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Routine high-precision analysis of triple water-isotope ratios using cavity ring-down spectroscopy

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RATIONALE: Water isotope analysis for δ^2H and δ^{18}O values via laser spectroscopy is routine for many laboratories. While recent work has added the δ^{17}O value to the high-precision suite, it does not follow that researchers will routinely obtain high precision ^{17}O excess (Δ^{17}O). We demonstrate the routine acquisition of high-precision δ^2H, δ^{17}O, δ^{18}O, d, and Δ^{17}O values using a commercially available laser spectroscopy instrument.

METHODS: We use a Picarro L2140-*i* cavity ring-down spectroscopy analyzer with discrete liquid injections into an A0211 vaporization module by a Leap Technologies LC PAL autosampler. The instrument is run in two modes: (1) as recommended by the manufacturer (default mode) and (2) after modifying select default settings and using alternative data types (advanced mode). Reference waters analyzed over the course of 15 months while running unknown samples are used to assess system performance.

RESULTS: The default mode provides precision for δ^2H, δ^{17}O, δ^{18}O, d, and Δ^{17}O values that may be sufficient for many applications. When using the advanced mode, we reach a higher level of precision for δ^2H, δ^{17}O, δ^{18}O, d, and Δ^{17}O values (0.4 mUr, 0.04 mUr, 0.07 mUr, 0.5 mUr, and 8 μUr, respectively, where mUr = 0.001 = ‰, and μUr = 10^{-6}) in a shorter amount of time and with fewer syringe actuations than in the default mode. The improved performance results from an increase in the total integration time for each injected water pulse.

CONCLUSIONS: Our recommended approach for routine δ^2H, δ^{17}O, δ^{18}O, d and Δ^{17}O measurements with the Picarro L2140-*i* is to make use of conditioning vials, use fewer injections (5 per vial) with greater pulse duration (520 seconds (s) per injection) and use only the first 120 s for δ^2H measurements and all 520 s for δ^{17}O and δ^{18}O measurements. Although the sample throughput is 10 unknowns per day, our optimal approach reduces the number of syringe actuations, the effect of memory, and the total analysis time, while improving precision relative to the default approach.

The first complete water stable isotope analysis (^{1}H, ^{2}H, ^{16}O, ^{17}O, ^{18}O) from a single water parcel was made by infrared laser absorption spectrometry (LAS).[1–4] LAS pioneers, as reviewed by Kerstel,[5] have moved the technology in the latest commercial versions of LAS instruments from the physics lab to stable isotope ratio facilities.[6,7] The laser spectroscopy physics lab is equipped with clean rooms, optical benches, and completely adjustable software appropriate for LAS pioneering work. Commercial LAS instruments, by contrast, present limited options to the user and, instead, manufacturers provide a software package with recommended default settings and very little room for optimization. Indeed, for most researchers interested in the δ^2H and δ^{18}O values of water, the default mode is sufficient, provided that care is taken with the influence of memory[8–11] and organic contaminants.[12,13] Researchers have suggested optimization strategies for water injection,[14] run design,[15] and data reduction.[14,16] It remains poorly documented, however, how a researcher should use the current generation of LAS instruments on a routine basis to obtain the highest possible precision for all three water isotope ratios and their derived quantities (δ^2H, δ^{17}O, δ^{18}O, d, and Δ^{17}O values). The definitions of δ^2H, δ^{17}O, δ^{18}O, d, and Δ^{17}O values are as in Steig *et al*.[7] and reproduced here:

$$\delta^i = \frac{{}^iR_{sample}}{{}^iR_{reference}} - 1, \quad (1)$$

where i is the rare isotope species of interest, $^2R = N(^2\mathrm{H})/N(^1\mathrm{H})$, $^{17}R = N(^{17}\mathrm{O})/N(^{16}\mathrm{O})$, $^{18}R = N(^{18}\mathrm{O})/N(^{16}\mathrm{O})$, and N is the abundance. The derived quantity d (deuterium excess) is defined as:

$$d = \delta^2\mathrm{H} - 8\left(\delta^{18}\mathrm{O}\right), \quad (2)$$

and the derived quantity Δ^{17}O (^{17}O excess) is defined as:

$$\Delta^{17}\mathrm{O} = \ln\left(\delta^{17}\mathrm{O} + 1\right) - 0.528^* \ln\left(\delta^{18}\mathrm{O} + 1\right). \quad (3)$$

Engineers and researchers will often assess the highest possible precision that an LAS instrument can provide by using Allan variance[17] which can be estimated with a loaded sample in a closed cavity[18] or with a continuously provided isotopically homogenous sample.[19] While very helpful when designing an instrument,[6,7] or for continuous samplers,[19,20]

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it is unclear how the optimal integration time derived from the Allan variance translates to discrete injection sampling methods. Liquid water-isotope LAS instruments require the system to be purged between sample injections. The laser cavity, then, is necessarily disturbed (e.g., dramatic pressure fluctuations) between samples. Here, we treat discrete water injections as if they are a continuous stream of isotopically homogenous water vapor to estimate Allan variance by adding the residence time of the samples, excluding the sampling change event between samples.

Furthermore, we evaluate different methods for obtaining a recommended integration time (1) by varying the pulse duration – the time spent measuring an individual injection of water, (2) by varying the fraction of data from a single pulse used for further calculations, and (3) by varying the number of pulses used per vial of sample water. Each of these represents a potential compromise of data quality with respect to memory, sample throughput, and instrument usage.

This paper is for users wanting to obtain maximum precision from their LAS instrument. Our approach should be widely applicable to all manufacturers' current general LAS instruments. The intent is not to provide a "standard operating procedure" but rather to describe what is required to make the greatest-possible precision measurements of δ^2H, δ^{17}O, δ^{18}O, d, and Δ^{17}O values with the current commercial varieties of LAS instrumentation. Ideas in the paper, while specific to a certain instrument, could be applied to other commercial instruments.

Over a 15-month period, we routinely ran unknown samples and conducted short calibrations and experiments using a Picarro L2140-*i* LAS instrument, with two different approaches: a default mode and an advanced user mode. An approach is considered "default" if the instrument is used as recommended by the manufacturer, with the possibility of modifying the number of injections from a single sample vial. An "advanced" approach is defined as one in which the configuration files of the instrument have been modified, or where data are used that are not normally accessed by users. We report the accuracy and precision of δ^2H, δ^{17}O, δ^{18}O, d, and Δ^{17}O values for reference waters measured with our LAS instrument for different default and advanced modes, and with each mode testing several data-processing options.

EXPERIMENTAL

Setup

Our instrumentation was previously described by Steig *et al*.[7] Briefly, 1.8 μL (to target 20,000 ppm H_2O) of water is injected using a 10-μL syringe (002986, SGE, Ringwood, Vic, Australia) into a vaporization module (A0211, Picarro, Santa Clara, CA, USA) with a liquid autosampler (LC PAL, Leap Technologies, Carrboro, NC, USA). In our experience, a 10-μL syringe has a longer lifetime (relative to the recommended 5-μL syringe) and sufficient volume reproducibility. The autosampler was fitted with a 98-position sample tray, although in practice we rarely used all 98 positions. The vaporizer-provided mixture of water vapor and dry air[10] is pulled into the cavity of a cavity ring-down spectrometer (L2140-*i*, sn HBDS2171, Picarro[7] based on earlier designs described by Crosson[21]) with a diaphragm four-head pump (PB 2 k424, Picarro, or OEM part number 0110039573, KNF Neuberger, Trenton, NJ, USA). Dry carrier air is building-sourced whole compressed air that has been cleaned via molecular sieve 5 A and magnesium perchlorate.

Run architecture

A "run" is defined as a set of vials automatically sampled sequentially from start to finish. Each run containing unknown samples was organized by having a set of five reference waters, n samples (typically $n \sim 30$ vials), and then another set of five reference waters. An example run layout is shown in Table 1. Two reference waters (high and low δ values) were used to normalize while 2–3 reference waters were used for quality assurance/quality control (QA/QC) (Table 1). All independently measured reference waters used in this study are listed in Table 2 with their VSMOW-SLAP normalized isotopic ratios.

Occasionally, we conducted drift runs and calibration runs containing reference waters only. A drift run would resemble the architecture of Table 1 but, in place of the unknowns, we would insert a QA/QC standard. The calibration runs were organized from high to low δ values (or vice versa) for the purposes of measuring reference waters against our in-house reference waters primarily used for normalization (SW and VW) or the reference waters VSMOW2 and SLAP (not SLAP2). An example calibration run would have proceeded as such: KD, USGS45, VSMOW2, SW, GISP, WW, WGW, VW, SLAP.

Prior to each run, proper movement of the syringe plunger was ensured and the vaporizer septum (IceBlue 27159, Restek, Bellefonte, PA, USA) was changed. All reference and sample water vials in this study were 2-mL vials with 300-μL fused inserts (9532S-0CV, Microsolv Technology Group, Leland, NC, USA) and were capped with red rubber/PTFE layered septum caps (C4000-51B, Thermo Fisher Scientific, Waltham, MA, USA). The vials were filled with 200 μL of water. We choose these smaller volume vials over the standard 2-mL vials because many of our samples are quantity limited and we also wish to reduce the quantity of reference water being used. Each injection included purging the syringe twice with sample vial water (filled and injected to waste) and then rinsed 10 times within the sample vial water (i.e. plunger strokes) at 10 μL/s. This strategy, in our experience, removes the presence of the bubble that is often between the bottom of the plunger and the sample water. No rinse aid such as the commonly used NMP (1-methyl-2-pyrrolidinone) was used at any point in these experiments.

Data types

The L2140-*i* produces four levels of data: (1) *coordinator data*, (2) *user data*, (3) *private data*, and (4) *spectral data*. The *coordinator data* are what most users post-process to VSMOW-SLAP scales and publish; the coordinator file contains a single row of data for every injection and is readily imported into a Laboratory Information Management System (LIMS) such as LIMS for Lasers 2015.[16] Each datum in the *coordinator data* is the average, variance estimate, or otherwise-summarized value across the 120–500 s duration of usable data from an injection, and originates from the *user data*. The *user data* file is typically used if the pulse analysis

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Table 1. Example run architecture

Description	Vial/run order	Number of injections	Autosampler job number	Purpose
High δ standard	1	10	1	Conditioning vial
High δ standard	2	5	2	Normalization
Floating Control Standard	3	10	3	Conditioning vial
Floating Control Standard	4	5	4	QA / QC
Control Standard	5	10	5	Conditioning vial
Control Standard	6	5	6	QA / QC
Low Δ^{17}O Control Standard	7	10	7	Conditioning vial
Low Δ^{17}O Control Standard	8	5	8	QA / QC
Low δ standard	9	10	9	Conditioning vial
Low δ standard	10	5	10	normalization
sample	11	15	11	Conditioning vial
samples	12–44	5	12	unknowns
High δ standard	45	10	13	Conditioning vial
High δ standard	46	5	14	Normalization
Floating Control Standard	47	10	15	Conditioning vial
Floating Control Standard	48	5	16	QA / QC
Control Standard	49	10	17	Conditioning vial
Control Standard	50	5	18	QA / QC
Low Δ^{17}O Control Standard	51	10	19	Conditioning vial
Low Δ^{17}O Control Standard	52	5	20	QA / QC
Low δ standard	53	10	21	Conditioning vial
Low δ standard	54	5	22	normalization

All reference-water vials used for normalization or quality assurance/quality control (QA/QC) were preceded by a vial of identical water (conditioning vial) to ameliorate the effects of memory. The High δ-value standard was SW, the control standard was WW, the low Δ^{17}O control standard was WGW, and the low δ-value standard was VW. The Floating Control Standard was one of five reference waters ranging from high δ values (e.g. USGS45) to low δ values (CPH_4, shown in Supplementary Table S1, Supporting Information) and "floats" in their location in the run order such that the order of all standards follows high δ value to low δ value. Each row in this table requires its own autosampler job number unlike default methods where a single job is used to process an entire run of samples and reference waters.

Table 2. Values of the reference waters included in this study

	δ^2H_{VSMOW} (mUr)	$\delta^{17}O_{VSMOW}$ (mUr)	$\delta^{18}O_{VSMOW}$ (mUr)	d_{VSMOW} (mUr)	$\Delta^{17}O_{VSMOW}$ (μUr)
International reference waters					
VSMOW2[a]	0	0	0	0	0
SLAP[a]	−428	−29.6986	−55.5	16	0
GISP[a,b]	−189.7	−13.1337	−24.78	8.54	28
USGS45[a,c]	−10.3	−1.1703	−2.24	7.60	12
In-house reference waters					
KD	1.03	0.0126	0.02	0.87	2
SW	−75.55	−5.5558	−10.56	8.93	34
WW	−268.15	−17.9710	−33.81	2.33	26
WGW	−318.78	−21.1903	−39.78	−0.54	15
VW	−438.65	−30.2926	−56.60	14.15	3

Internal reference water values were obtained by DI-IRMS (reduction with Cr for δ^2H values, CO_2-H_2O equilibration for $\delta^{18}O$ values, H_2O fluorination for $\Delta^{17}O$ values), OA-ICOS, and CRDS. No data obtained from the L2140-*i* were used to calculate these values. The $\delta^{17}O$ value is calculated from the $\Delta^{17}O$ and $\delta^{18}O$ values and is shown to four decimal places as recommended by Schoenemann *et al.*[29] VSMOW2 is the second generation of Vienna Standard Mean Ocean Water, SLAP is the original version of Standard Light Antarctic Precipitation, GISP is the original generation of Greenland Ice Sheet Precipitation, USGS45 is a U.S. Geological Survey water, KD is a single parcel of the commercial Kona Deep drinking water, SW is Seattle deionized tap water, WW is West Antarctic Ice Sheet water, WGW is West Antarctic Ice Sheet Divide Ice core water from the last glacial time period, and VW is surface snow from near the Vostok ice-core site.

[a] δ^2H and $\delta^{18}O$ values from Brand *et al.*[30]

[b] $\Delta^{17}O$ value from Steig *et al.*;[7] note that the weighted average of all known GISP $\Delta^{17}O$ values is 27 μUr.[6,7,35]

[c] $\Delta^{17}O$ value from Berman *et al.*;[6] $\delta^{17}O$ value calculated from $\delta^{18}O$ and $\Delta^{17}O$ values.

fails and a user employs the pulse analysis software to redefine the peaks. The *private data* are high-resolution unprocessed data with all instrument parameters recorded at a frequency of approximately 1 Hz but are still a reduction from the *spectral data*. The *spectral data* are the measured absorbances during each ring-down and have a frequency of approximately 500 Hz. We use the *coordinator data* file for our default mode but use the *private data* for our advanced user mode. We also have employed the *private data* throughout this study in order to track instrument performance with the diagnostic parameters. The *private data* are stored in Hierarchical Data Format (HDF) with the .h5 extension by time and, unlike the *coordinator data*, are continuously logged when the analyzer is running (see Appendix for the location of, and details related to, the *private data*). Many software packages can read in HDF files and we use MATLAB (MathWorks, Natick, MA, USA) to accomplish this task. We have provided our MATLAB code to load the .h5 files of a run in the Supporting Information (importPicarroh5.m). This MATLAB code file is readily opened in any text editor for viewing. Our aim in providing the MATLAB code is to allow readers to understand and to replicate our processing calculations, whether nor not MATLAB is used. Many other software languages could be used, such as R or Python.

We use the *private data* to track such parameters as sampling frequency or spectral duration (stored as "spect_duration"), cavity length control (stored as "PZT_offsets"; PZT is lead zirconate titanate, a piezoelectric material used to vary the length of the cavity), and to calculate isotope ratios based on the absorption "strengths", independently of the default calculation as provided in the *coordinator data*.

Note that when *user data* or *private data* are being employed independently of the Picarro software, one must define the water pulses using custom software. Our custom MATLAB script, which imports the *private data*, finds all the injections in a way that is indistinguishable from those defined by the coordinator software. Furthermore, the MATLAB script provides easy access to three levels of reduced data. First, the high-resolution data are taken directly from the HDF files and have a frequency of about 1 Hz. Second, injection-level data are obtained by taking the mean and standard deviation of the high-resolution data over the stable region of a water pulse originating from a single injection. Third, vial-level data are obtained by taking the mean and standard deviation of the injection level data over all injections from a single vial.

All instruments have a unique factory calibration and the measured values for $\delta^{18}O$, $\delta^{17}O$ and $\delta^{2}H$, as reported by the instrument, may resemble values on the VSMOW scale but have not been formally normalized. Furthermore, the measured $\Delta^{17}O$ values displayed on the instrument software or within any of the above-mentioned data types are insufficient in accuracy and should not be used. While the instrument software does allow for user-imposed calibration coefficients, they do not adhere to the Identical Treatment (IT) principle[22] and, as such, it is our practice to leave the factory calibration values intact and use our own software calibration strategies as initially described in Steig *et al.*,[7] and detailed below in the Calibration section, and more exhaustively in the supplemental MATLAB code text (Supporting Information).

Pulse duration

Can the pulse duration be increased as a way to increase the amount of data obtained per injection, without a precision cost? The time allowed for water to move from the vaporizer to the measurement cavity is the *pulse duration*. The default software allows users to select among several different modes that, among other things, change the pulse duration (e.g., "high throughput", "high precision", "O17HighPrecision"). The timing of all processes associated with an injection is dictated for all these modes within the appropriate coordinator configuration file (the location of these files and this value are detailed in the Appendix). We will refer to the value that we modified as the *sample duration*. The *sample duration* in the configuration file has a default value of 1320 and is proportional to the duration of a pulse in quarter second units (units specified by the manufacturer's software engineers). When this value is set to 1320, the entire injection time (including pumping away the sample and purging with dry air) is about 536 s, yielding about 200 s of useful data. By increasing or decreasing the *sample duration*, users can increase or decrease the amount of time for which an injection is measured without changing the intra-pulse details (e.g., pump and purge timing).

Total sample integration time

In addition to changing the measurement duration of an individual injection, one can also change the number of injections as a way to modify the total amount of data gathered per sample. This is accomplished by changing the count within the operation of the LC PAL autosampler. In the interest of obtaining acceptable $\Delta^{17}O$ results, we wanted to gather enough data over the course of a vial, consistent with the optimal integration time of ~10^3 s indicated by the Allan-variance calculations in Steig *et al.*[7] Ideally Allan-variance tests are conducted with a continuous stream of constant water vapor over a long period of time. However, to be able to assess our system's performance during routine operation, we approximate a conventional Allan-variance calculation using discrete water injections. To this end, we conducted runs where a single reference water was loaded into 50 vials and injected 25 times per vial. Note here, with two 1.8-µL syringe purges to waste and one 1.8-µL injection for measurement, repeated 25 times, this yields a total of 135 µL of water from a 200-µL volume in a 300-µL insert. Supplementary Fig. S1 (Supporting Information) shows the expected decrease in water vapor concentration due to decreasing pressure in the vial but no effect on the $\delta^{2}H$, $\delta^{17}O$, $\delta^{18}O$, d, or $\Delta^{17}O$ values. The *sample duration* was default and the run lasted for approximately 8 days. For Allan-variance purposes, the high-resolution data are used but we first find all the water pulses in the dataset and then remove the interstitial data. The high-resolution pulse-plateau data are pasted together as if they were continuous and the frequency of measurement is retained at ~1 s. In this way, we obtain an estimate of the optimal integration time when data are gathered in an identical fashion to routine sample measurements.

Overcoming memory

In contrast to the above system assessment where a single water sample is injected for prolonged periods of time, routine analysis requires users to switch among disparate waters. One

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cannot assume that all injections from each vial of water are usable, because of sample memory where "memory" or carry-over is the fraction of water or otherwise exchangeable oxygen and hydrogen left in the instrument after an injection that influences subsequent injections. The manufacturer-recommended default protocol for handling this effect is to ignore the first n injections of a vial (e.g., ignore the first 3 from a total of 6 injections). Others have demonstrated success in using a numerical memory correction for δ^2H and δ^{18}O values.[9,10,15,23,24] Given the high-precision effort of this work and the particularly small signal sought when measuring terrestrial Δ^{17}O values, we attempt to push our measurements towards "memory-free" rather than using a correction. Our goal is to use a strategy similar to the default (i.e., ignoring the first few injections) by adding conditioning vials (described below) but also to monitor memory using a method similar to that given by Groning.[24]

In routine sample analysis, we varied the number of injections taken from a vial from 5 to 30 as we evaluated different approaches to handling memory. Reference waters are particularly disparate and, as such, another strategy that we employed was to precede a reference water vial with a vial of identical water (or near-identical in the case of VSMOW2 and SLAP) to act as a conditioner. This increases the number of injections of that specific water, ameliorating the effects of memory. Data from conditioner vials were not included in the data analysis.

Three main approaches can be used to address memory: (a) conditioning, by injecting a sample of similar composition prior to the sample of interest; (b) estimation, in which memory is characterized by measuring known samples to develop a memory-correction equation; and (c) ordering, in which care is taken that adjacent samples do not vary significantly in composition. Because the best approach, or combination of approaches, will depend on the types of samples being measured, we cannot recommend a specific strategy for this, and do not claim that our approach fully addresses memory. In the present study, our most effective tools against memory are the conditioning vial and the selective sequence of waters. Reference waters were always run in sequence of δ^2H value (e.g., highest to lowest). We minimized the δ^2H difference between adjacent waters to 200 mUr or less. (Note here we are using the urey unit instead of ‰ (per mil).[25]). We choose the δ^2H value to order our reference waters because it is most affected by memory. We always included a conditioning vial for reference waters with at least 10 injections and sometimes up to 30 injections.

Calibration

Most researchers adhere to the IT Principle[22] and normalize their samples on the basis of individual runs, whether they use mass spectrometry or laser spectrometry. For reasons that are also well articulated in Thompson,[26] a run is typically assumed to comprise the samples and reference materials analyzed from the time at which the instrument is started until it stops. All the reference materials needed to make all appropriate corrections are included in a run and, thus, a run is a single window within which all samples are calibrated. Given the longer analysis time required for a high-precision Δ^{17}O measurement, we wanted to assess the possibility of combining multiple runs into a "calibration window". Here again we can use a non-traditional approach to an Allan-variance analysis. If we use all the vial level data (mean values for each vial, not high resolution data) from a single reference water collected over the entire 15-month study and leave those data as un-normalized measured values (i.e., not normalized to reference waters included in the runs) we will have a measure of long-term instrument drift. We can then construct a very long-term Allan-variance plot, which we can use to determine the appropriate duration for a calibration window.

Once we have our calibration windows defined, we use all the non-conditioning vials from the two normalization reference waters to generate a single calibration over that entire window. We use VSMOW2 and SLAP when measuring in-house reference waters and two flanking in-house reference waters (e.g., SW and VW) when measuring samples to normalize data to the VSMOW-SLAP scale.[27–29] Current accepted values (Table 2) are taken from the literature (generally from Brand *et al.*[30] but also from others,[6,7] see Table 2 for details) or determined by dual-inlet isotope ratio mass spectrometry (DI-IRMS) (reduction with Cr for δ^2H values,[31] CO_2-H_2O equilibration for δ^{18}O values,[32] H_2O fluorination for Δ^{17}O values[29]), off-axis integrated cavity output spectroscopy (OA-ICOS, using an DLT-100 by Los Gatos Research, San Jose, CA, USA (for δ^2H and δ^{18}O values[33])), and cavity ring-down spectroscopy (CRDS)[10] (L1102-*i*, L2120-*i*). No data obtained from the L2140-*i* in this study (or any L2140-*i*) were used to calculate these values.

We use the VSMOW-SLAP normalized vial-level data from all QA/QC reference waters combined over the 15-month study to calculate the root mean square error (RMSE) to evaluate our precision and accuracy. We also use the mean signed difference (MSD) to provide an additional bias evaluation of accuracy. The root mean square error is calculated as:

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{n}\left(y_i - \hat{y}_i\right)^2}{n-1}} \tag{4}$$

where n is the total number of reference water vials, y_i is the individual vial isotope ratio estimate (e.g., δ^{18}O value), and $\hat{y}_i$ is the current accepted value for that particular reference water. The mean signed difference is calculated as:

$$\mathrm{MSD} = \frac{\sum_{i=1}^{n}\left(y_i - \hat{y}_i\right)}{n} \tag{5}$$

The RMSE is the standard deviation from a current accepted value while the MSD is an estimate of bias and these together provide us with our estimates of precision and accuracy combined across the reference water isotopic composition.

RESULTS AND DISCUSSION

Pulse duration

We ran the instrument with a default *sample duration* as well as with a long *sample duration*. As already noted, the default *sample duration* value of 1320 in the configuration file corresponds to approximately 200 s of integrated data

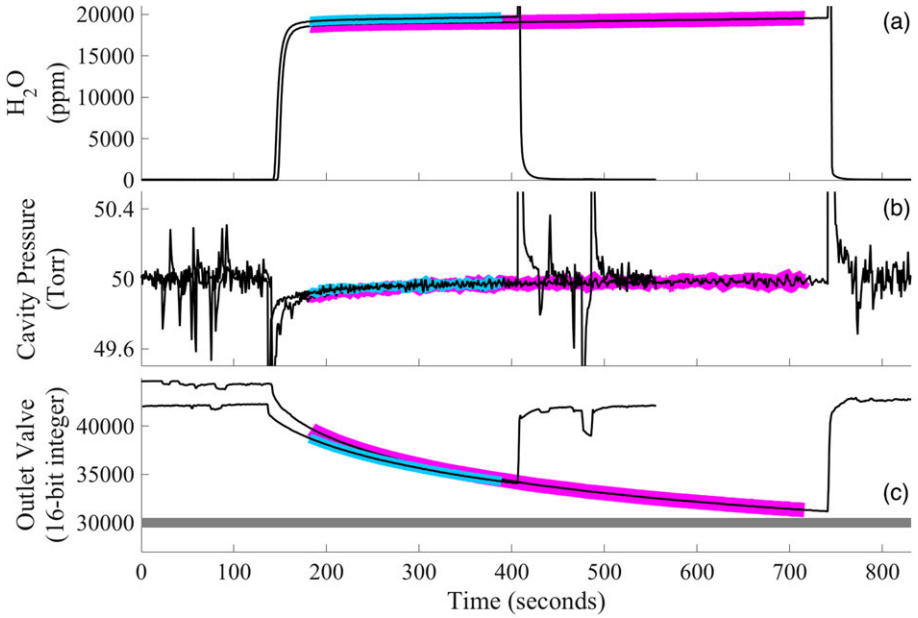

Figure 1. Injection examples illustrate the two types of pulses used in this study where blue is the usable data from a default pulse length and magenta is the usable data from a long pulse length: (a) water vapor concentration; (b) cavity pressure; and (c) outlet valve position and minimum orifice size (horizontal line) below which cavity pressure is no longer stable.

(Fig. 1(a)). Our long-pulse *sample duration* value is 3000, which corresponds to approximately 500 s of integrated data (Fig. 1(a)).

Note that the *sample duration* cannot be increased indefinitely. The quantity of air in the vaporizer chamber is finite. A position-controlled valve located downstream of the spectrometer cavity is used to maintain the cavity pressure at 50 Torr (Fig. 1(b)) and continuously closes while a pulse proceeds (Fig. 1(c)). We tried longer pulse times by changing the *sample duration* value to 5000 and 10000 but the cavity pressure became erratic after the outlet valve was below 30000 (Fig. 1(c), horizontal bar) and it was evident

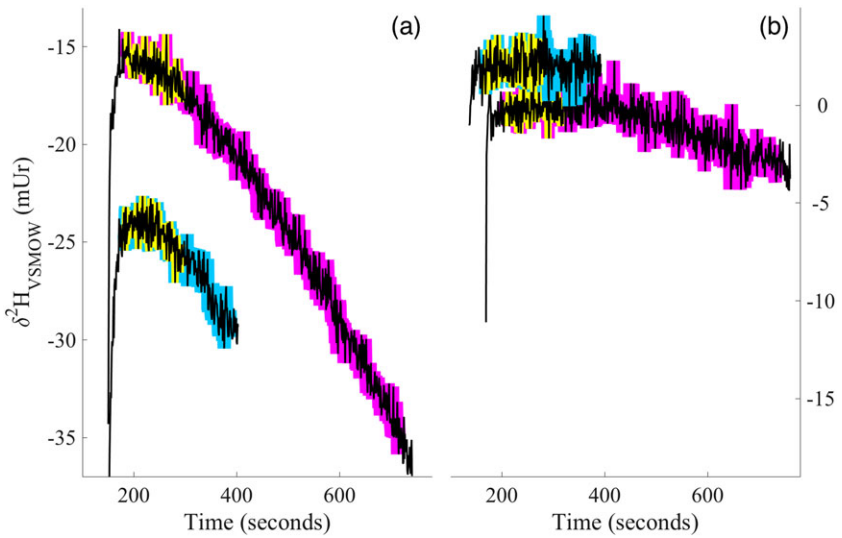

Figure 2. (a) δ^2H values from the same default and long pulse examples shown in Fig. 1. Both default and long pulses are from different runs and are the first injections of a high δ-value reference water (KD) following a low δ-value reference water (VW) (data not shown). Blue and magenta shading are as in Fig. 1. Yellow shading shows the first 120 s of data that comprise "short" integrations throughout this study. The colors in this figure are used throughout the paper for clarity. (b) The same KD water from the same two runs as (a) 40 injections later (i.e. 40 injections of KD after VW). Both (a) and (b) y-axes have a range of 24 mUr. Both the short-integrations in (b) are within a 95% confidence interval of the accepted value of KD. Note the reduced, but still present, effect of memory with longer pulse duration in (b).

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that the outlet valve was unable to control the cavity pressure under these conditions. The outlet valve position number is a 16-bit value and thus ranges from 0 to 65535; where 0 is theoretically all the way closed and 65535 is theoretically all the way open. We have assigned an arbitrary minimum threshold of 30000 for the outlet valve position. However, this is not a fixed value for any single instrument and should be reevaluated routinely, as changes in vacuum due to pump age can influence the outlet valve and hence the cavity pressure.

Another side effect to sampling from a parcel of air while continuously removing it via bulk flow is isotope fractionation. The pump can be assumed to remove proportionally more of the lighter water isotopologues and, as such, we should observe a gradual isotope enrichment of the heavier water isotopologues in the measurement of a single injection with increased sampling time. However, in practice we find that this effect is generally overwhelmed for longer integration times by the more problematic effect of memory.

An increase in pulse duration increases the impact of memory (Fig. 2) because the longer that a single injection resides in and among the vaporizer, cavity and associated valves and plumbing, the more the injected water is affected by carry-over from previous injections. Figure 2(a) shows both default (blue) and long (magenta) pulses from the first injection of a high δ-value reference water (KD) (these are the pulses that are shown) following a low δ-value reference water (VW) (data not shown). This is an interesting illustration of the memory effect and with the following simple calculation suggests incomplete pumping of vapor. We observe an increase in the water vapor concentration from 18500 to 19500 for the long pulse in Figs. 1(a) and 2(a). Using a two-source mixing model, 18500 ppm of vapor with a δ^2H value of −15 mUr (uppermost value from Fig. 2(a)) plus 1000 ppm of vapor that elicits a 20 mUr decrease (from −15 to −35 mUr in Fig. 2(a)) yields a vapor with a δ^2H value of approximately −400 mUr which is remarkably close to the VW δ^2H value of about −439 mUr (from Table 2). This is most certainly an oversimplification but it is suggestive and it is likely that multiple reservoirs exist as previously described.[9]

Regardless of the exact reservoir, to reduce the impact of memory, one can avoid long integration and execute short pulses (as in "high-throughput" mode) or, to save the syringe life, one can still perform long pulses but use only the first 120 s for δ^2H measurements (Fig. 2, yellow). Even default mode (manufacturer's "High Precision" mode in this case) has an integration time longer than 120 s and is thus overly affected by memory, particularly for δ^2H values (Fig. 2(a)). Note that this cannot be corrected for if the *coordinator data* are used, as the high-resolution data are not available. Also note that even after 40 injections of the in-house reference water KD, we do not observe the expected isotopic enrichment in ^{2}H with continued sampling of the same water injection (Fig. 2(b)); this clearly implicates the continued memory influence of the previous (isotopically more negative with respect to ^{2}H) sample. The expected observance of ^{2}H and ^{18}O within-injection enrichment due to bulk-flow removal of water vapor from the cavity was observed after 540 injections of a single water using a separate instrument (L2120-*i*) (data not shown).

Total sample integration time

Based on the Allan-variance data in Steig *et al.*,[7] the optimal integration time for Δ^{17}O measurements with the L2140-*i* is 1200 s, which provides a precision of approximately 10 μUr. Figure 3 shows the truly continuous data from Steig *et al.*[7] as well as a series of discrete injections from a single reference water (SW). Several observations can be made from this dataset. First, this particular L2140-*i* using discrete injections performed slightly better with respect to Δ^{17}O than the instrument used in Steig *et al.*[7] Second, Δ^{17}O data generally exhibit a white noise pattern with few perturbations, which is unlike the δ^{18}O, δ^{17}O and δ^2H data from 20 to 200 s. The δ^{18}O, δ^{17}O, δ^2H, and *d* values all show oscillations due to noise imposed by the discrete sampling. In the Allan-variance calculation, we are assuming that the data are continuous, but between 20 and 200 s, we are estimating variance across the boundary of an injection cycle and are observing increased noise because of this. Indeed, if the injection-level data are

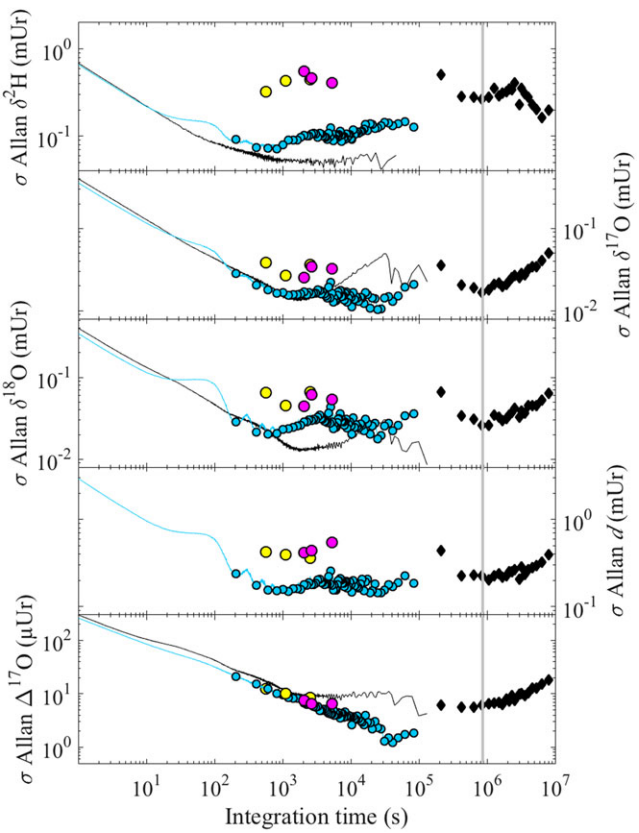

Figure 3. Allan standard deviation for δ^2H, δ^{17}O, δ^{18}O, *d*, and Δ^{17}O values. The black line is from Steig *et al.*[7] and represents truly continuous measurements collected from a distinct L2140-*i*. The blue line is an SW discrete-injection run. Blue dots are the injection-level data from that same SW run. The yellow dots are calibrated short-integration vial-level standard deviations for all reference waters at varying numbers of injections over the course of the 15-month study period. The magenta dots are calibrated long-integration vial-level standard deviations for all reference waters at varying numbers of injections over the 15-month study period. The black diamonds are results from un-normalized WW vials over the course of 15 months. The gray vertical bar shows 10 days.

used to construct an Allan-variance plot (Fig. 3, blue dots) the first few troughs of the high-resolution data are occupied by the interval over which injections are averaged. Third, the optimal time over which to integrate is different for δ^2H, δ^{17}O, δ^{18}O, and Δ^{17}O measurements. The δ^2H value appears to have the shortest optimal integration time, with 500 to 900 s showing the lowest Allan deviation (Fig. 3, top). The δ^{17}O value has the lowest Allan deviation between 1000 and 2000 s. The δ^{18}O value appears to have its minimum between 600 and 900 s, while d has a minimum integration between 800 and 1500 s. Lastly, Δ^{17}O reaches its lowest Allan deviation after 10000 s. The absorption lines for each isotopic ratio are evidently affected differently by instrument conditions (e.g., temperature and pressure fluctuations in the cavity). Thus, to obtain the highest level of precision, different integrations times need to be used for each isotope, which is not possible with *coordinator data*.

Finally, it is of interest how the results of our Allan-variance tests compare with actual sample reproducibility in routine practice. Figure 3 (yellow and magenta symbols) compares the compiled standard deviations for all waters run over the course of our experiment with the Allan-variance results. The results show that the Allan-variance results are optimistic: that is, we tend to obtain results less precise than would be suggested by the manufacturer-specified instrument precision based on Allan variance of a single water analyzed over a long period of time.

Overcoming memory

Probably the main reason why it is a challenge for routine sample analysis to attain manufacturer-specified precision is the toggling among disparate waters and hence, memory. We monitor memory as a way to monitor run quality, vaporizer cleanliness, and general performance. Figure 4 shows the contribution of previous injections to the current injection as estimated by both δ^2H and δ^{18}O values. While our unknown samples are especially clean, as they are Antarctic ice-core water, and it is apparent when we ran samples containing more solutes (Fig. 4, March–April 2015), the important part of Fig. 4 is an alternative presentation of the long *vs* default *vs* short integration of the δ^2H data. Note that the short integration results in reduced impact of memory, as would be expected from the findings in Fig. 2.

Calibration

We combined between 1 and 6 runs into a calibration window such that our calibration windows were typically 10 days in duration. This is based on the long-term Allan variance of our WW reference water (Fig. 3, black diamonds, vertical bar). If the instrument experienced a calibration-changing event, the calibration window was adjusted accordingly. A calibration-changing event might be a software upgrade, a shift in the spectroscopy as noted by a shift in the PZT offset, or a sudden change in the spectral duration. The 15-month time period over which data in the paper were collected was divided into 31 calibration windows. We have provided data from a single calibration window as a supplementary comma separated values (CSV) file (Schauer_RCM_LASCompleteWater_ExampleCalibrationWindow_Data.csv, Supporting Information) that includes all pertinent injection level data. We also provide our normalized vial-level data from that same calibration window as Supplementary Table S1 (Supporting Information).

One potential improvement to our calibration approach would be to include a set of reference waters in the middle of the run, rather than only at the beginning and end. However, even if the set of reference waters was minimal (two for normalization, one for QA/QC), this would add 13 h to the run (Table 3). Also, although we are combining 2 to 3 runs into a calibration window, it is possible that the

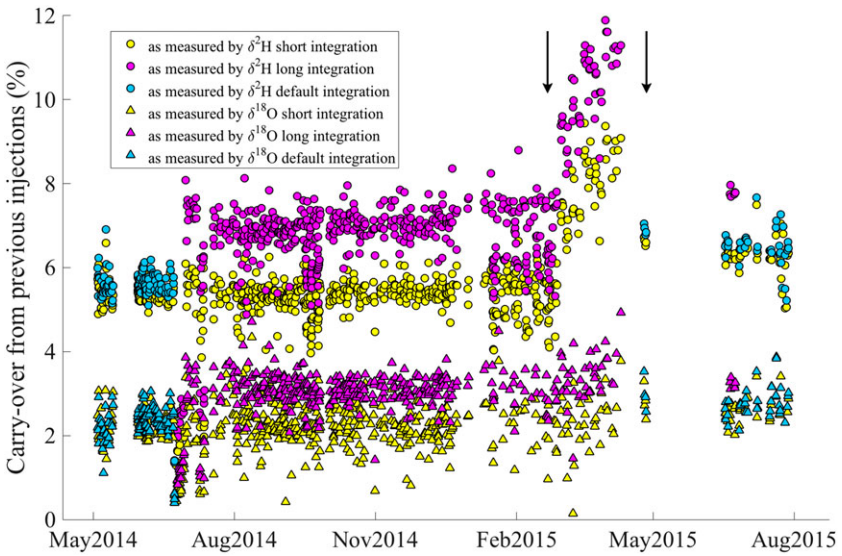

Figure 4. The contribution of previously injected water to the current measurement (carry-over or memory) as estimated by δ^2H and δ^{18}O values. The first arrow indicates the onset of injecting salty samples while the second arrow shows when the vaporizer was cleaned. The δ^2H colors are as in Fig. 2 and reflect default integration (blue), long integration (magenta), and short integration (yellow).

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Table 3. Run accounting, timing and sample throughput

	Default pulse, 10 inj	Default pulse, 20 inj	Long pulse, 5 inj
Number of conditioning vials	11	11	11
Number of injections per conditioning vial	10	20	10
Number of reference waters vials	10	10	10
Number of injections per reference water vial	10	20	5
Number of unknown vials	33	33	33
Number of injections per unknown vial	10	20	5
Total time per injection (minutes)	8.82	8.82	14.38
Total amount of usable data per injection (seconds)	200	200	520
Total injections in run	540	1080	325
Length of run (days)	3.3	6.6	3.2
Usable data generated per day (hours)	7.2	7.2	9.6
Time associated with 3 reference waters (hours)	10.3	20.6	13.2
Total number of unknowns run per day	10	5	10

The default pulse is the preset condition when ^{17}O-high precision has been selected while starting the coordinator software. Users typically prefer to have a single autosampler job for their run, which is represented with the 10 inj and 20 inj columns below, where inj is injections. The long pulse 5 inj is the advanced user mode and represents the conditions responsible for the optimal results in Table 4.

startup procedures (i.e., changing septum, cleaning syringe, restarting the coordinator software) introduces a within-run drift that is correctable but only with regularly spaced reference waters. However, given that we see drift after 10 days (Fig. 3, black diamonds), and that our runs are an average of 3.5 days long, it seems unlikely that within-run drift is significant if present.

Table 4 shows the overall performance as assessed by six reference waters. This dataset shows that acceptable data can be obtained in default mode and optimal data are obtained by using long pulses and subsampling those long pulses into short integration for δ^2H and d values. The optimal data show that the δ^2H value is within 0.42 mUr of the accepted values and with an apparent bias of 0.2 mUr (i.e., the mean is 0.2 mUr higher than the nominally accepted values). The δ^{17}O and δ^{18}O values are within 0.04 and 0.07 mUr, respectively, of the accepted value with no measurable bias. The d value is within 0.46 mUr of the accepted values with no bias. The Δ^{17}O is within 8 μUr of the accepted values with an apparent +3 μUr bias. Note here that all of our estimates of bias for Δ^{17}O are positive, suggesting a small mis-measurement or mis-assignment of the accepted Δ^{17}O values of the reference waters. Lastly, we measure GISP and USGS45 to within error of previously reported values (Table 5).

The long pulse data are also optimal for two practical reasons: (1) the syringe is actuated only one-half to one-quarter as many times as in the default mode, and (2) the total time required to obtain data is reduced. Short pulse injections with 10 injections per vial require 1.5 h per vial. Short pulse injections with 20 injections per vial require 3.0 h per vial. Long pulse injections with 5 injections per vial require 1.2 h per vial. While all these time periods are long relative to previously published works reporting δ^2H and δ^{18}O values,[8] our optimal method for the complete water-isotope ratio measurements with the L2140-*i* requires only 25% of the time required for

Table 4. The combined root mean square error (RMSE) and mean signed difference (MSD) (given in parentheses) for all GISP, USGS45, KD, SW, WW, WGW, and VW waters run over the course of the 15-month study

Method	n	δ^2H (mUr)	δ^{17}O (mUr)	δ^{18}O (mUr)	d (mUr)	Δ^{17}O (μUr)
Default pulse, default integration, 10 injs	62	0.63 (−0.1)	0.05 (0.0)	0.09 (0.0)	0.82 (−0.2)	9 (4)
Default pulse, short integration, 10 injs	62	0.48 (−0.1)	0.05 (0.0)	0.09 (0.0)	0.76 (−0.2)	13 (4)
Default pulse, default integration, 20 injs	50	0.69 (0.0)	0.04 (0.0)	0.08 (0.0)	0.58 (−0.2)	10 (4)
Default pulse, short integration, 20 injs	50	0.54 (0.0)	0.04 (0.0)	0.06 (0.0)	0.51 (−0.2)	11 (4)
Long pulse, long integration, 5 injs	250	0.66 (0.3)	0.04 (0.0)	0.07 (0.0)	0.59 (0.2)	8 (3)
Long pulse, short integration, 5 injs	250	0.42 (0.2)	0.04 (0.0)	0.07 (0.0)	0.49 (0.1)	14 (4)
Optimal	**250**	**0.42 (0.1)**	**0.04 (0.0)**	**0.07 (0.0)**	**0.46 (0.0)**	**8 (3)**

Waters used to normalize within a calibration window (e.g., VSMOW2/SLAP or SW/VW) are excluded. RMSE is the standard deviation difference from the accepted value and MSD is the average difference from the accepted value; see text for formulas. "Optimal" uses short integration on long pulses for δ^2H values and long integration for δ^{17}O, δ^{18}O, and Δ^{17}O values while d is a combination of short integration for δ^2H values and long integration for δ^{18}O values. The number of reference water vials incorporated into the RMSE and MSD is n.

Table 5. Measured value means and standard deviations (given in parentheses) of the widely dispersed secondary reference waters included in this study using the optimal sampling approach

	n	δ^2H_{VSMOW} (mUr)	$\delta^{17}O_{VSMOW}$ (mUr)	$\delta^{18}O_{VSMOW}$ (mUr)	d_{VSMOW} (mUr)	$\Delta^{17}O_{VSMOW}$ (μUr)
GISP[a]		-189.7 (0.9)	-13.1337 (0.02)	-24.78 (0.08)	8.54 (0.93)	28 (9)
GISP[b]	10	-189.37 (0.25)	-13.1219 (0.04)	-24.76 (0.07)	8.72 (0.47)	29 (8)
USGS45[a]		-10.3 (0.4)	-1.1703 (0.03)	-2.24 (0.01)	7.60 (0.40)	12 (5 [c])
USGS45[b]	25	-10.48 (0.39)	-1.1371 (0.04)	-2.18 (0.06)	6.99 (0.37)	17 (8)

The $\delta^{17}O$ value is shown to four decimal places as recommended by Schoenemann *et al*.[29]
[a]Current literature values, see Table 1.
[b]Measured in this study.
[c]Estimated from Berman *et al*.[6]

IRMS $\Delta^{17}O$ methods.[29] The precision and accuracy of this optimal method surpass and are competitive with those obtained by IRMS.

CONCLUSIONS

We show long-term high-precision performance for water δ^2H, $\delta^{17}O$, $\delta^{18}O$, d, and $\Delta^{17}O$ values from routine injections of discrete water samples. It is possible to obtain acceptable data in default instrument mode, and slightly more precise data by increasing the number of injections. We find that the optimal approach for our L2140-*i* instrument is to use fewer injections but increase the integration time. This reduces the number of syringe actuations and the total analysis time without compromising precision. The main reason that very long runs fail, in our experience, is syringe failure in the middle of a run. Syringe actuation and usage are important. This optimal approach deals with this main concern. Increasing the integration time does not lead to increased isotope fractionation, but does increase the effect of memory, which is addressed by using instrument conditioning. Using our optimal approach, a sample requires 1.2 h to analyze and yields RMSE values of 0.42 mUr, 0.04 mUr, 0.07 mUr, 0.46 mUr, and 8 μUr for δ^2H, $\delta^{17}O$, $\delta^{18}O$, d, and $\Delta^{17}O$ values, respectively (Table 4). To obtain these values, the data used for δ^2H values are calculated with short integrations while d is a combination of short integration for δ^2H values and long integration for $\delta^{18}O$ values, and the $\delta^{17}O$, $\delta^{18}O$, and $\Delta^{17}O$ values are calculated with long integrations from the same pulse of water. We also find good agreement with accepted values of GISP and USGS45 using our optimal method (Table 5).

Our optimal approach is more than a strategy to use a Picarro L2140-*i*. It is a suggestion to mine the data of any commercially available LAS instrument, customize the manufacturer-specified settings, and find the highest possible precision. While we chose to use MATLAB for our data processing, this is not a requirement for this approach. Many other software packages exist that are free and open-source (e.g. R and python). Most data-processing software packages allow for direct reading-in of HDF format files. The idea of tweaking the pulse duration could be applied to any LAS instrument. Indeed, the same strategy of modifying the integration time was applied in a DI-IRMS system with great success.[34]

Our optimal sample throughput is lower than in previous LAS method papers (e.g. [16]). However, considering that all the metrics reported here (δ^2H, $\delta^{17}O$, $\delta^{18}O$, d, and $\Delta^{17}O$ values) are more or as precise as those obtained by IRMS, the sample throughput is competitive with any existing method at 10 samples per day. While we cannot measure any sample or reference water better than the current precision of our normalization reference waters, perhaps, in the future, we will know our reference materials better by using techniques similar to what we have presented here. Furthermore, better precision leads to signals that were heretofore undetectable.

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APPENDIX

The *private data* used in this study are located within the main computer hard drive here:

C:\Picarro\G2000\Log\Archive\DataLog_Private \[YEAR]\[MONTH]\[DAY]\. Within each [DAY] folder are two or three compressed files (*.zip) that are written every 12 hours. Each compressed file contains 10 HDF files (.h5).

The *sample duration* in this study is within the coordinator initialization file "CoordinatorLIMS_G2000_lct.ini". This file is located on the main computer hard drive here:

C:\Picarro\G2000\AppConfig\Config\Coordinator\. A coordinator initialization file exists for each of the selectable protocols that are presented to the user upon launching the Coordinator software. This particular file is read by selecting "O17 High Precision". Line 45 of this file is called "sample" and has a value 0xFF,0x04,1320 as a default. Note, a coordinator configuration file exists for each mode of running (high throughput, etc.) and the same value on Line 45 in each of these files exists.

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