro Inc.(using Wavelength Scanned Cavity Ring Down Spectroscopy). However, the performance of our instrument can certainly also be further increased, both by optimizing the functioning of the present instrument, and by a further optimized design, of the sample inlet system.

Applying the SLW and DLW techniques, with their use of water with enriched levels of the rare stable isotopes of hydrogen and/or oxygen, requires well-characterized enriched reference waters. The International Atomic Energy Agency (IAEA, Vienna) had such reference waters

available, but these are exhausted. New reference waters thus had to be produced in sufficient quantity, and a higher characterization quality was desired.

In chapter 4 of this work, we report the production and certification of one set of singly,  $^2\text{H}$ -enriched waters, produced in batches of 20 liters each, with nominal values for  $\delta^2\text{H}$  of 800 ‰, 6000 ‰ and 16000 ‰, and one set of doubly labelled ones, 10 liters each, with approximately the same  $\delta^2\text{H}$  values and with  $\delta^{18}\text{O}$  values of nominally 100 ‰, 750 ‰ and 2000 ‰. The reference waters were prepared by mixing well-characterized original waters gravimetrically: distilled natural water, isotopically pure  $^2\text{H}$  water, and highly  $^{18}\text{O}$  enriched water. We characterized the isotopic composition of the natural water through a ring test and that of the pure  $^2\text{H}$  and enriched  $^{18}\text{O}$  using dilutions with well known natural and depleted natural water. It turned out that the accurate characterization of the original parent waters was crucial. The isotopic abundances of both the pure  $^2\text{H}$  water and the highly  $^{18}\text{O}$  enriched water that we purchased were not accurately enough known for our purpose from the product certifications; the non-enriched isotopes of these waters were not specified at all, and yet probably enriched to some extent as well (and indeed turned out to be enriched as well).

On top of that, we have thoroughly discussed how the assigned values to the new reference waters are coupled to the accepted values for the isotope ratios of VSMOW( Vienna Standard Mean Ocean Water) and SLAP (Standard Light Antarctic Precipitation), and in particular to the "consensus" isotopic difference between VSMOW and SLAP. To ensure the correctness of our gravimetric mixing procedure, validation measurements have been carried out on the isotopic composition of the produced reference waters using different techniques, including our new OF-CEAS laser spectrometer. The produced new reference waters will be made available worldwide by the IAEA, they will be distributed in 5-mL aliquots.

To facilitate the isotope mixing calculations for all mixtures that had to be prepared and to avoid computational mistakes, we developed a user-friendly computation tool in an excel spreadsheet. With this spreadsheet the isotope values and corresponding isotopic abundances for any mixture of waters with different isotopic compositions can be computed. This is reported in chapter 5. The spreadsheet we produced allows the mixing of up to 10 different waters, of which up to five can be specified using their isotopic abundances and also up to five using their isotope delta values. This spreadsheet is the first that facilitates specification of the mixing components in both

isotope delta and isotope abundance scales. The tool has been thoroughly validated using three independently developed similar (but less user-friendly and less flexible) calculation spreadsheets. Several other applications of the tool are presented in the chapter.

In chapter 6 and 7 we focussed on quantification of isotope effects on the temperature of the triple point of water (TPW). The triple point is the physical state of a pure substance in which all the three phases coexist in thermodynamic equilibrium. The temperature of this triple point for water is the basis of the SI definition of the kelvin, and furthermore for the practical realization of the International Temperature Scale of 1990 (ITS-90). Any ITS-90 temperature in the range between 13.8033 K and 1234.93 K is realised using platinum resistance thermometers calibrated at the TPW. Therefore, any uncertainty in the realization of the TPW temperature is propagated to any temperature over this range. The isotopic composition of water was found to be one of the two major sources of uncertainty in the realization of TPW temperature (the other one is water impurities). Although this effect has been known for years (and has been incorporated in the definition by prescribing the isotopic composition of the used water to be that of VSMOW), thorough experimental investigations of this effect had not been carried out to date. In this work, we present a complete, detailed, and accurate experimental study of this subject in co-operation with VSL, the Netherlands' national metrology institute (NMI) in Delft, using their knowledge of, and state-of-the-art instrumentation for TPW temperature measurements. The production of waters with well-known isotopic composition, and subsequent isotope analysis was done in our group, using both IRMS and the OF-CEAS laser spectrometer. We present the hydrogen isotopic composition dependence of the TPW temperature in chapter 6 and the oxygen one in chapter 7. As all triple point cells to realize the TPW temperature contain water with an isotopic composition that is not equal to that of VSMOW, the realized temperature has to be corrected for that isotopic composition. Using the results of our experiments, we recommend a new, more accurate correction equation.

To conclude, the isotope community (the doubly labelled studies) and thermometry community will benefit from the outcomes of this thesis work. This new high-quality set of reference waters will help the DLW laboratories to accurately calibrate their unknown enriched waters by interspersing aliquots of these reference materials among water sample unknowns. A reliable tool is now available for calculations of both naturally occurring and laboratory mixing of isotopically different waters. Improved accuracy and reproducibility of the TPW temperature

will lead to both a general higher quality of temperature measurement, and to a higher quality of the realization of the kelvin according to the SI definition. As to the latter, this improvement comes timely in the light of discussions to redefine the kelvin based on Boltzmann's constant.

**References:**

[1] van Trigt R, Kerstel E. R. Th., Visser G H and Meijer H A. J **2001** *Anal. Chem.* **73**, 2445

