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Water enriched in the rare stable isotopes

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Chapter 8

Conclusions and outlook

This thesis focuses on using the stable isotopes of water in two distinctly different fields of study: Body composition and energy expenditure studies using the Singly and Doubly labelled water (DLW) methods and the accurate realization of the triple point of water (TPW). For the first application we presented the development and characterization of a prototype laser-based spectrometer using Optical Feedback Cavity Enhanced Absorption technology (OF-CEAS) in chapter 2 and 3, production of a high-quality set of singly and doubly stable isotope labelled reference waters for the isotope community (chapter 4), and development of a spreadsheet for isotope calculations of water mixtures (chapter 5). Regarding the second application, we studied the dependence of the TPW on the isotopic composition of the water (in chapter 6 and 7). Here we summarize the main results of the thesis, draw conclusions about our achievements, and outline some possible directions for future research.

In chapter 2, we presented the development of our "SARA" (Spectroscopy by Amplified Resonant Absorption) OF-CEAS prototype instrument for water isotope ratio measurements in biomedical research. We characterized the instrument and showed the preliminary results in chapter 3. The current laser spectrometer is capable of real-time, simultaneous measurements of $^2\text{H}/^1\text{H}$, $^{18}\text{O}/^{16}\text{O}$, and $^{17}\text{O}/^{16}\text{O}$ from enriched water samples with an accuracy and precision comparable to (or especially for ^2H isotope even better than) pyrolysis-IRMS. The performance of the instrument has been evaluated over a wide range of isotopic abundances that cover the whole range of possible enrichment levels of the DLW-derived specimens. The performance of the newest versions of two commercially available laser spectrometers from LGR Inc. [1] and Picarro Inc. [2] surpasses our instrument in precision and accuracy for the isotope ratios in natural water. However, as far we know they have not been examined for enrichment levels as high as we assessed on our OF-CEAS system. We have shown that throughout the whole range of enrichment levels, the achieved accuracy of our instrument is sufficient for the DLW method. More importantly, the calculation of energy expenditure does not depend on the absolute isotope ratios, but rather on the ratio of initial and final enrichment, and as such requires a good linearity

with a stable slope. This has been assured by the excellent linear and stable correlation between the measured and known isotope values over a wide range of isotopic abundances in our experimental assessment. Furthermore, the relative measurement precision increases with increasing enrichments.

Our instrument still suffers from considerable sample-to-sample memory. This is common for instruments dealing with water. For better accuracy and faster measurements, however, this memory must be minimized, for example by coating the inner surface of the cavity and the evaporation chamber with a hydrophobic coating.

As is described in chapter 4, we managed to produce a new set of singly and doubly stable isotope labelled reference waters (called IAEA-604 to IAEA-609) with unprecedented quality in terms of the accuracy by which the isotope ratios of these waters are known. They are being put to use as international reference materials for the calibration of isotope measurements of primarily SLW and DLW-related samples. They cover $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in the range of 800–16000 ‰ and 100–2000‰, respectively. They are being distributed by the International Atomic Energy Agency (IAEA) in 5-mL aliquots in borosilicate ampules. Thanks to their high quality, they can serve other purposes as well. The IAEA-604, with the lowest enrichment has been already used to connect the $\delta^2\text{H}$ scale of solid materials to the VSMOW-SLAP scale [3]. As a future work, CIO plans to establish the $\delta^{18}\text{O}$ value of SLAP (Standard Light Antarctic Precipitation) using the close relation between the $\delta^{18}\text{O}$ values of the new reference waters and the $\delta^{18}\text{O}$ of SLAP.

Through the work presented in chapter 5, a thoroughly tested spreadsheet is now available to calculate the isotopic composition for a mixture of waters (up to 10 different waters), expressed both in delta-values and isotopic abundances. This spreadsheet can be easily extended to include other isotopes, should the need arise.

The dependence of the temperature of triple point of water (TPW) on its exact isotopic composition has been discussed in second part of this thesis, in chapter 6 and 7. The TPW was selected to define the unit of thermodynamic temperature, the kelvin, by the 10th General Conference on Weights and Measures in 1954 [4]. The kelvin was defined as 1/273.16 fraction of the TPW temperature. In 1996, it was found that the isotopic composition (and the purity of the used water) influences the TPW significantly. To tackle this problem, the isotopic composition of the water was included in the kelvin definition. It must be identical to that of

VSMOW. As in practice, water in a triple point cell will never have that exact composition, an isotope effect correction was included.

Our work presented in chapter 6 and 7 presented the most complete, detailed, and accurate experimental study on this subject so far. The result of this research is a realization of the triple point of water with reduced uncertainty. The low uncertainty achieved in our correction coefficients resulted in an uncertainty $< 1 \mu\text{K}$ for triple point cell waters used around the world.

Our work is timely, as in 2011, a new definition of the kelvin, based upon the value of the Boltzmann constant was proposed [5]. For such a transition, the best possible realization of the kelvin using the present definition is crucial, and we contributed to achieving that.

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