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High resolution, high precision, simultaneous measurements of δD and δ^{18}O using a CRDS analyzer with an ultrasonic nebulizer sample preparation module.

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The recent advent of commercial Cavity Ring Down Spectroscopy (CRDS) has initiated the development of numerous new Continuous Flow Analysis (CFA) methods for high resolution, high precision measurements of greenhouse gas concentrations and isotopic ratios of water from ice cores. Depending on the sample preparation method and the calibration schemes applied, these new systems have proved to be precise, accurate and extremely versatile, allowing for high quality measurements performed in the field.

However there are still challenges to be addressed. Measurements need to be accurately calibrated with respect to international standards (SMOW – SLAP in the case of water). A proper characterization of the precision and the accuracy of a system is another task that needs to be performed. Apparent sample diffusion affects the produced signals in ways that are unique not only to different systems but also to different implementations of the same system, reducing the resolution that can be obtained. Parameters such as melt rate, sample flow, cavity volume and the method of sample preparation can significantly alter the performance of the analytical method. These effects can be accurately characterized with a series of experiments and consequently corrected for using spectral filtering techniques. Last but not least, proper monitoring of the melting process is necessary in order to assign an ice core depth scale on the data produced.

In this work we present an integrated system for high resolution, high precision water isotopic analysis from a continuously melted ice core sample, using a commercial CRDS analyzer (Picarro $L2130-i$) . The system utilizes an ultrasonic concentric nebulizer in order to achieve complete fractionation free vaporization of the continuous flow water sample. An adjacent home made calibration module allows for the injection of local standards accurately characterized with respect to the SMOW – SLAP scale. The system has been used for the high resolution isotopic analysis of $13\times13\mathrm{mm}$ ice rods sampled from the WAIS divide ice core. We present how we progress from raw data to SMOW and depth calibrated simultaneous measurements of δD and δ^{18}O). We discuss the achieved precision for the second order parameter of the Deuterium excess and propose ways to deconvolve the produced data for apparent smoothing effects using a Wiener filtering ap