



Development and evaluation of a spectral analysis method to eliminate organic interference with cavity ring-down measurements of water isotope ratios

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Cavity ring-down spectroscopy (CRDS) is a technology based on the spectral absorption of gas molecules of interest at specific spectral regions. The CRDS technique enables the analysis of hydrogen and oxygen stable isotope ratios of water by directly measuring individual isotopologue absorption peaks such as H₁₆OH, H₁₈OH, and D₁₆OH. Early work demonstrated that the accuracy of isotope analysis by CRDS and other laser-based absorption techniques could be compromised by spectral interference from organic compounds, in particular methanol and ethanol, which can be prevalent in ecologically-derived waters.

There have been several methods developed by various research groups including Picarro to address the organic interference challenge. Here, we describe an organic fitter and a post-processing algorithm designed to improve the accuracy of the isotopic analysis of the “organic contaminated” water specifically for Picarro models L2130-i and L2140-i. To create the organic fitter, the absorption features of methanol around 7200 cm⁻¹ were characterized and incorporated into spectral analysis. Since there was residual interference remaining after applying the organic fitter, a statistical model was also developed for post-processing correction. To evaluate the performance of the organic fitter and the postprocessing correction, we conducted controlled experiments on the L2130-i for two water samples with different isotope ratios blended with varying amounts of methanol (0-0.5%) and ethanol (0-5%).

When the original fitter was not used for spectral analysis, the addition of 0.5% methanol changed the apparent isotopic composition of the water samples by +62‰ for $\delta^{18}\text{O}$ values and +97‰ for $\delta^2\text{H}$ values, and the addition of 5% ethanol changed the apparent isotopic composition by -0.5‰ for $\delta^{18}\text{O}$ values and -3‰ for $\delta^2\text{H}$ values. When the organic fitter was used for spectral analysis, the maximum methanol-induced errors were reduced to +4‰ for $\delta^{18}\text{O}$ values and +5‰ for $\delta^2\text{H}$ values, and the maximum ethanol-induced errors were unchanged. When the organic fitter was combined with the post-processing correction, up to 99.8% of the total methanol-induced errors and 96% of the total ethanol-induced errors could be corrected. The applicability of the algorithm to natural samples such as plant and soil waters will be investigated.