

# High-Precision Laser Spectroscopy D/H and $^{18}\text{O}/^{16}\text{O}$ Measurements of Microliter Natural Water Samples

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Newly available gas analyzers based on off-axis integrated cavity output spectroscopy (OA-ICOS) lasers have been advocated as an alternative to conventional isotope-ratio mass spectrometers (IRMS) for the stable isotopic analysis of water samples. In the case of  $\text{H}_2\text{O}$ , OA-ICOS is attractive because it has comparatively low capital and maintenance costs, the instrument is small and field laboratory portable, and provides simultaneous D/H and  $^{16}\text{O}/^{18}\text{O}$  ratio measurements directly on  $\text{H}_2\text{O}$  molecules with no conversion of  $\text{H}_2\text{O}$  to  $\text{H}_2$ ,  $\text{CO}$ , or  $\text{H}_2/\text{CO}_2$ —water equilibration required. Here we present a detailed assessment of the performance of a liquid-water isotope analyzer, including instrument precision, estimates of sample memory and sample mass effects, and instrumental drift. We provide a recommended analysis procedure to achieve optimum results using OA-ICOS. Our results show that, by using a systematic sample analysis and data normalization procedure routine, measurement accuracies of  $\pm 0.8\text{‰}$  for  $\delta\text{D}$  and  $\pm 0.1\text{‰}$   $\delta^{18}\text{O}$  are achievable on nanoliter water samples. This is equivalent or better than current IRMS-based methods and at a comparable sample throughput rate.

The past decade has witnessed the ongoing development and evolution of new laser gas analyzers based on off-axis integrated-cavity output spectroscopy (OA-ICOS) to the point of offering a commercially viable alternative to conventional stable isotope-ratio mass spectrometers (IRMS) for isotopic assays of selected environmental gas matrixes such as  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ .<sup>1–8</sup> A number of advantages of OA-ICOS technology over IRMS systems

have been identified.<sup>6</sup> For the purposes of stable isotope assays of natural waters discussed here, these advantages include the following: considerably lower upfront capital cost, benchtop size, field laboratory portability, few moving parts requiring regular maintenance (e.g., no high-vacuum pump inlet systems), no isobaric interferences with the gas of interest that requires a separate purification and analysis, and no costly external preparation systems for the conversion of  $\text{H}_2\text{O}$  to pure  $\text{H}_2$ ,  $\text{CO}$ , or water equilibration with  $\text{CO}_2$  or  $\text{H}_2$ . The elimination of reference and carrier gases required by continuous-flow IRMS (CF-IRMS) furthermore reduces daily operational costs. Finally, when used for stable isotopic measurements of waters, OA-ICOS measures D/H and  $^{18}\text{O}/^{16}\text{O}$  directly and simultaneously on  $\text{H}_2\text{O}$  molecules from a single injection, which is impossible with conventional IRMS systems. This simplification reduces both the time for sample analysis and error intrinsic to the conversions of  $\text{H}_2\text{O}$  to  $\text{H}_2$  or  $\text{CO}/\text{CO}_2$ . The primary disadvantage of laser-based gas isotope analyzers compared to IRMS is decreased analytical flexibility because these instruments are generally dedicated to a single gas isotopic species of interest (e.g.,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , or  $\text{CH}_4$ ). Further, optical laser measurements for other gas species of immense isotopic interest (e.g.,  $\text{O}_2$ ,  $\text{SO}_2$ ,  $\text{CO}$ ,  $\text{N}_2$ ) are not currently available.

The objective of this study was to independently assess a commercially available OA-ICOS system for the analysis of natural waters for high-precision stable isotope assays of  $^2\text{H}$  and  $^{18}\text{O}$  and its potential for use as a routine analytical tool in a stable isotope laboratory operation. For this study, we used a Los Gatos Research Liquid Water Analyzer model 908-0008 ([www.lgrinc.com](http://www.lgrinc.com)) for the direct D/H and  $^{18}\text{O}/^{16}\text{O}$  isotopic ratio measurements of natural waters. The Liquid Water Analyzer instrument uses OA-ICOS<sup>9</sup> and, compared to previous spectrometers that use laser spectroscopy,<sup>5,10–12</sup> relies on spatial separation of reflections from highly reflective mirrors installed within the cavity. The use of highly reflective off-axis mirrors effectively extends average optical path length to  $\sim 3000$  m. This extensive path length for light results in increased

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- (1) Barbour, M. M.; McDowell, N. G.; Tcherkez, G.; Bickford, C. P.; Hanson, D. T. *Plant Cell Environ.* **2007**, *30*, 469–482.
- (2) Bowling, D. R.; Sargent, S. D.; Tanner, B. D.; Ehleringer, J. R. *Agric. For. Meteorol.* **2003**, *118*, 1–19.
- (3) Crosson, E. R.; Ricci, K. N.; Richman, B. A.; Chiles, F. C.; Owano, T. G.; Provencal, R. A.; Todd, R. A.; Glasser, J.; Kachanov, A. A.; Paldus, B. A.; Spence, T. G.; Zare, R. N. *Anal. Chem.* **2002**, *74*, 2003–2007.
- (4) Griffiths, T. J.; Baker, J. M.; Sargent, S. D.; Tanner, B. D.; Zhang, J. *Agric. For. Meteorol.* **2004**, *124*, 15–29.
- (5) Kerstel, E. R. T.; Gagliardi, G.; Gianfrani, L.; Meijer, H. A. J.; van Trigt, R.; Ramaker, R. *Spectrochim. Acta, Part A* **2002**, *58*, 2389–2396.
- (6) Kerstel, E. R. T.; Piersma, T.; Gessaman, J. A. *Isot. Environ. Health Stud.* **2006**, *42*, 209–209.
- (7) Kerstel, E. R. T.; van der Wel, L. G.; Meijer, H. A. J. *Isot. Environ. Health Stud.* **2005**, *41*, 207–216.

- (8) Lee, X.; Sargent, S.; Smith, R.; Tanner, B. J. *Atmos. Oceanic Technol.* **2005**, *22*, 1305–1305.
- (9) Baer, D. S.; Paul, J. B.; Gupta, J. B.; O'Keefe, A. *Appl. Phys. B: Lasers Opt.* **2002**, *75*, 261–265.
- (10) Kerstel, E. R. T.; van Trigt, R.; Dam, N.; Reuss, J.; Meijer, H. A. J. *Anal. Chem.* **1999**, *71*, 5297–5303.
- (11) Gianfrani, L.; Gagliardi, G.; van Burgel, M.; Kerstel, E. R. T. *Opt. Express* **2003**, *11*, 1566–1576.
- (12) Kerstel, E. R. T.; Iannone, R. Q.; Chenevier, M.; Kassi, S.; Jost, H.-J.; Romanini, D. *Appl. Phys. B: Lasers Opt.* **2006**, *85*, 397–406.

absorption, thereby allowing the use of more economical industrial grade infrared diode lasers that can be operated at room temperature and do not require liquid nitrogen cooling. The laser wavelength is tuned over the absorption spectra of the gas species and the isotopologues of interest, here  $\text{H}_2\text{O}$ . During the measurement, the cavity temperature, cavity pressure, laser path length, and absorptions are recorded and used to calculate isotopologue concentrations and the corresponding ratios of interest. Instrument details, theory of operation, and method description are fully described elsewhere<sup>9,13</sup> and at the manufacturers web site ([www.lgrinc.com](http://www.lgrinc.com)).

## METHODS

An OA-ICOS water isotope analyzer (Los Gatos model 908-0008) was coupled to a CTC LC-PAL liquid autosampler for simultaneous D/H and  $^{18}\text{O}/^{16}\text{O}$  ratios measurements of  $\text{H}_2\text{O}$ . The liquid autosampler, which can hold up to 200 samples, was interfaced to the laser analyzer via a heated (70 °C) septum injection port and  $\sim 1$  m of  $1/8$ -in.-o.d. Teflon transfer tubing that was wrapped with heating tape and also kept at 70 °C to facilitate vapor transfer. The liquid autosampler was programmed using the analyzer software to inject from 0.2 to 1.0  $\mu\text{L}$  of  $\text{H}_2\text{O}$  using a 1.2- $\mu\text{L}$  Hamilton microliter syringe (model 7701.2N). The analyzer software interface allowed the user to enter sample lists for analyses, and data output was imported through an interface to LIMS for Light Stable Isotopes (U.S. Geological Survey, <http://isotopes.usgs.gov>) for data normalization and storage.

As noted above, the OA-ICOS instrument does not make use of a comparative reference gas of known isotopic composition, although such ICOS configurations exist, are more complex, and have been described elsewhere.<sup>10</sup> Hence, to determine the  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  of unknown samples, it was necessary to include at least two widely separated and previously calibrated stable isotope working standards or primary isotopic water references within and throughout each autorun. Further, unlike IRMS methods, the OA-ICOS instrument measures the concentrations of the individual isotopologues of  $\text{H}_2\text{O}$  and calculates absolute ratios. Hence, to convert isotopic ratios to the conventional  $\delta$  notation relative to the VSMOW standard, the absolute ratios must be recalculated using the conventional  $\delta$  equation and the known isotopic ratios of Vienna standard mean ocean water (VSMOW) or through the use of calibrated laboratory working standards and their ratios relative to VSMOW.

All water samples and calibrated laboratory working standard waters were pipetted into Waters 12  $\times$  32 mm screw-top 2-mL vials capped with preslit PTFE/silicone septa. Water samples (0.2–1.0  $\mu\text{L}$ ) were injected through a septum port in the liquid autosampler and dynamically transferred as vapor through the Teflon tube into the analyzer cavity for measurement. The liquid autosampler injector was maintained at 70 °C to ensure complete sample evaporation and gaseous transfer through the Teflon tube to the pre-evacuated optical cavity where laser absorption specific to the isotope composition was measured. Expansion of sub-microliter injections into the large optical chamber ensured no liquid water remained in the injection and transfer line.

In this study, we did not presume that the OA-ICOS measured sample isotopic ratios could be unquestioningly related to VS-

MOW absolute ratios. All measured water samples were instead calibrated and normalized to internal laboratory water standards that were previously calibrated relative to VSMOW (0‰) and VSLAP ( $\delta\text{D}$  –428‰ and  $\delta^{18}\text{O}$  –55.5‰) using conventional IRMS systems. Consequently, all measured values reported here are relative to VSMOW.

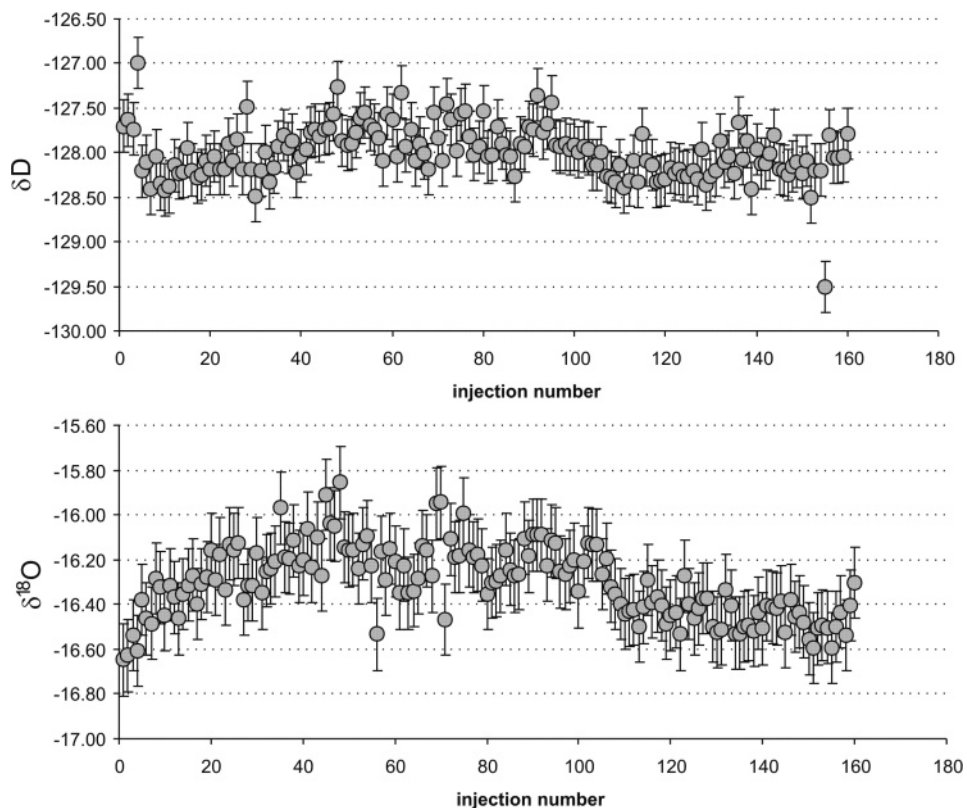
## RESULTS AND DISCUSSION

**Sample Precision.** Experiments of 160 consecutive injections of ultrapure water (known  $\delta\text{D}$  = –128‰,  $\delta^{18}\text{O}$  = –16.3‰ VSMOW) were conducted to assess the analytical precision of the instrument (Figure 1). In these experiments, 0.75- $\mu\text{L}$  samples were injected sequentially over a period of  $\sim 11$  h. In Figure 1, we present the typical results of one representative experiment. A high precision of measurement for both  $\delta\text{D}$  and  $\delta^{18}\text{O}$  with a very low standard deviation of  $\pm 0.29\text{‰}$  for  $\delta\text{D}$  and  $\pm 0.16\text{‰}$  for  $\delta^{18}\text{O}$  measurements ( $n$  = 160) was obtained. Of the 160 single injections for  $\delta\text{D}$ , 8 samples (5%) differed from the mean value of –128‰ by  $>0.5\text{‰}$  and 1 sample (1%) differed by  $>1\text{‰}$ . For  $\delta^{18}\text{O}$  measurements, 8 samples (6%) differed from the mean value of –16.3 by  $>0.3\text{‰}$  and none of the samples differed by  $>0.5\text{‰}$ . To improve precision, the 3 nearest injection results were grouped and average values calculated (Figure 2). This procedure slightly improved the precision for the  $\delta\text{D}$  measurements, lowering standard deviation from  $\pm 0.29$  to  $\pm 0.22\text{‰}$ , whereas standard deviation for  $\delta^{18}\text{O}$  remained unchanged. This suggested that variations in  $\delta\text{D}$  measurements are attributed to measurement imprecision in large part, whereas  $\delta^{18}\text{O}$  variations are related mostly to slow instrumental drift over time in the measured values (see below).

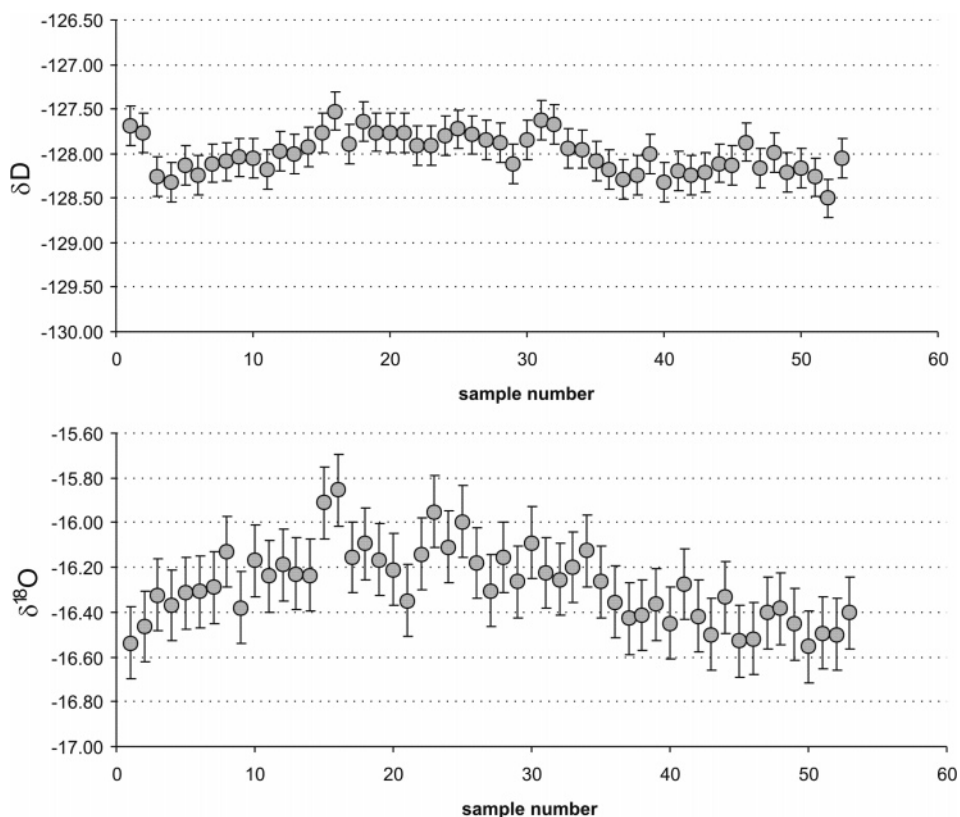
**Instrumental Drift.** A slow and temporal instrumental drift was observed for both  $\delta\text{D}$  and  $\delta^{18}\text{O}$  with an increased number of 0.75- $\mu\text{L}$  sample injections (Figures 1 and 2). The magnitude of drift for  $\delta\text{D}$  and  $\delta^{18}\text{O}$  was about 0.6 and 0.4‰, respectively, over 11 h. However, based on more than 6 months of testing, this drift was random in any direction at a magnitude similar to that shown in Figure 1, and drift in  $\delta\text{D}$  and  $\delta^{18}\text{O}$  was generally correlated. For the representative example shown in Figure 1, the isotopic values between sample injections 40 and 100 were more positive than the overall mean, whereas sample values between 110 and 160 injections were more negative than the mean for both  $\delta\text{D}$  and  $\delta^{18}\text{O}$  measurements, although this effect was more pronounced in the  $\delta^{18}\text{O}$  measurements (Figure 1, lower panel).

This observed instrumental drift can be easily corrected by systematically spacing standard injections within the autorun and conducting linear interpolations. For example, using the same data in Figure 1, we assumed that every third sample was a “reference” injection, starting from the first three injections. In this case, our sample list was composed of standard (3 injections), sample A (3 injections), sample B (3 injections), standard (3 injections), sample C (3 injections), and so on. Sample isotopic values were corrected by assuming a linear drift interpolated between adjacent identical standards. After this linear drift correction was applied, the precisions improved significantly for both  $\delta\text{D}$  and  $\delta^{18}\text{O}$  measurements (Figure 3). The standard deviation decreased to  $\pm 0.13\text{‰}$  for  $\delta\text{D}$  and  $\pm 0.06\text{‰}$  for  $\delta^{18}\text{O}$ . For the 34 calculated  $\delta\text{D}$  sample values, 2 differed by  $>0.3\text{‰}$  from the mean. For the 34 calculated  $\delta^{18}\text{O}$  sample values, none of the values differed from the mean by  $>0.2\text{‰}$  and only 4 values differed by  $>0.1\text{‰}$ .

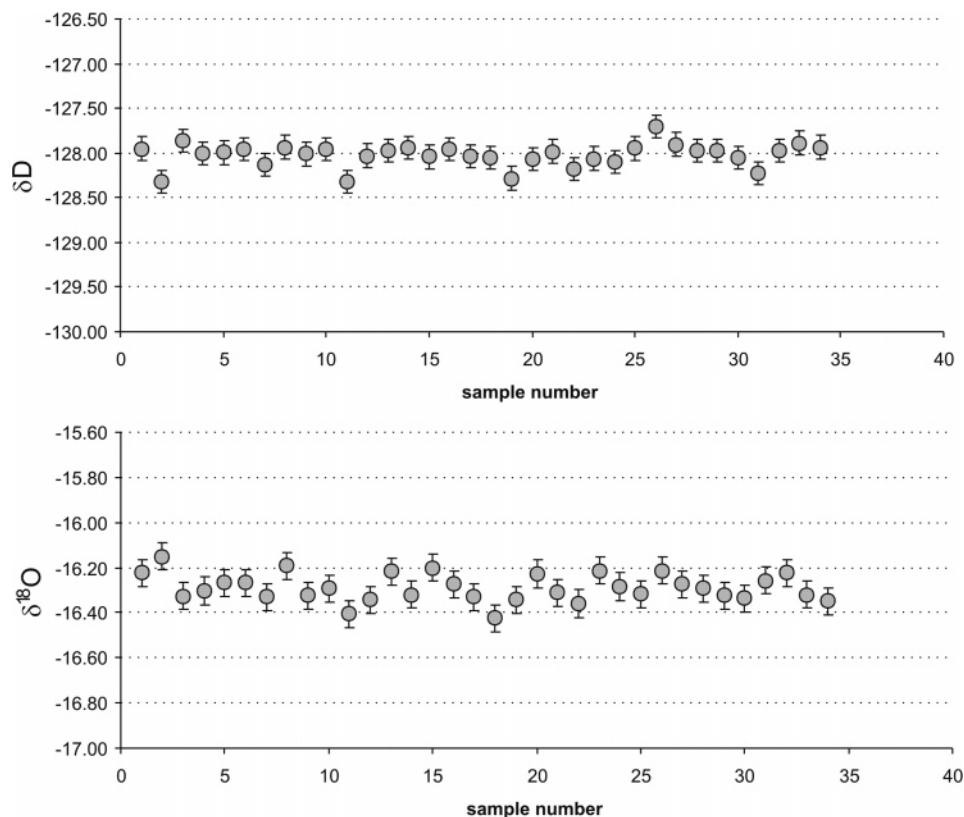
(13) Paul, J. B.; Lapson, L.; Anderson, J. G. *Appl. Opt.* **2001**, *40*, 4904–4910.



**Figure 1.**  $\delta D$  and  $\delta^{18}O$  values for 160 sequential 0.75- $\mu L$  injections of an ultrapure water sample over an 11-h period (0–160). Slow drift was evident for both isotopes, but are more pronounced for  $\delta^{18}O$ . Values between 40 and 100 injections were more positive than the mean, whereas values between 110 and 160 were more negative than the mean. Error bars equal standard deviations  $\pm 0.29$  and  $\pm 0.16\text{‰}$  for  $\delta D$  and  $\delta^{18}O$ , respectively.



**Figure 2.**  $\delta D$  and  $\delta^{18}O$  values of ultrapure water samples calculated from a running mean of 3 injections ( $t = 11$  h). The drift in the measured values is more pronounced than in Figure 1. Error bars equal standard deviations  $\pm 0.22$  and  $\pm 0.16\text{‰}$  for  $\delta D$  and  $\delta^{18}O$ , respectively.



**Figure 3.**  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of 0.75- $\mu\text{L}$  ultrapure water samples calculated from a running average of 3 injections and corrected for instrumental drift ( $t = 11$  h). Error bars equal standard deviations  $\pm 0.13$  and  $\pm 0.06\text{‰}$  for  $\delta\text{D}$  and  $\delta^{18}\text{O}$ , respectively.

**Sample Memory Effects.** Because the physical transfer of liquid water vaporized in the heated liquid autosampler port and transfer tubing was by static expansion into the previously evacuated OA-ICOS chamber, the potential for intersample memory effects due to the “stickiness” of water was considered. Further, the potential for mixing of water samples in the syringe and adsorption of sample water onto the inner surfaces transfer tubing could also result in intersample memory effects, as had been previously documented in IRMS preparation systems.<sup>14</sup> As a result, tests were conducted to assess the intersample memory effects exhibited by the OA-ICOS-liquid autosampler setup.

For this test, two isotopically separated laboratory water standards were used: INV1 with a  $\delta\text{D}$  value of  $-217\text{‰}$  and  $\delta^{18}\text{O}$  value of  $-28.6\text{‰}$ , and ROD2 with a  $\delta\text{D}$  value of  $+6\text{‰}$  and  $\delta^{18}\text{O}$  of  $-0.6\text{‰}$ , relative to VSMOW. These laboratory standards were each measured in a continuous series of 10 injections for each standard, and the two standard series was alternated 10 times (10 INV1, 10 ROD2, 10 INV1, etc.). The first, second, third, etc., injections following the standard change were grouped and their isotopic values averaged (Figure 4). For  $\delta\text{D}$ , the mean of the first injection following a standard switch deviated by 10‰ from the correct value, and the mean of the second injection deviated by 2.5‰ from reported  $\delta\text{D}$  value (Figure 4). By the third injection, the mean value was within an acceptable analytical error ( $\leq 1.1\text{‰}$ ) of the correct value. For  $\delta^{18}\text{O}$ , the mean value of the first injection differed from the correct value by 0.43‰. The mean values of the second and subsequent injections differed by  $<0.1\text{‰}$  from the correct value.

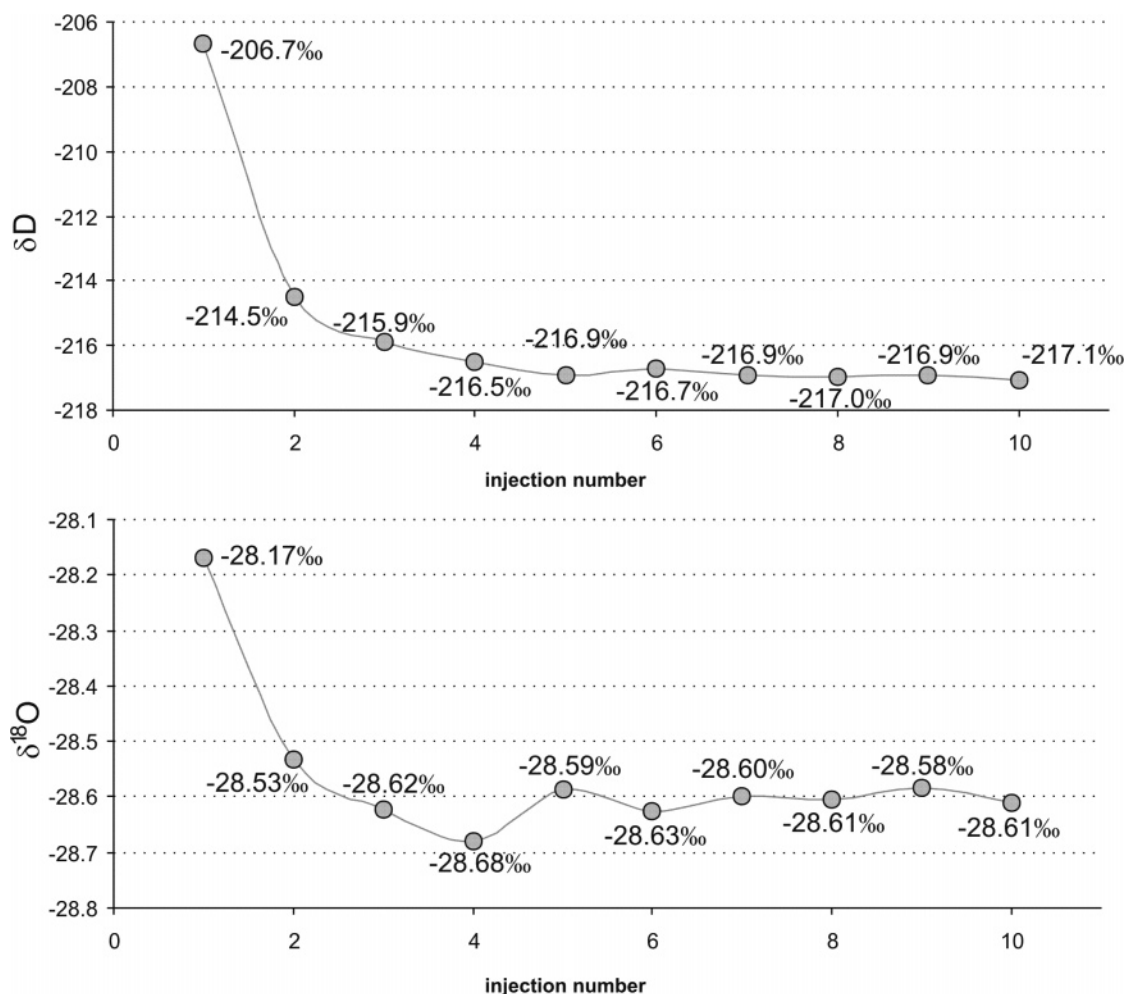
A second experiment was conducted using a set of two samples having smaller and more typical isotopic  $\delta\text{D}$  differences (B-73,  $\delta\text{D} = -73.0$ ; TAP,  $\delta\text{D} = -131.0\text{‰}$ ). As expected, the experiment showed that the memory effects were smaller when the isotopic differences between samples were much smaller. Specifically, for  $\delta\text{D}$ , the first injection after sample change differed by 2.8‰ from the correct value, the mean the second injection deviated by 0.8‰, and the mean values of the remaining injections deviated by less than 0.4‰.

In summary, our experiments here revealed that the number of injections required to overcome potential intersample memory effects and obtain accurate isotopic values depended on the isotopic difference between the samples and the working standards and was more pronounced for  $\delta\text{D}$ . Similar memory effects are observed for IRMS water preparation systems. Based on these findings, we recommend using five sequential injections of each sample or reference, with the first two injection results being discarded and the mean of the last three injections accepted as the final result for measuring natural waters. Furthermore, for all measurements, the final three injections must also be closely scrutinized for isotopic dependencies based on the actual mass of the injected sample (see below). Practically, this means that the highest precision throughput (with simultaneous  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) is  $\sim 20$  min/sample, which compares favorably to IRMS systems, and especially so since IRMS systems generally require separate assays or preparations for each isotope.

**Sample Mass Effects and Outliers.** Measurements with sample injection volumes of 0.2, 0.4, 0.6, 0.8, and 1.0  $\mu\text{L}$  were performed to investigate the effect of sample mass on the measured isotopic ratios. Each sample volume experiment con-

(14) Morrison, J.; Brockwell, T.; Merren, T.; Fourel, F.; Phillips, A. M. *Anal. Chem.* **2001**, *73*, 3570–3575.





**Figure 4.** Isotopic values of 0.75- $\mu$ L injections of “light” laboratory standard INV1 ( $\delta D = -217\text{‰}$ ,  $\delta^{18}O = -28.6\text{‰}$ ) followed by “heavier” laboratory standard ROD-2 ( $\delta D = +6\text{‰}$ ,  $\delta^{18}O = -0.6\text{‰}$ ). Memory effects were negligible after the third injection.

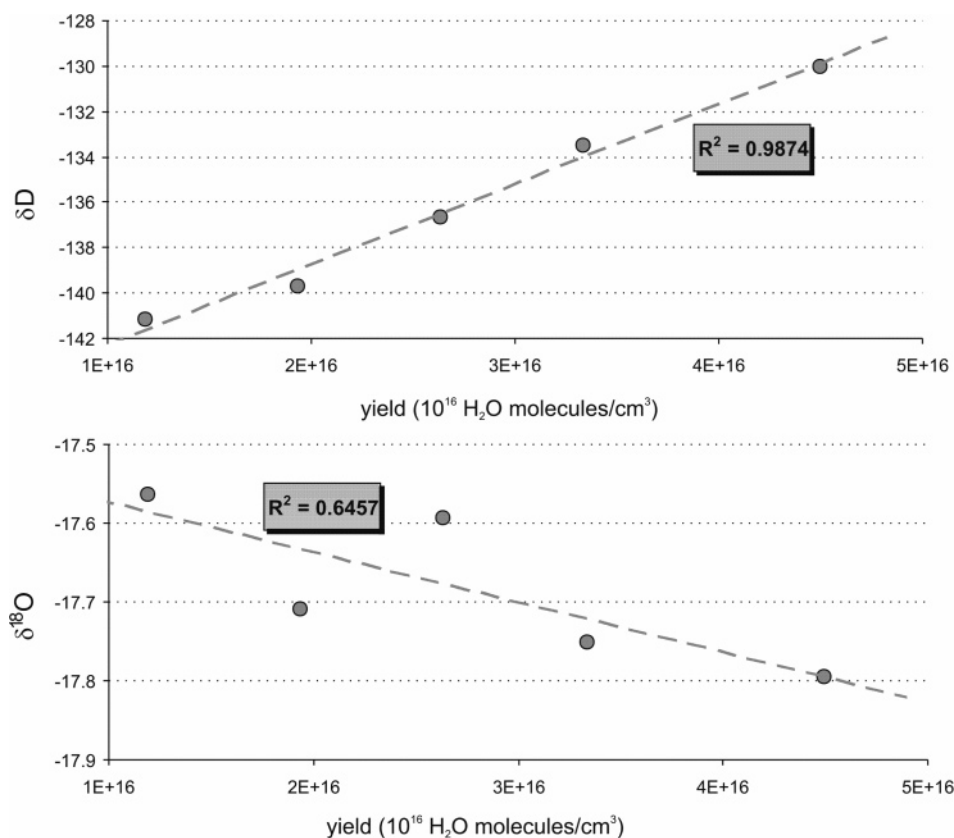
sisted of 10 injections preceded and followed by 0.75- $\mu$ L injections of established laboratory water standards in order to normalize the results and correct for drift. Of the 10 sample injections at these various volumes, the first 3 results were discarded because of potential memory effects described above and the remaining 7 injections were averaged. In all cases, and in order to clearly illustrate the dependency of the ratios on  $H_2O$  volume, the isotopic working standards injection volumes were held constant at 0.75  $\mu$ L. Figure 5 clearly illustrates dependencies of calculated isotopic values on mass of water molecules entering and measured within the optical cavity. Hydrogen isotopic values exhibited a highly linear trend with  $\delta D$  values becoming more positive with increasing sample volume or  $H_2O$  mass. An 11‰ increase was observed in  $\delta D$  values for this spread in sample volume, expressed as mass from  $1.2 \times 10^{16}$  to  $4.5 \times 10^{16}$   $H_2O$  molecules/ $cm^3$  present within the optical cavity. For  $\delta^{18}O$ , the observed change was much smaller (Figure 5, lower panel), ranging from  $-17.56\text{‰}$  for the smallest injection volume to  $-17.80\text{‰}$  for the largest injection volume. Thus, it is apparent that highly precise injection volumes are required and a heightened vigilance to factors that can affect the mass of water injected are critical (septum leakage, syringe jamming).

For the purpose of measuring natural water samples, we adopted the protocol of accepting only the results for which the

measured  $H_2O$  sample mass was within an acceptable range of  $(3.1 \times 10^{16}) \pm 0.1$   $H_2O$  molecules/ $cm^3$  (this exact determination is likely to be instrument specific). Although the volume of injected water samples and standards was set to be constant for routine operation, we observed that small variations in the injected mass can occur within a routine sample autorun. These small mass variations can adversely and dramatically affect measured isotopic ratios as demonstrated above. Variations in sample size during analysis may be due to a number of factors including the following: (1) septum failure or leakage, (2) septum under- or overtightening; (3) natural salt precipitates formed within the syringe causing needle partial jamming or malfunction, and (4) extended use of a syringe (i.e., physical wear). These factors ultimately affect  $H_2O$  transfer issues and can be avoided by regular septum changes and operational diligence.

#### Data Normalization Procedures for Optimum Results.

Based on our testing of an OA-ICOS optical laser system, we recommend a systematic approach to stable isotopic assays of natural water samples using this new technology. Our approach consisted of injecting every sample and isotope laboratory standard sequentially five times. Isotopic ratios from the first two injections were rejected because of the potential for intersample memory effects. The sample masses of the last three injections were then scrutinized for mass yield. If  $H_2O$  mass yield fell outside the



**Figure 5.** Influence of sample injection volume (expressed as mass yield) on the measured  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values. From left to right, sample injection volumes were 0.2, 0.4, 0.6, 0.8, and 1.0  $\mu\text{L}$  and results were normalized to 0.75- $\mu\text{L}$  injections of two laboratory standards.

specified range of  $(3.1 \times 10^{16}) \pm 0.1 \text{ H}_2\text{O molecules/cm}^3$ , the sample results were discarded and this sample was repeated in another run. If mass yield was within acceptable limits,  $\delta$  values of samples and standards were then calculated using the mean of the last three injections. In order to correct for instrumental drift, each autorun consisted of alternating injections of working standards at the beginning of the run and repeated after every two unknown samples. Autoruns may therefore have to be limited to 200–230 injections in order to avoid septum failure, which translates to  $\sim 26$ –30 unknown samples. Increasing the number of injections was not recommended as we observed that septa often became leaky after  $>250$  injections as revealed by variable mass yields. Finally, we recommend routinely including 10 injections of ultrapure water following injection of the last sample in order to wash out salt buildup in the needle and to improve the functional lifetime of costly microliter syringes. While we did not test salty and brine water samples, we found no adverse effects using groundwater samples having up to 15 000 mg/L TDS.

Using the above recommended procedure, we measured four samples from the international Interlaboratory Comparison of Water Samples—WICO 2002.<sup>15</sup> Internationally accepted values for WICO waters and results obtained from OA-ICOS water isotope analyzer procedure are presented in Table 1. For  $\delta\text{D}$ , the mean differences ranged from  $-0.4$  to  $+1.1\text{‰}$ , with the standard deviation of measurement being  $\pm 0.8\text{‰}$ . For  $\delta^{18}\text{O}$ , mean differences between accepted and measured values ranged from  $+0.03$

**Table 1. Comparison of Mean ( $n = 3$ )  $\delta\text{D}$  and  $\delta^{18}\text{O}$  Values Using the OA-ICOS Water Isotope Analyzer with WICO2002 Interlaboratory Comparison of Water Samples<sup>15</sup> Following the Recommended Analysis Procedure**

sample	Wico 2002 Report $\delta\text{D}$	$\delta^{18}\text{O}$
OH 5	−2.1	−0.26
OH 6	−39.1	−4.22
OH 7	−77.8	−10.72
OH 8	−122.0	−16.27
sample	OA-ICOS Water Isotope Analyzer $\delta\text{D}$	$\delta^{18}\text{O}$
OH 5	−2.5	−0.38
OH 6	−38.3	−4.19
OH 7	−77.7	−10.87
OH 8	−120.7	−16.21
sample	Mean Isotopic Difference $\Delta\text{D}$	$\Delta^{18}\text{O}$
OH 5	−0.4	−0.12
OH 6	0.8	0.03
OH 7	−0.2	−0.15
OH 8	1.1	0.06

to  $-0.15\text{‰}$  with standard deviation of the measurement being  $\pm 0.11\text{‰}$ .

## CONCLUSION

Results show that OA-ICOS laser technology for the measurement of liquid water isotopes yields comparable or better accuracy

(15) Gröning, M.; Graeber, S.; Bhattacharya, S. K.; van Duren, M.; Andreescu, L. IAEA, Vienna, May 2003.

for  $\delta D$  compared to both offline dual-inlet (e.g., zinc or uranium reduction) and continuous flow IRMS methods (e.g., C reduction, Cr reduction), which are generally on the order of  $\pm 0.5$  to  $\pm 4\%$ .<sup>14,16–21</sup> For  $\delta^{18}O$ , the OA-ICOS gas analyzer yielded accuracies that were comparable to or better than current automated CF-IRMS methods such as C-reduction to CO and CO<sub>2</sub>–H<sub>2</sub>O equilibration, which generally range between  $\pm 0.1$  and  $\pm 0.4\%$ .<sup>20–25</sup> Conventional IRMS, however, requires chemical conversion or isotopic equilibration of water molecules with other gas species. Measurement of both D/H and  $^{18}O/^{16}O$  ratios directly on water molecules via OA-ICOS laser spectroscopy fully eliminates the need for chemical conversions and thereby avoids errors intrinsic to such conversions.

In addition to the demonstrated precision and accuracy of OA-ICOS, there are additional benefits to this technology over IRMS. These include lower upfront capital cost, simplicity, field laboratory portability, few consumables, and elimination of reference and carrier gases. We therefore conclude that OA-ICOS is fully suitable for high-precision routine isotopic analysis of natural waters and thereby provides an attractive lower cost option to IRMS systems for this specific assay. Additional benefits include the option of field or ship portability for tracer and in-field experiments or use in laboratories that cannot meet the stringent environmental and electrical conditions required by complex IRMS systems.

- (16) Eiler, J. M.; Kitchen, N. *Geochim. Cosmochim. Acta* **2001**, *65*, 4467–4479.
- (17) Kelly, S. D.; Heaton, K. D.; Brereton, P. *Rapid Commun. Mass Spectrom.* **2001**, *15*, 1283–1286.
- (18) Kelly, S. D.; Parker, I. G.; Sharman, M.; Dennis, M. J. *J. Mass Spectrom.* **1998**, *33*, 735–738.
- (19) Karhu, J. A. *Anal. Chem.* **1997**, *69*, 4728–4730.
- (20) Begley, I. S.; Scrimgeour, C. M. *Rapid Commun. Mass Spectrom.* **1996**, *10*, 969–973.
- (21) Gehre, M.; Geilmann, H.; Richter, J.; Werner, R. A.; Brand, W. A. *Rapid Commun. Mass Spectrom.* **2004**, *18*, 2650–2660.
- (22) Fessenden, J. E.; Cooks, C. S.; Lott, M. J.; Ehleringer, J. R. *Rapid Commun. Mass Spectrom.* **2002**, *16*, 1257–1260.
- (23) Socki, R. A.; Romanek, C. S.; Gibson, Jr. E. K. *Anal. Chem.* **1999**, *71*, 2250–2253.
- (24) Begley, I. S.; Scrimgeour, C. M. *Anal. Chem.* **1997**, *69*, 1530–1535.
- (25) Sharp, Z. D.; Atudorei, V.; Durakiewicz, T. *Chem. Geol.* **2001**, *178*, 197–210.

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