



Very high precision and accuracy analysis of triple isotopic ratios of water. A critical instrumentation comparison study.

Vasileios Gkinis (1), Christian Holme (1), Valerie Morris (2), Abigail Grace Thayer (2), Bruce Vaughn (2), Helle Astrid Kjaer (1), Paul Vallelonga (1), Marius Simonsen (1), Camilla Marie Jensen (1), Anders Svensson (1), Niccolo Maffezzoli (1), Bo Vinther (1), and Remi Dallmayr (3)

(1) University of Copenhagen, Niels Bohr Institute, Copenhagen, Denmark, (2) Institute for Arctic and Alpine Research, University of Colorado, Boulder, USA, (3) National Institute for Polar Research, Tokyo, Japan

We present a performance comparison study between two state of the art Cavity Ring Down Spectrometers (Picarro L2310-i, L2140-i). The comparison took place during the Continuous Flow Analysis (CFA) campaign for the measurement of the Renland ice core, over a period of three months. Instant and complete vaporisation of the ice core melt stream, as well as of in-house water reference materials is achieved by accurate control of microflows of liquid into a homemade calibration system by following simple principles of the Hagen-Poiseuille law. Both instruments share the same vaporisation unit in a configuration that minimises sample preparation discrepancies between the two analyses.

We describe our SMOW-SLAP calibration and measurement protocols for such a CFA application and present quality control metrics acquired during the full period of the campaign on a daily basis. The results indicate an unprecedented performance for all 3 isotopic ratios ($\delta^2\text{H}$, $\delta^{17}\text{O}$, $\delta^{18}\text{O}$) in terms of precision, accuracy and resolution. We also comment on the precision and accuracy of the second order excess parameters of HD^{16}O and H_2^{17}O over H_2^{18}O (D_{xs} , $\Delta^{17}\text{O}$). To our knowledge these are the first reported CFA measurements at this level of precision and accuracy for all three isotopic ratios. Differences on the performance of the two instruments are carefully assessed during the measurement and reported here.

Our quality control protocols extend to the area of low water mixing ratios, a regime in which often atmospheric vapour measurements take place and Cavity Ring Down Analysers show a poorer performance due to the lower signal to noise ratios. We address such issues and propose calibration protocols from which water vapour isotopic analyses can benefit from.