



## Laser-based stable hydrogen and oxygen analyses: How reliable can measurement results be?

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A comparison of stable hydrogen and oxygen isotope-ratio analyses by dual inlet isotope-ratio mass spectrometry (IRMS) and laser absorption spectrometry indicates that laser-based analyses of filtered, low salinity, environmental waters can be substantially biased. For example, the IRMS and laser-based  $\delta^2\text{H}$  values of a Mississippi River sample collected November 26, 2007 at Thebes, Illinois were  $-49.6 \pm 0.2$  ‰ ( $N = 2$ ) and  $-36.8 \pm 0.9$  ‰ ( $N = 6$ ), respectively, which differ by more than 12 ‰. Comparative  $\delta^{18}\text{O}$  values for IRMS and laser-based measurements are  $-7.04 \pm 0.08$  ‰ ( $N = 2$ ) and  $-0.58 \pm 0.14$  ‰ ( $N = 6$ ), which differ by more than 6 ‰. Even larger  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  differences of 14.5 and 7.8 ‰ were determined from a Mississippi River sample collected December 19, 2007. Of comparative IRMS and laser-based  $\delta^2\text{H}$  measurements of a wide variety of ground-water, surface-water, precipitation, and tap-water samples (total = 588), 5 differed by more than 3 ‰. Each was measured at least twice by both techniques on different days. Of these 5 samples, 2 were Mississippi River samples, as described above and 3 were ground-water samples from wastewater sites or from sites contaminated with organic wastes. Of comparative  $\delta^{18}\text{O}$  measurements of 403 water samples measured at least twice by both techniques on different days, 14 differed by more than 0.40 ‰ and 3 differed by more than 1 ‰. These three sites, including two as described above, were all Mississippi River surface-water network samples collected in autumn or winter. Nevertheless, for the majority of samples, the differences in IRMS and laser-based measurements are small. For example, for 90 percent of the samples, the difference in  $\delta^2\text{H}$  measurements is less than 2 ‰ and that of  $\delta^{18}\text{O}$  is less than 0.3 ‰. The differences between the results appear to be due primarily to bias in the laser-based measurements caused by dissolved organic carbon (DOC). Addition of activated carbon granules to samples prior to analysis absorbs DOC and substantially improves agreement between the measurement techniques, but the addition of activated carbon to samples has yet to become common practice in the isotope community. Samples that are analyzed using only laser-based spectrometry might yield inaccurate results.

LIMS (Laboratory Information Management System) for Light Stable Isotopes was essential to the production, monitoring and maintenance of results from the laser based spectrometric system (Los Gatos Research Liquid-Water Isotope Analyzer). Using the latest version of LIMS for Light Stable Isotopes (<http://isotopes.usgs.gov/Research%20Highlights%20Pages/LIMS.htm>), the 1-sigma standard deviations of  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of a control water sample analyzed by laser spectrometry on 80 separate days between July 26, 2008 and November 26, 2008 were 0.54 and 0.15 ‰ respectively.

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