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Approaches for Achieving Long-Term Accuracy and Precision of $\delta^{18}O$ and $\delta^{2}H$ for Waters Analyzed using Laser Absorption Spectrometers

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Abstract

The measurement of δ^2H and δ^{18}O in water samples by laser absorption spectroscopy (LAS) are adopted increasingly in hydrologic and environmental studies. While LAS instrumentation is easy to use, its incorporation into laboratory operations is not as easy, owing to extensive offline data manipulation required for outlier detection, derivation and application of algorithms to correct for between-sample memory, correcting for linear and non-linear instrumental drift, VSMOW-SLAP scale normalization, and in maintaining long-term QA/QC audits. Here we propose a series of standardized water isotope LAS performance tests and routine sample analysis templates, recommended procedural guidelines, and new data processing software (*LIMS for Lasers*) that altogether enables new and current LAS users to achieve and sustain long-term δ^2H and δ^{18}O accuracy and precision for these important isotopic assays.

Keywords: oxygen-18, deuterium, hydrology, water isotopes, laser spectroscopy, methods, stable isotopes

Introduction

Although isotope-ratio mass spectrometry (IRMS) is a traditional way to conduct stable hydrogen and oxygen isotope (δ^2H and δ^{18}O) analysis of water, since 2007 their measurement for hydrologic studies are increasingly conducted by tuneable diode infrared laser absorption spectroscopy (LAS), and is fast replacing IRMS in many areas[1]. LAS technology measures optically the concentrations of water stable isotopologues from nanoliter liquid water injections (e.g. on the vaporized H_2O molecules) by using cavity ring-down laser spectroscopy (CRDS) or off-axis integrated cavity output laser spectroscopy (OA-ICOS). Previous studies described LAS technology and performance compared to IRMS[2-9]. Because LAS performance equals or exceeds IRMS for δ^2H or δ^{18}O measurements of environmental water samples at lower cost, this technology is quickly expanding into laboratories that do not have isotopic analysis experience. Comparative benefits over IRMS include small bench-top footprint, portability, and modest laboratory infrastructure requirements. LAS technology may not be suitable for water samples having high salinity or interfering organic compounds for which interferences in the isotopologue infrared absorption intensities cannot be corrected for[4, 10].

While LAS instrumentation is easy to operate, obtaining accurate δ^2H and δ^{18}O results is not straightforward. Currently, there are several challenges in obtaining high-quality LAS δ^2H and δ^{18}O results, which differ markedly from IRMS (e.g. strong between-sample memory, molecular optical interferences) and are especially difficult for users with little measurement experience. Currently, LAS instruments produce large output files in comma-separated value (CSV) format that requires considerable offline processing[3, 9]. This processing includes (i) assessing samples for infrared spectral interferences, ii) screening for

poor sample injections with high isotopic variance, (iii) derivation of algorithms to correct for between-sample carryover , (iv) correcting for instrumental isotopic drift, (v) normalizing the δ^2H and δ^{18}O data to the VSMOW-SLAP scales through the use of laboratory measurement standards[11], and (vi) tracking QA/QC of the instrument on a daily basis and the long-term[7, 9, 12]. Unfortunately, the software currently provided by LAS manufacturers is incapable of fulfilling these data correction and long-term data management needs. Some users developed fixed-template Microsoft Excel spreadsheets for processing LAS data[9, 13]; however, complex spreadsheets are ill-suited to be quickly modified by inexperienced users, and data stored in spreadsheets are difficult to manage for long-term laboratory QA/QC and audit purposes. Here, we recommend *LIMS for Lasers (v 10)*; a Microsoft Access™ relational database application developed specifically for LAS users as a joint effort between the U.S. Geological Survey (USGS)[14] and the International Atomic Energy Agency (IAEA). This new software application automates all LAS data corrections, and provides a Laboratory Information Management System (LIMS) for LAS users to manage clients, projects, samples, and instrumental data; furthermore, it is cost-free from the USGS (http://isotopes.usgs.gov/research/topics/lims.html) and the IAEA (http://www-naweb.iaea.org/napc/ih/IHS_resources_sampling.html#lims).

Our experience shows many new LAS users with interests in water isotope measurements are increasingly from developing countries, or in non-traditional research facilities, including water-management authorities and private firms, often with limited isotopic measurement experience. Accordingly, the aim of this paper is to assist LAS users to obtain best results by (i) reviewing the fundamental aspects of LAS instrumentation, sample handling, and data calibration practices, (ii) proposing robust standardized LAS

performance-assessment templates that will enable users to evaluate their instrument's accuracy and precision, and (iii) providing standardized daily-use templates to automate many of the required LAS data corrections (e.g. memory, drift) by using LIMS for Lasers software. We endorse and summarize systematic procedures that are easily implemented by all LAS users, which help avoid mistakes and improve long-term, accurate performance, independently of which LAS instrument is used.

Materials and Methods

LAS Water Isotope Instrumentation. Currently, water isotope LAS suppliers include Los Gatos Research Inc. (www.lgrinc.com), which provides off-axis integrated cavity output laser spectroscopy (OA-ICOS), and Picarro Inc. (www.picarro.com), which provides cavity ring-down laser-based spectroscopy (CRDS).

Laboratory Measurement Standards. Carefully maintained laboratory standards are critical to the isotope laboratory. Currently, VSMOW (Vienna Standard Mean Ocean Water), VSMOW2, and SLAP2 (Standard Light Antarctic Precipitation) are the primary isotope reference waters available for δ^{2}H and δ^{18}O (and δ^{17}O) measurements[15,16,17]. They are available from the IAEA (www.iaea.org), NIST (www.nist.gov/srm/), or the USGS (http://isotopes.usgs.gov/), in limited quantities every 3 years, and are intended for the calibration of daily-use laboratory standards.

Daily-use standard waters and a control standard may be obtained locally or from commercial sources (e.g. imported or local bottled water), preferably in large quantities (e.g. 20 L), and should fully bracket the isotope-delta range of the samples to be measured. At least three daily-use δ^{2}H and δ^{18}O standards should be sought: a high delta end-member

value (positive delta) and low delta end-member value (negative delta) to be used for data normalization[11] and a mid-point measurement standard as a long-term control. Laboratories must carefully calibrate their daily-use standards by using VSMOW2/SLAP2 primary standards or VSMOW/SLAP (see below).

The handling and long-term storage of reference and calibration waters is a crucial consideration. The IAEA water isotope inter-comparison[1] revealed a leading cause of inaccurate LAS (and IRMS) performance stemmed from poor storage of primary or daily-use standards, resulting in enrichment of ^{2}H and ^{18}O by evaporation that adversely affects outcomes. It is critical to pay attention to maintaining and monitoring the integrity of primary and daily-use standards, and to minimize or eliminate evaporation and leakage. Use of flame-sealed glass-storage ampoules or nitrogen or argon gas over-pressurized large-volume (10–50 L) stainless steel or aluminium casks are strongly preferred over inexpensive plastic bottles for long-term storage of standards[18-20]. For daily pipetting into LAS vials, smaller sub-samples of standards stored in tightly in sealed HDPE or ground glass stoppered containers (e.g. 50–100 mL) suffice[18].

For laboratories that cannot seal in-house standards in glass ampoules, daily-use secondary standards covering a sufficiently appropriate isotopic range are available from the IAEA Water Resources section or the USGS (http://isotopes.usgs.gov/lab/referencematerials.html). The USGS daily-use ampoules are extremely useful because each fills exactly three 2-mL LAS autosampler vials (e.g. suited for one autorun). The isotopic compositions of USGS45/46/47/48 are carefully calibrated to the VSMOW-SLAP scales and span a large $\delta^{2}H_{VSMOW}$ (and $\delta^{18}O_{VSMOW}$) range (–2 to –235 ‰). Each case of ampoules lasts for 1–2 years of typical LAS operation, eliminating evaporative loss

and isotopic fractionation. The recommendation for daily usage is two USGS ampoules with isotopic compositions fully bracketing the samples for data normalization, and a mid-point standard that serves as an independent control not used in data normalization. The 2-mL septum capped autosampler vials containing the dispensed standards and control should not be used for more than 2–3 days after the septa are punctured and stored not longer than one month in non-punctured vials.

Unknown Water Samples. LAS technology requires that unknown water samples be suited to analytical purpose. Generally, clean environmental freshwaters (e.g. rain, surface and groundwater) pose few analytical problems for LAS instruments. Samples should be field collected in 25–125 mL, tightly closed, glass (with inner conical cap liners) or HDPE bottles (with cap liner inserts) to minimize evaporation and leakage during transit and storage prior to analysis[18]. Sample bottles should be reliably labeled and stored at room temperature and in the dark to avoid algal growth. For shipping, precautions must be taken to avoid sample bottle breakage or freezing during transport. Turbid water samples should be filtered (0.45-300 μm filters), preferably in the field.

Analyzing water with total dissolved solids (TDS) above around 25,000 mg/L (Conductivity >40,000 μS/cm) may cause seizing of the syringe, or salt build-up within the heated liquid-water injection unit. An inexpensive conductivity probe therefore provides a useful sample pre-screening tool. Salty samples should be avoided, distilled, or pooled for discrete short analytical runs, and the heated injector block and syringes should be cleaned thereafter. Alternatively, salt water and brines can be measured by LAS by using H_2O head-space equilibration[21].

A major concern are water samples that contain significant amounts of volatile organic compounds (VOCs) that are vaporized with the water sample and enter the LAS cavity, causing isotopologue spectral interference. Organic contamination may not be apparent from visual inspection of water samples. Some volatile organics at low concentrations (e.g. alcohols, some hydrocarbons, in plant water extracts), can cause serious spectral interference, leading to highly erratic isotopic measurement results[4, 10, 12, 22-24]. Therefore, samples from contaminated sites (e.g. solvents, oil-field waters, landfill leachates) and plant water extracts are best avoided, or approached with caution[25]. For sample analyses that may be used in court or legal cases, an IRMS confirmation is recommended. To address the spectral interference problem, Los Gatos and Picarro provide users with offline software that can be used to post-process autorun outputs by comparing sample spectra to that of clean standard water. This software can be used to help identify bad results, and potentially correct via a spectral library, some specific VOC interferences[23, 26]. However, the range of volatile organic molecules in water that may cause infrared spectral interference patterns are practically unlimited; caution is advised, and we recommend that all autorun output should be scanned for spectral interferences. Any sample identified by the spectral evaluation software as a bad result should never be reported or used, and these compromised samples should instead be measured by IRMS.

LAS autosamplers use 2 mL septum screw-capped (preferably Teflon lined septum) glass sample vials. Typically, 1–1.5 mL of water is dispensed by pipette into each vial, by using a new pipette tip for each sample. Approximately 0.5 mL headspace must be left in the vial to avoid suction on the syringe to minimize variable water yields on the instrument. Dispensed samples can be stored in vials tightly capped (frozen or at room temperature) for

over 1 month before use, although it is preferable to dispense samples into vials just before analysis. Re-runs of measured samples in punctured vials should be completed within a few days to minimize evaporation through punctured septa, or immediately recapped with non-punctured septa for later analysis. One helpful laboratory policy is to run all samples twice, dispensed in separate vials, measured on different days, and a third time if the duplicate analyses do not agree within acceptable criteria (see below). This will ensure high quality results, quantify external reproducibility, and help to identify the most common user mistakes, like mislabeled or switched vials.

Number of Samples Measured. One productivity consideration is how many samples can be measured per autorun. Laboratories prefer autoruns that are optimized for daily work cycles (10, 20, or 50 samples plus standards per autorun). However, two hardware elements constrain the length of LAS analysis templates. First, the injection port septum (e.g. pre-drilled long-life Restek Blue Ice™ or Supelco LB-2 Thermogreen™) can fail after approximately 500–800 injections (note: a sample is defined as 8 sequential injections from the same vial, see below). As a result, it is recommended that LAS autoruns comprise no more than 500–800 injections, after which the heated septum must be changed. Second, the high precision microliter syringes used by LAS autosamplers can fail, or badly underperform, after as few as a dozen injections. Unsurprisingly, syringe underperformance is a leading cause of poor LAS isotopic outcomes. Generally, the higher dissolved solute concentration, the sooner a syringe will be compromised by solute precipitation, plunger stickiness, or jamming of the plunger in the barrel. Syringe performance should be verified by manually priming offline with deionized water before each autorun to ensure it is functioning smoothly, and thereafter monitored for signs of failure. Syringe performance

degradation is usually manifested by variable or unexpectedly decreased H_2O yields (and concomitant high delta variance) or by complete jamming. These two hardware elements combined effectively constrain the practical length of each autorun to no more than 500–800 injections. Several strategies have been proposed to prolong the life of costly syringes, including solvent cleaning and storage in deionized water between autoruns[9].

Systematic Analysis Templates: LIMS for Lasers. Systematic templates based on Identical Treatment (IT) principles are recommended to give optimal outcomes[27]. The use of *LIMS for Lasers* and its flexibly structured analysis templates make it easy for LAS operators to apply systematic IT data corrections and to identify problems when changes in sample and control analysis patterns are observed. Structured LAS templates employ appropriately distributed (beginning, middle, end of autorun) multiple occurrences of two measurement-standards, a control, and 5–10 samples located in-between. The control standard should be placed within groups of unknown samples (or randomized); not following the same reference waters, which produces placement biased results. This template arrangement facilitates using *LIMS for Lasers* to automatically and accurately quantify between-sample memory, determine instrumental drift, and normalize data[11] to the VSMOW-SLAP scales by using assigned values of high and low reference waters via bracketed normalization. The suitably placed control standard(s) monitors daily and long-term QA/QC and laboratory performance. Further, it is recommended that each LAS instrument be tested periodically for accuracy performance by using a wide isotopic range of sample and standards having known δ^2H and δ^{18}O values.

A LAS accuracy performance testing procedure is proposed by using known reference waters (Table 1), a testing analysis template (Table 2) and instrumental scoring

matrix (Table 3). It is recommended that this LAS performance template be run periodically per year in triplicate over several days on the same instrument to enable incorporation of all daily variations inherent in laboratory operations (e.g. different users, temperature changes, repeats). Results from each of the three autoruns are normalized individually, with the final results pooled for reporting the mean and standard deviation (SD) of each known test sample. Reported mean values are compared to their known values for a scoring-based assessment. The template illustrated in Table 2 is compatible with automated data processing in *LIMS for Lasers*. The use of externally obtained independent calibration standards and two or more test samples stored in glass ampoules along with in-house standards is encouraged in case there are systematic problems with sample and standard storage within the laboratory that need to be rectified (e.g. standards have partly evaporated).

For routine daily autoruns of samples, a robust analysis template is illustrated in Table 4, instead using well characterized local laboratory reference waters and not primary isotopic standards (Table 5). By using *LIMS for Lasers*, this template automates outlier identification, between-sample memory, drift correction, and bracketed normalization to the VSMOW-SLAP scales. The number of unknown samples placed between high and low standard-triplet groupings should not exceed 5–10 samples. The high and low standard triplets should be alternated (e.g. high/low/low and low/high/high) to provide robust quantification of between-sample memory across the autorun that is not biased by isotopic directionality[7]. The control used for monitoring performance should succeed or be amongst samples to avoid bias. The control facilitates independent monitoring of QA/QC performance on a daily and long-term basis. Preferably, but not essential, is that the

isotopic composition of the control standard be known, e.g. obtained from an external source (e.g. USGS glass ampoules, IAEA, other laboratory). This will help identify over the long-term whether in-house standards were compromised during their storage. Depending upon the type of LAS instrument and mode (e.g., age, high throughput versus high precision mode), a reliable analysis procedure is to use 8 injections per sample vial, and to ignore the first 3-4 results. While fewer injections may be employed as new LAS instruments evolve, rigorous testing to ensure that between-sample memory is corrected for is required[9].

Between-Sample Memory and Instrumental Drift. Two inherent instrumental factors affect the quality of LAS isotope measurements: between-sample carry-over and instrumental drift. Between-sample carry-over (or memory) is residual H_2O molecular (isotopologue) contamination stemming from the prior sample in the syringe, laser cavity, or transfer lines. Both factors must be examined, quantified, and corrected for; both of these corrections are automated by using *LIMS for Lasers*.

For most LAS instruments, between-sample carryover is around 15 per cent following the first injection, to <1–2 per cent after 4 sequential injections of the same sample[3, 8]. If the delta value change between two water samples is large, a 1-2 per cent carryover can have a significant detrimental impact. Overcoming between-sample memory requires either (i) many injections (>9-16 injections) from the same sample vial to fully be rid of memory of the previous sample[7], or (ii) some form of calculated memory-correction algorithm using 10 or fewer sample injections[9, 13]. Between-sample memory is further minimized by discarding the results of the first 3-4 injections of 8 (or more) injections, which is customarily recommended by both manufacturers. In *LIMS for Lasers,* between-sample memory is quantified by comparing the average of all non-ignored delta values of one

laboratory standard vial (e.g. high δ value) to the average values of two successive vials of a second (e.g. low δ value) laboratory standard, or vice-versa. For autoruns containing appropriately distributed (start, middle, end) groupings of high/low standard followed by two identical low/high standards (e.g. high, low1, low2), the between-sample memory is calculated by using the average of all non-ignored injections as follows:

$$\text{Memory} = (\overline{\delta}_{\text{low1}} - \overline{\delta}_{\text{low2}}) / ((\overline{\delta}_{\text{high}} - \overline{\delta}_{\text{low2}}))$$

where $\overline{\delta}_{\text{low1}}$, $\overline{\delta}_{\text{low2}}$, and $\overline{\delta}_{\text{high}}$ are the mean values of all non-ignored injections of the low1, low2, and high water standard vials, respectively. Equivalent symbols apply for high1, high2, and low standard triplets.

Example:

$$\text{Memory} = (-401.57\ ‰ - (-404.03\ ‰)) / (-41.89\ ‰ - (-404.03\ ‰))$$

$$\text{Memory} = 0.0068 = 0.68 \text{ per cent}$$

To make a correction, the memory-corrected δ of a sample or reference water, $\delta_{\text{memory-corrected}}$, is determined by the relationship:

$$\delta_{\text{memory-corrected}} = \overline{\delta}_{\text{sample}} + \text{Memory} \times (\overline{\delta}_{\text{sample}} - \overline{\delta}_{\text{previous sample}})$$

where $\overline{\delta}_{\text{sample}}$ and $\overline{\delta}_{\text{previous sample}}$ are the mean delta values of all non-ignored injections for each vial. For example, a sample with measured mean δ^2H delta of –200 ‰ immediately following standard water having the above value of –404.03 ‰ may be corrected as follows:

$$\delta_{\text{memory-corrected}} = -200\ ‰ + 0.0068 \times (-200\ ‰ - (-404.03\ ‰)) = -200\ ‰ + 1.39\ ‰$$

$$\delta_{\text{memory-corrected}} = -198.61\ ‰$$

Some LAS instruments were prone to significant temperature dependent instrumental drift over the course of an autorun[3]. Because LAS analysers do not use a comparative reference gas like IRMS to counteract drift, drift might be observed over the course an autorun. To overcome drift, most users recommend placement of small groups of samples (max 5–10 samples) between groupings of water standards, by using "bracketed normalization", which assumes linear drift (or none) occurred between these smaller groupings of samples and standards over a short time period. Linear drift may be observed for some LAS instruments; allowing users to construct a least squares time-based drift correction to the entire autorun by using the distributed measurement standards, and no need for bracketing. We recommend bracketed normalization because it handles bi-directional drift over the course of an autorun; however, all possible drift correction options can be assessed by using *LIMS for Lasers* or offline by spreadsheet. The bracketed memory and drift correction approach recommended here is analogous to that used in laser ablation ICPMS data processing software[28].

Bad Sample Injections. The most common LAS problems stem from poor analyses, such as low or variable H_2O yields from micro-syringe underperformance, septa failure, over- or under-filled or skipped vials, or some other malfunction. Locating faulty or identifying missing injections among hundreds of rows of CSV data is time consuming by using spreadsheets. *LIMS for Lasers* automatically pre-screens imported data with graphical summary plots of the H_2O yield and isotopic data versus injection number, warns users about missing sample analyses, flags samples whose water yield is less than 85 per cent of the expected mean, and culls null-data results. This pre-screening feature of *LIMS for Lasers*

aids to ensure users do not mistakenly import or process bad data, and signals that consideration should be given to replacing the syringe when many samples are flagged.

Accuracy and Precision Performance Assessment Criteria. Unacceptable LAS isotopic performance criteria are herein defined as water samples (or the test standards) having more than a 0.15 ‰ and 1 ‰ disparity in either direction from their known $\delta^{18}O$ and $\delta^{2}H$ values, respectively (e.g. Table 1 or 5). These performance criteria generally are considered acceptable by historical precedents for hydrologic applications. Additionally, a weighted-instrumental scoring scheme is proposed whereby higher scores are given for accurate performance (closer to known value), and lower scores for poor performance (farther from known value, but still acceptable), and zero when results are outside the target range. A 0.15 ‰ disparity from the known value for $\delta^{18}O$ is worse than achievable by dual-inlet IRMS based CO_2- H_2O equilibration methods (e.g. $\pm$ 0.05 ‰), but sufficiently accommodates $\delta^{18}O$ performance of current and previous generation LAS instruments. A higher standard of $\delta^{18}O$ accuracy and precision may be required for applications such as high-resolution ice cores for climatic reconstructions, which is currently not as easily achievable by LAS[29, 30].

Poor precision (repeatability) on averaged pooled sample results (N, ±1 sigma SD) results in further reduction in score, allowing that it is better to be accurate (and less precise), than precisely inaccurate. The proposed LAS accuracy and precision performance-scoring scheme is summarized in Table 3.

Daily and Long-term QA/QC Monitoring. On a daily and monthly basis, there is no need to conduct intensive accuracy performance testing of the laser instrument. Instead, laboratories can routinely, during daily analysis, track short-term and longer-term QA/QC by using a control standard, appropriately or randomly placed within each autorun template

(Table 4), noted above. The control standard is not used for data normalization, and functions as an overseer to signal when LAS performance has significantly altered or drifted[27]. The long-term mean and external precision of a control offers parsimonious performance metrics to the laboratory and its users[4]. Importantly, the control standard must be as vigilantly maintained as calibration standards through proper storage and dispensing.

Results and Discussion

Several current and older LAS instruments from Los Gatos Research Inc. and Picarro Inc. were tested for accuracy and external precision with analysers that spanned several generations (2007–2013). All instruments were set up for liquid water $\delta^{18}O$ and $\delta^{2}H$ analysis, following the manufacturer directions. In all cases, carrier gas supplied to each instrument was dry air via Drierite™ air-dryer canisters (water-volume fraction < 250 ppm). Where appropriate, software settings were changed to optimize the instrument's spectral fitting for dry-air, instead of high-purity N_2 carrier gas. Testing procedures are summarized in Tables 2 and 3. All instrument-testing configurations and results are reported in Table 6. All data corrections (e.g. between-sample memory, instrument drift, and normalization) were assessed and conducted by using default settings in the *LIMS for Lasers* (v10.066). The scoring scheme in Table 3 was applied to the normalized data summaries obtained from three test runs for each instrument (Table 6), which also includes additional details, e.g., number of injections, etc.

By using *LIMS for Lasers*, data compilations in Table 6 revealed all LAS instruments passed the accuracy and precision performance criteria, and produced satisfactory $\delta^{2}H$ and $\delta^{18}O$ results for hydrologic purposes. For the instruments tested, sample $\delta^{2}H$ performance

outcomes were within 1 ‰ of known δ^2H values, indicating excellent δ^2H performance regardless of age. For δ^{18}O, the performance outcomes were within the stated 0.15 ‰ acceptance criteria, which is satisfactory for most environmental and water resource studies. Unsurprisingly, the 2012 Los Gatos instrument performed significantly better than its older 2007 sibling, revealing performance improvements over time. The Picarro L2120i model performed equally accurately in high-throughput mode versus high-precision mode, albeit with better δ^2H reproducibility in high-precision mode (note: the recommended Picarro N_2 carrier-gas option was not tested in HT mode). Sample-throughput productivity ranged from 23–30 samples per 24 hours on the Picarro instrument and to 90 samples per 24 hours on the newest Los Gatos instrument, when each sample was comprised of 8 injections.

Several caveats can be levied against these systematic performance evaluation tests. One critique is that the standards and test waters were low TDS or distilled waters. Conducting similar systematic testing, by using a diverse isotopic array of waters having a wide range of TDS, or containing calibrated spikes of common problematic VOCs to check how well spectral-interference software identified problems might be useful for targeted user-specific scenarios. Higher TDS water chemistry or trace VOCs could result in poorer performance. However, pure waters, like those employed here, form the fundamental foundation for all water isotope LAS testing that can be easily adopted by all users.

Performance may also depend on the isotopic range of samples and standards being tested, primarily due to the robustness of between-sample memory corrections, drift, and bracketed normalization outcomes for each instrument [9]. By design, the samples and standards in Tables 1 and 5 span the terrestrial δ^2H and δ^{18}O range of natural waters to

encompass all possibilities, an extreme testing scenario that is unlikely to be encountered in laboratories measuring smaller delta ranges of local water samples on a regular basis. Although untested, one might predict that a similarly designed systematic-performance test, but spanning a less extreme isotopic range (thus lowering between-sample memory impacts) and tailored towards what is actually required by the LAS user, could produce better results by further minimizing between-sample memory impact.

We stress the importance of using an independent control standard to monitor daily- and long-term LAS performance, which is easily accomplished with *LIMS for Lasers*. For example, a time series and running mean of $\delta^{2}H$ and $\delta^{18}O$ results for the IAEA control standard (W-31) from the Isotope Hydrology Laboratory is shown in Figure 1, and is obtained quickly by the "Track My Laboratory QA/QC" function of *LIMS for Lasers*. Graphical QA/QC plots like these should be examined daily following the processing of each autorun, and on a weekly and longer basis. Outliers from an autorun are quickly spotted, and help inform where common mistakes are made (e.g. misplaced vials), and where corrective actions need to be taken (e.g. repeat, check standard integrity, etc.). Concomitantly, good long-term control standard data summaries provide parsimonious metrics of how well a laboratory performs isotopic analyses by LAS over the longer-term. Reporting, for example, the 1-year running average and SD of the control provides a realistic indicator of everyday laboratory performance than the reporting the analytical precisions of standards from single autoruns, as is commonly done.

Regarding potential problem areas, poor LAS performance is most often the result of syringe underperformance, manifested by variable water yields and poor delta reproducibility. This is an easily resolved hardware issue that should always be checked as a

starting point whenever LAS performance degrades. Syringe lifetime may be extended by using a larger size syringe, if possible, and by completing autoruns with a deionized water sample wash, and offline syringe cleaning[9]. However, over time there could be a variety of other causes for poor LAS outcomes in the periodic accuracy testing with test waters of known delta values, or in routine sample analysis. A control standard of known isotopic composition that gives increasingly inaccurate results could be an indication that its container is compromised by evaporation or leakage, particularly if the δ^2H and δ^{18}O values trend to more positive delta values than expected. Conversely, increasingly evaporated calibration standards will lead to results that are too negative. If a group of known test samples produce final δ^2H and δ^{18}O results biased in one direction (either too positive or negative or diverging at one extreme), this could arise from one or more of the standards being compromised by evaporation or leakage in storage, or by using incorrectly assigned values for one or more of the standards.

Poor overall sample precision (per or among autoruns) is usually from syringe underperformance, but can also arise from excessive salt build-up over time in the injection vaporizer (which especially impacts δ^{18}O values), or from other instrumental malfunction or leak. Spurious δ^2H and δ^{18}O results for individual samples that grossly deviate from the expected local meteoric linear relationship may be spectrally compromised by VOCs; therefore, results of LAS data autoruns containing suspicious or organic-rich samples should always be scanned by using the manufacturers' offline spectral software before importing and processing the data. Other poor-performance outcomes can stem from user inattention, which may include insufficient instrumental warm-up time, incorrect carrier-gas or flow rate , over- or under-filling of sample and standard vials, loose or leaky sample

transfer lines, exhausted Drierite, high H_2O background carrier gas, incorrect laser-spectrum offsets and calibration, or compromised laser mirrors from internal condensation from improper shut downs. Los Gatos and Picarro provide extensive troubleshooting tips and procedures in their user manuals that should be consulted regularly, and they should be contacted directly when all of the usual performance-impacting suspects have been eliminated.

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Table 1. Recommended reference and test waters of known $\delta^{18}O$ and $\delta^{2}H$ composition for evaluation of LAS instrumental performance. This set should be run several times annually using USGS standard ampoules (or every 3 years using VSMOW2/VSLAP2) using the template in Table 2. Assigned target values for the high and low In-house laboratory standards are pre-determined by measuring them repeatedly against VSMOW2 and SLAP2. Current USGS laboratory standards and their assigned values are from http://isotopes.usgs.gov/lab/referencematerials.html.

References	Sample ID	$\delta^{18}O_{(VSMOW)}$	$\delta^{2}H_{(VSMOW)}$	Comment
low standard	SLAP2/USGS46	–55.5 ‰ / –29.80 ‰	–427.5 ‰ / –235.8 ‰	From ampoule
high standard	VSMOW2/USGS48	0 / –2.22 ‰	0 / –2.0 ‰	From ampoule
Test Samples				
Sample A	Lab standard high	pre-determined	pre-determined	In-house standard
Sample B	GISP / USGS47	–24.8 ‰ / –19.8 ‰	–190 ‰ / –150.2 ‰	From ampoule
Sample C	USGS45	–2.24 ‰	–10.3 ‰	From ampoule
Sample D	Lab standard low	pre-determined	pre-determined	In-house standard

Table 2. LAS Instrumental Accuracy Performance Template. Use measurement standards and samples from Table 1. Each sample comprises 8 injections; the first 4 injections are ignored. The template is run in triplicate over several days, and results for each LAS autorun normalized separately. This template is compatible with automated data processing using *LIMS for Lasers*, which (1) corrects for between-sample memory, (2) applies instrumental drift corrections (if applicable), (3) and normalizes data to the VSMOW-SLAP scales using the assigned values of the high and low References using bracketed normalization.

Sample	Run Order	Primary Function	Secondary Function	Tertiary Function
Deionized Water	1	Pre-Conditioning		
Deionized Water	2	Pre-Conditioning		
low standard	3	Normalization	Between Sample Memory	Instrumental Drift
high standard	4	Normalization	Between Sample Memory	Instrumental Drift
high standard	5	Normalization	Between Sample Memory	Instrumental Drift
Sample A*	6	Test Sample		
Sample A	7	Test Sample		
Sample A	8	Test Sample		
Sample B*	9	Test Sample		
Sample B	10	Test Sample		
Sample B	11	Test Sample		
high standard	12	Normalization	Between Sample Memory	Instrumental Drift
low standard	13	Normalization	Between Sample Memory	Instrumental Drift
low standard	14	Normalization	Between Sample Memory	Instrumental Drift
Sample C*	15	Test Sample		
Sample C	16	Test Sample		
Sample C	17	Test Sample		
Sample D*	18	Test Sample		
Sample D	19	Test Sample		
Sample D	20	Test Sample		
low standard	21	Normalization	Between Sample Memory	Instrumental Drift
high standard	22	Normalization	Between Sample Memory	Instrumental Drift
high standard	23	Normalization	Between Sample Memory	Instrumental Drift
Deionized Water	24	Final Rinse		

*Adjacent test sample groupings in the autorun should differ by >3 ‰ for $\delta^{18}O$, as per Table 1.

Table 3. Scoring matrix for LAS instrumental performance. Acceptable accuracy is defined as less than 0.15 ‰ and 1 ‰ difference from known $\delta^{18}O$ and $\delta^{2}H$ values, respectively. These performance criteria are considered reasonable for most but not all hydrological studies[1]. Poor precision (n, ±1 sigma SD) results in score reductions.

Accuracy		
$\delta^{18}O$	**Points**	**Criteria**
Excellent	10 Points	<= 0.08 ‰ difference from known value
Acceptable	5 Points	<= 0.15 and >0.08 ‰ difference from known value
Unacceptable	0 Points	> 0.15 ‰ difference from known value
$\delta^{2}H$		
Excellent	10 Points	<= 0.4 ‰ difference from known value
Acceptable	5 Points	<= 1.0 ‰ and >0.4 ‰ difference from known value
Unacceptable	0 Points	> 1.0 ‰ difference from known value
Precision		
Unacceptable	-5 Points	> 0.2 ‰ for $\delta^{18}O$ or >1.0 ‰ for $\delta^{2}H$
Final Assessment:		
Pass	>= 20 points for $\delta^{18}O$ and >= 20 points for $\delta^{2}H$	
Fail	< 20 points for $\delta^{18}O$ or < 20 points for $\delta^{18}O$	

Table 4. Example 20-sample daily-use template for all LAS instruments. Procedure is 8 sequential injections per sample, ignoring the first 4 injections. This analysis template contains 32 rows of 8 injections each, or 256 individual injections. The pattern can be modified to create a 10, 30, or 40-sample templates, but should contain fewer than 500–800 injections. This template facilitates automated memory and drift corrections and bracketed normalization using *LIMS for Lasers*. The control standard facilitates monitoring QA/QC performance outcomes. The number of samples emplaced between high and low standard groupings should not exceed 5–10 unknown waters.

Sample	Tray Position	List #	Function
high δ standard	1-1	1	Memory/Normalization
low δ standard	1-2	2	Memory/Normalization
low δ standard	1-3	3	Normalization/Drift
Sample 1	1-4	4	Unknown Sample
Sample 2	1-5	5	Unknown Sample
Sample 3	1-6	6	Unknown Sample
Sample 4	1-7	7	Unknown Sample
Sample 5	1-8	8	Unknown Sample
Sample 6	1-9	9	Unknown Sample
Sample 7	1-10	10	Unknown Sample
Sample 8	1-11	11	Unknown Sample
Sample 9	1-12	12	Unknown Sample
Sample 10	1-13	13	Unknown Sample
control standard	1-14	14	QA/QC Tracking
low δ standard	1-15	15	Memory/Normalization
low δ standard	1-16	16	Memory/Normalization
high δ standard	1-17	17	Normalization/Drift
Sample 11	1-18	18	Unknown Sample
Sample 12	1-19	19	Unknown Sample
Sample 13	1-20	20	Unknown Sample
Sample 14	1-22	22	Unknown Sample
Sample 15	1-23	23	Unknown Sample
Sample 16	1-24	24	Unknown Sample
Sample 17	1-25	25	Unknown Sample
Sample 18	1-26	26	Unknown Sample
Sample 19	1-27	27	Unknown Sample
Sample 20	1-28	28	Unknown Sample
Control standard	1-29	29	QA/QC Tracking
high δ standard	1-30	30	Memory/Normalization
low δ standard	1-31	31	Memory/Normalization
low δ standard	1-32	32	Normalization/Drift

Table 5. Example instrumental test and calibration samples comprised of IAEA and USGS references with known $\delta^{18}O$ and $\delta^{2}H$ values for evaluating LAS accuracy and precision. The analysis template in Table 2 was applied (three times); results for several laser instruments using these waters are summarized in Table 6.

References	**Sample ID**	$\delta^{18}O_{(VSMOW)}$	$\delta^{2}H_{(VSMOW)}$	**Comment**
low standard	IHL W-35	–50.87 ‰	–397.9 ‰	IAEA Lab Std.
high standard	IHL W-36	+0.08 ‰	–0.1 ‰	IAEA Lab Std.
Test Samples				
Sample A	IHL W-31	–8.64 ‰	–61.5 ‰	IAEA Lab Control
Sample B	IHL W-37	–12.03 ‰	–86.4 ‰	IAEA Lab Control
Sample C	IHL W-34	–24.76 ‰	–189.2 ‰	IAEA Lab Control
Sample D	USGS45	–2.24 ‰	–10.3 ‰	USGS Ampoule

Table 6. Instrumental performance results for several LAS instruments, tested over a 3-day period (January–June 2013) using the analysis template in Table 2; assessment criteria in Table 3; known value calibration standards and samples from Table 5. Instruments were configured as recommended with elimination of between-sample washes. Carrier gas was dry air with water volume fraction < 250 ppm. Pull-up strokes=4. HT = high-throughput mode. HP = High-performance mode. *Note: these test results are not transferrable to other LAS instruments; each instrument must be tested by its user.*

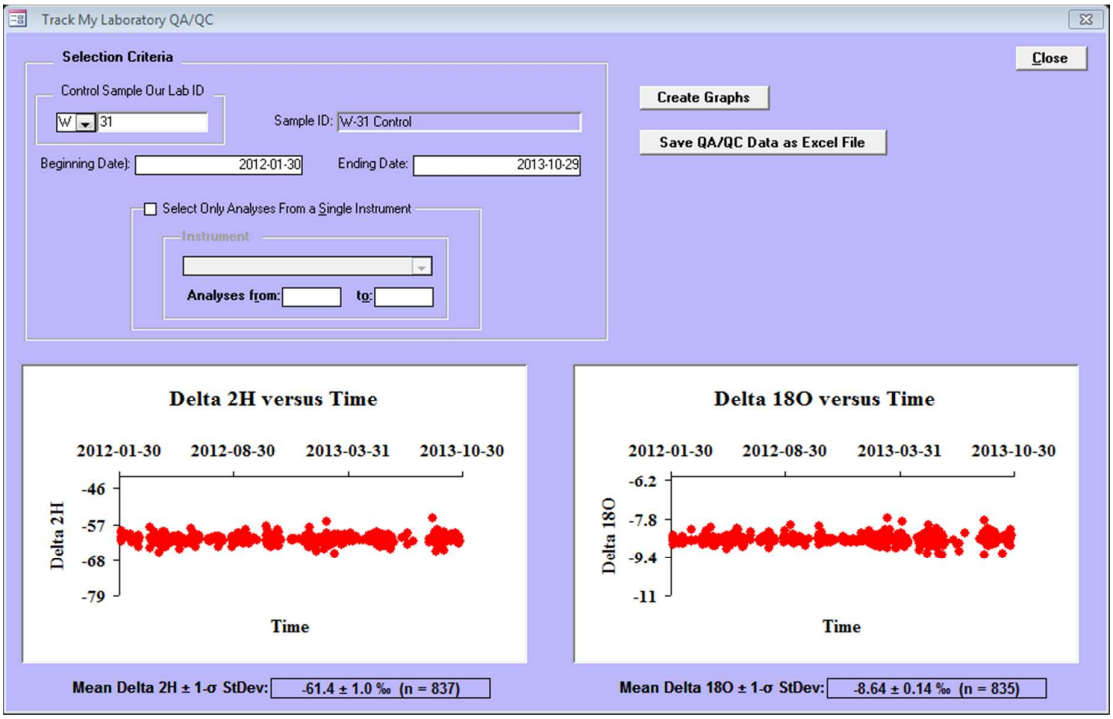
Instrument 1	**Supplier: Los Gatos**	**Model: LWIA-24d**	**Injections per sample: 8**	**Mode: HP**	**Sample Rate: 90 per 24h**	**Carrier: Dry Air**	**Built: 2012**		**Score: PASS**
δ^{18}O(VSMOW)	Known δ	Meas. Mean δ	Difference, ‰	Score	# Samples	1σ SD, ± ‰	Score	Subtotal	Final
Sample A	–8.64	–8.55	+0.09	5	9	0.06	-	5	**30**
Sample B	–12.03	–11.94	+0.09	5	9	0.07	-	5	
Sample C	–24.76	–24.73	+0.03	10	9	0.10	-	10	
Sample D	–2.24	–2.20	+0.04	10	9	0.11	-	10	
δ^{2}H (VSMOW)									
Sample A	–61.5	–61.3	+0.2	10	9	0.1	-	10	**35**
Sample B	–86.4	–86.0	+0.4	10	9	0.3	-	10	
Sample C	–189.2	–189.3	–0.1	10	9	0.2	-	10	
Sample D	–10.3	–11.2	–0.9	5	9	0.4	-	5	

Instrument 2	**Supplier: Los Gatos**	**Model: LWIA v1**	**Injections per sample: 8**	**Mode: HP**	**Sample Rate: 55 per 24h**	**Carrier: Dry Air**	**Built: 2007**		**Score: PASS**
δ^{18}O(VSMOW)	Known δ	Meas. Mean δ	Difference, ‰	Score	# Samples	1σ SD, ± ‰	Score	Subtotal	Final
Sample A	–8.64	–8.59	+0.05	10	9	0.06	-	10	**25**
Sample B	–12.03	–12.09	–0.06	10	9	0.10	-	10	
Sample C	–24.76	–24.46	+0.30	0	9	0.08	-	0	
Sample D	–2.24	–2.31	–0.07	10	9	0.33	–5	5	
δ^{2}H (VSMOW)									
Sample A	–61.5	–60.7	+0.8	5	9	0.9	-	10	**25**
Sample B	–86.4	–85.9	+0.5	5	9	0.6	-	10	
Sample C	–189.2	–189.7	–0.5	5	9	0.5	-	10	
Sample D	–10.3	–9.9	+0.4	10	9	0.3	-	10	

Instrument 3	**Supplier: Picarro**	**Model: L2120i**	**Injections per sample: 8**	**Mode: HP**	**Sample Rate: 23 per 24h**	**Carrier: Dry Air**	**Built: 2013**		**Score: PASS**
δ^{18}O(VSMOW)	Known δ	Meas. Mean δ	Difference, ‰	Score	# Samples	1σ SD, ± ‰	Score	Subtotal	Final
Sample A	–8.64	–8.66	–0.02	10	9	0.04	-	10	**30**
Sample B	–12.03	–12.02	+0.01	10	9	0.08	-	10	
Sample C	–24.76	–24.65	+0.11	5	9	0.04	-	5	
Sample D	–2.24	–2.38	–0.14	5	9	0.10	-	5	
δ^{2}H (VSMOW)									
Sample A	–61.5	–60.7	+0.8	5	9	0.5	-	5	**25**
Sample B	–86.4	–85.3	+1.1	0	9	0.4	-	0	
Sample C	–189.2	–189.3	–0.1	10	9	0.4	-	10	
Sample D	–10.3	–10.7	–0.4	10	9	0.4	-	10	

Instrument 4	**Supplier: Picarro**	**Model: L2120i**	**Injections per sample: 8**	**Mode: HT**	**Sample Rate: 30 per 24h**	**Carrier: Dry Air**	**Built: 2013**		**Score: PASS**
δ^{18}O(VSMOW)	Known δ	Meas. Mean δ	Difference, ‰	Score	# Samples	1σ SD, ± ‰	Score	Subtotal	Final
Sample A	–8.64	–8.66	–0.02	10	9	0.09	-	10	**30**
Sample B	–12.03	–12.11	–0.08	10	9	0.07	-	10	
Sample C	–24.76	–24.63	+0.13	5	9	0.14	-	5	
Sample D	–2.24	–2.33	–0.09	5	9	0.07	-	5	
δ^{2}H (VSMOW)									
Sample A	–61.5	–60.9	+0.6	5	9	0.5	-	10	**30**
Sample B	–86.4	–86.0	+0.4	10	9	0.6	-	10	
Sample C	–189.2	–188.9	+0.3	10	9	0.9	-	10	
Sample D	–10.3	–11.0	–0.7	5	9	0.5	-	5	

Figure 1. Screenshot of control standard QA/QC monitoring using *LIMS or Lasers (v 10),* which allows users to track daily- and long-term performance of their LAS instrument(s). Outliers are easily detectable. Long-term performance statistics offer a more realistic report of how well the LAS laboratory performs.



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