Laser absorption spectrometry for δ^{18}O and δ^{2}H measurements in environmental studies: Part I, Experiences and comparisons with dual-inlet isotope-ratio mass spectrometry*,†

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The measurement of the same water sample by any laboratory worldwide should yield the same δ^{2}H and δ^{18}O values, within analytical uncertainty. In most studies of clean water, the agreement between the "gold standard" dual-inlet isotope-ratio mass spectrometry (DI-IRMS) and laser absorption spectrometry (LAS) is good. However, in some cases, it is not satisfactory. Figure 1 shows measurements by LAS and DI-IRMS of a Mississippi River water sample collected by the U.S. Geological Survey (USGS) during regular surface-water network sampling. Differences in δ^{2}H and δ^{18}O values were as much as 22 and 6.5 ‰, respectively, between DI-IRMS and LAS measurements for this surface-water sample that contained a small amount of residual methanol from cleaning the compositing churn prior to sample collection for pesticides. For a landfill water sample, δ^{2}H and δ^{18}O differences of ~10 and ~0.4 ‰, respectively, were observed. Adding activated carbon to samples from landfills, sewage sites, and those containing volatile organic compounds, does not assist LAS to achieve "true" δ values (Figure 2).

Because of these observations and discussions with manufacturers at the European Geophysical Union meeting in Vienna in 2009, spectral interference software was developed by all LAS manufacturers. Nevertheless, LAS may determine erroneous δ values for some water samples with no indication that spectral interference remains. Figure 3 shows a comparison of

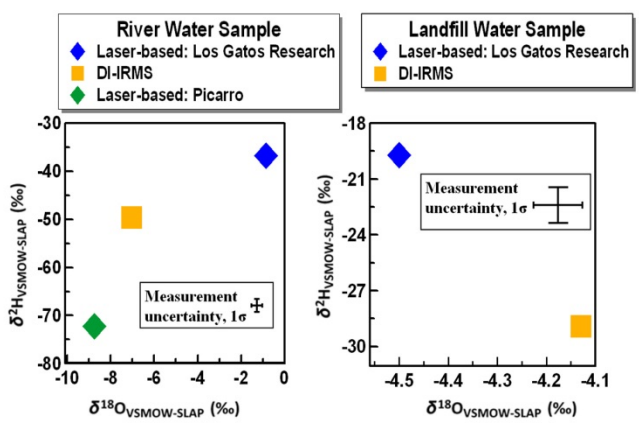

Figure 1. Comparison of δ^{2}H and δ^{18}O measurements of a Mississippi River water sample and a landfill water sample by laser absorption mass spectrometry and "gold standard" dual-inlet isotope-ratio mass spectrometry (modified from Singleton and others, 2009).

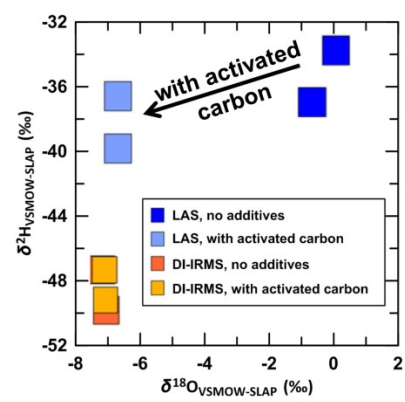

Figure 2. Shift in δ^{2}H and δ^{18}O by treatment of Mississippi River water samples with activated carbon. Although the δ^{18}O agreement improved substantially, δ^{2}H differences still exceed ~10 ‰ (modified from Singleton and others, 2009).

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* Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

† January 27, 2014 presentation for Laser Specs for Field Hydrology and Biogeochemistry: Lessons Learned and Future Prospects, A Virtual Workshop exploring the potential and pitfalls of a revolutionary technology, Organized by CUAHSI (Consortium of Universities for the Advancement of Hydrologic Sciences, Inc.) and the U.S. Geological Survey.

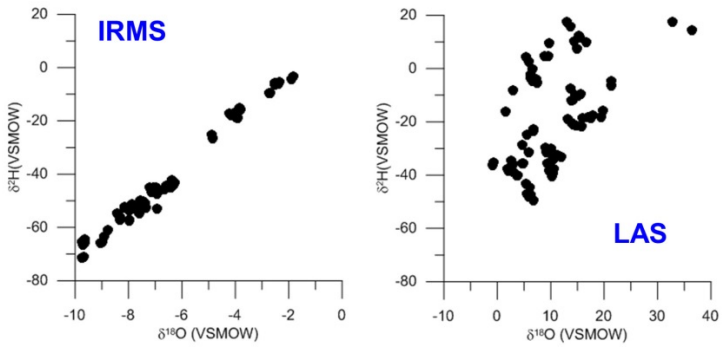

Figure 3. Comparison of δ^2H and δ^{18}O IAEA (International Atomic Energy agency) GNIP (Global Network of Isotopes in Precipitation) samples from Costa Rica during 2013. Two different LAS instruments indicated no spectral interference. Only the mass-spectrometric measurements were accurate.

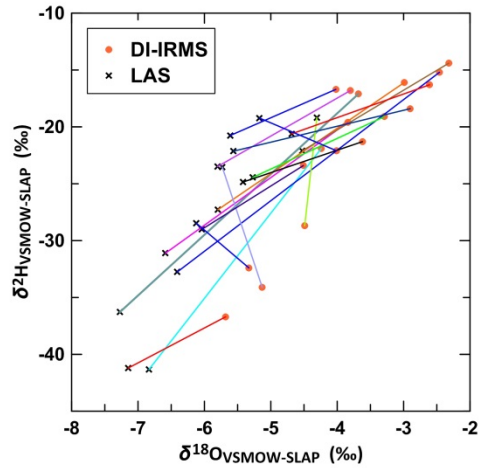

Figure 4. Comparison of LAS measurements by an unspecified laboratory and DI-IRMS measurements of low tannin surface-water samples collected in 2011 and 2012 that should have given identical results.

IRMS and LAS measurements of Costa Rica precipitation samples collected following a standard protocol using paraffin oil in the rain totalizer to minimize sample evaporation. Only the IRMS results were accurate, and the reason for the difference remains unknown. Two different LAS instruments indicated no spectral interference. The LAS measurements had excellent reproducibly on replicate samples, but accuracy was very poor with some δ^{18}O values being too positive by ~30 ‰ as compared with mass-spectrometric measurements (Figure 3).

Figure 4 shows comparison δ^2H and δ^{18}O measurements of low tannin surface-water samples by LAS from an unnamed laboratory and DI-IRMS by the Reston Stable Isotope Laboratory of the USGS. Only the DI-IRMS are accurate, and δ^2H and δ^{18}O differences were as large as 15 and 4 ‰, respectively.

If the isotope results must hold up in court, DI-IRMS is strongly preferred. An effective quality-assurance strategy used at both the IAEA and the RSIL is to analyze samples twice, once by LAS and once mass spectrometrically.

LAS users would benefit greatly if their LAS instruments informed them of problematic samples with a flag in a data output column of the comma separated variable file used by LIMS (Laboratory Information Management System) for Lasers. Users would not need to resort to using offline spectral interference identification programs. In such a case, problematic samples could be analyzed by mass-spectrometric methods. **LAS vendors are encouraged (1) to incorporate spectral interference identification software into their data acquisition and control software, and (2) to append a column in the data file to identify samples with spectral interference.**

Reference

Singleton, G., Coplen, T. B., Qi, H, and Lorenz, J. M., 2009, Laser-based stable hydrogen and oxygen analyses: How reliable can measurement results be?, European Geosciences Union, General Assembly, April 2009, Vienna, Austria. http://meetingorganizer.copernicus.org/EGU2009/EGU2009-3290.pdf