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Technical Note: Evaluation of between-sample memory effects in the analysis of δ^2H and δ^{18}O of water samples measured by laser spectroscopes

D. Penna[1,2], B. Stenni[3], M. Šanda[4], S. Wrede[5,8], T. A. Bogaard[6], M. Michelini[3], B. M. C. Fischer[7], A. Gobbi[1], N. Mantese[1], G. Zuecco[1], M. Borga[1], M. Bonazza[3], M. Sobotková[4], B. Čejková[9], and L. I. Wassenaar[10]

[1]Department of Land, Environment, Agriculture and Forestry, University of Padova, Italy
[2]Faculty of Science and Technology, Free University of Bozen-Bolzano, Italy
[3]Department of Mathematics and Geosciences, University of Trieste, Italy
[4]Faculty of Civil Engineering, Czech Technical University in Prague, Czech Republic
[5]Department of Hydrology, University of Trier, Germany
[6]Faculty of Civil Engineering and Geosciences, Delft University of Technology, The Netherlands
[7]Department of Geography, University of Zürich, Switzerland
[8]Department of Environment and Agro-Biotechnologies, Centre de Recherche Public – Gabriel Lippmann, Luxembourg
[9]Czech Geological Survey, Prague, Czech Republic
[10]Isotope Hydrology Laboratory, International Atomic Energy Agency, Vienna

Correspondence to: D. Penna (daniele.penna@unipd.it)

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Abstract. This study evaluated between-sample memory in isotopic measurements of δ^2H and δ^{18}O in water samples by laser spectroscopy. Ten isotopically depleted water samples spanning a broad range of oxygen and hydrogen isotopic compositions were measured by three generations of off-axis integrated cavity output spectroscopy and cavity ring-down spectroscopy instruments. The analysis procedure encompassed small (less than 2 ‰ for δ^2H and 1 ‰ for δ^{18}O) and large (up to 201 ‰ for δ^2H and 25 ‰ for δ^{18}O) differences in isotopic compositions between adjacent sample vials. Samples were injected 18 times each, and the between-sample memory effect was quantified for each analysis run. Results showed that samples adversely affected by between-sample isotopic differences stabilised after seven–eight injections. The between-sample memory effect ranged from 14 % and 9 % for δ^2H and δ^{18}O measurements, respectively, but declined to negligible carryover (between 0.1 % and 0.3 % for both isotopes) when the first ten injections of each sample were discarded. The measurement variability (range and standard deviation) was strongly dependent on the isotopic difference between adjacent vials. Standard deviations were up to 7.5 ‰ for δ^2H and 0.54 ‰ for δ^{18}O when all injections were retained in the computation of the reportable δ-value, but a significant increase in measurement precision (standard deviation in the range 0.1 ‰–1.0 ‰ for δ^2H and 0.05 ‰–0.17 ‰ for δ^{18}O) was obtained when the first eight injections were discarded. In conclusion, this study provided a practical solution to mitigate between-sample memory effects in the isotopic analysis of water samples by laser spectroscopy.

1 Introduction

The use of laser absorption spectroscopy for the determination of water stable isotopes (δ^2H and δ^{18}O, VSMOW-SLAP scale) in water samples is becoming increasingly common worldwide. The availability of lower cost off-axis integrated cavity output spectroscopy (OA-ICOS) instruments and cavity ring-down spectroscopy (CRDS) devices compared to isotope-ratio mass spectrometers (IRMS), allowed researchers to take greater advantage of water isotopes as tracers in hydrological studies. Several studies tested the

performance of OA-ICOS (Lis et al., 2008; Wassenaar et al., 2008; IAEA, 2009b; West et al., 2010; Schultz et al., 2011) and CRDS instruments (Brand et al., 2009; Chesson et al., 2010; Gkinis et al., 2010) for the analysis of water samples, revealing very good comparability with isotope-ratio mass spectrometric techniques. Given the relatively recent advent of laser spectroscopy in hydrological laboratories, some practical aspects and shortcomings in the field of water research remain unexplored.

Recently, a comparative study of OA-ICOS spectroscopes tested against a mass spectrometer found poor accuracy of laser spectroscopy results specifically for isotopically depleted water samples (Penna et al., 2010). This poor accuracy was related to between-sample memory effects (MEs) – defined as the carryover of the sample being measured by traces of the previous water sample(s) (Olsen et al., 2006). Here we assessed the practical implications of the analysis of water samples characterised by a wide range of isotopic values and different conditions (under which the occurrence of MEs might significantly influence the final isotopic measurement) on the performance of different laser spectroscopes. For this experiment we tested three OA-ICOS and CRDS instruments of different generations using a set of ten isotopically depleted water samples.

2 Materials and methods

2.1 Laser spectroscopes and mass spectrometer

The water samples were analysed by six laser spectroscopes (three OA-ICOS: Delft University of Technology, the Netherlands, Czech Technical University in Prague and Czech Geological Survey, Czech Republic; three CRDS instruments: University of Trieste, Italy, University of Zürich, Switzerland, International Atomic Energy Agency, Vienna, Austria) and one mass spectrometer (University of Trieste), used as reference. Due to the rapid evolution of laser spectroscopy technology, we tested early and new generation instruments. The spectroscopes included:

1. OA-ICOS: one Liquid Water Isotope Analyser, model DLT-100 version 908-0008 (first generation), one version 908-0008-2000 (second generation) and one version 908-0008-3000 (third generation), manufactured by Los Gatos Research Inc. (LGR, Mountain View, California, USA). These instruments are referred to as "LGR-1", "LGR-2" and "LGR-3", respectively. The volume of water for each injection was 750 nl. According to the manufacturer's specifications (Los Gatos Research, Inc., 2008), the 1-σ measurement precision was below 0.6 ‰ for δ^2H and 0.1 ‰ for δ^{18}O.

2. CRDS: two Picarro L1102-i liquid analysers (first generation) and one L2130-i (second generation), manufactured by Picarro (Picarro, Santa Clara, California, USA), named "PIC-1", "PIC-2" (first generation) and "PIC-3" (second generation). The volume of water for each injection was 2 µl. The manufacturer reported the 1-σ measurement precision below 0.5 ‰ for δ^2H and 0.1 ‰ for δ^{18}O (Picarro, Inc., 2008).

3. IRMS: one Thermo Fischer Delta Plus Advantage mass spectrometer (Thermo Fisher Scientific Inc., Massachusetts, USA) connected to a GFL 1086 equilibration device. The measurements were carried out with a classical dual-inlet system using a CO_2/H_2 water equilibration technique (Epstein and Mayeda, 1953; Horita et al., 1989). The external 1-σ precision of the instrument was $\pm$0.7 ‰ and $\pm$0.05 ‰ for δ^2H and δ^{18}O measurements, respectively.

For all instruments we used new syringes, adopting the analysis specifications as recommended by the manufacturers. Before each analysis run, we performed the standard maintenance, such as changing the injection port septum and checking that the transfer line and the injection block were cleaned.

Further information regarding the theory of operation of the two laser systems is reported elsewhere (OA-ICOS: Sayres et al., 2009; Wang et al., 2009; CRDS: Brand et al., 2009; Gkinis et al., 2010).

2.2 Samples and analysis scheme

The comparative test was performed on ten isotopically depleted samples derived from snow surface samples collected at different locations in Antarctica, provided by the Isotope Geochemistry Laboratory of the University of Trieste. The isotopic composition of the samples ranged from $-$231.7 ‰ to $-$421.1 ‰ for δ^2H and from $-$29.83 ‰ to $-$53.41 ‰ for δ^{18}O. Each sample was analysed ten times by IRMS and the average and standard deviation values were reported (Table 1). Three laboratory measurement standards that bracketed the isotopic composition of the samples were used. These measurement standards were calibrated against IAEA (International Atomic Energy Agency) water standards (Gonfiantini, 1978) in relation to the VSMOW-SLAP scale and normalised adopting the procedure described in IAEA (2009a). All samples and standards were pipetted into ND8 32 $\times$ 11.6 mm screw neck 1.5 ml vials with PTFE/silicone/PTFE septa with 1 ml of water sample. Vial filling was done in the same laboratory to ensure sample consistency at all test locations. The samples were measured following the procedure suggested by the Isotope Hydrology Laboratory at IAEA (IAEA, 2009b) and tested by Penna et al. (2010). The scheme consisted of two measurement standards, interpolated by a linear regression, and a control standard not included in the calibration. The regression between measurements and known δ-values for calibration standards was used to convert the measured absolute isotopic ratios to respective δ-values. We adopted a modified version of this template, sampling each vial 18 times instead of six times in

Table 1. Isotopic compositions of samples and laboratory measurement standards. The reported values represent the average and the standard deviation of ten replicates.

ID	δ^2H (‰)	Std. dev. δ^2H (‰)	δ^{18}O (‰)	Std. dev. δ^{18}O (‰)
1	−231.7	0.5	−29.83	0.02
2	−258.7	0.4	−33.07	0.01
3	−277.5	0.5	−34.96	0.02
4	−303.8	0.4	−38.26	0.03
5	−312.2	0.6	−39.47	0.02
6	−334.7	0.4	−42.24	0.02
7	−338.5	0.5	−43.73	0.02
8	−373.1	0.4	−48.02	0.02
9	−390.4	0.5	−50.20	0.02
10	−421.1	0.5	−53.41	0.02
STD1	−221.8	0.5	−29.06	0.04
STD2	−313.8	0.4	−40.22	0.02
STD3	−422.8	0.4	−53.83	0.02

order to better observe the sequential trend of MEs. The water samples were grouped in two sets of five interposed by three triplets of laboratory measurement standards. Each run was started with a dummy sample to prime the transfer line and stabilise the machine and ended with deionised water to clean the syringe (IAEA, 2009b).

We took advantage of the wide isotopic range of the samples and measurement standards in designing the analysis sequence template presented in Table 2, where some adjacent vials were very close in isotopic composition, whereas others differed markedly. This allowed us to test the performance for a broad range of differences in isotopic compositions between adjacent vials (the lowest absolute difference between the heaviest and lightest water was approximately 2 ‰ for δ^2H and 1 ‰ for δ^{18}O, whereas the highest absolute difference between the isotopically heavier and lighter water was approximately 201 ‰ for δ^2H and 25 ‰ for δ^{18}O (Table 2).

ME was computed following Gröning (2011), assuming a constant memory decrease over time. For each pair of adjacent vials, we considered the isotopic difference (d) between the mean of the last three injections of the two samples as their true isotopic difference:

$$d = \left(\overline{i_{18}, i_{17}, i_{16}}\right)_k - \left(\overline{i_{18}, i_{17}, i_{16}}\right)_j \quad (1)$$

where i_{18}, i_{17} and i_{16} represent the isotopic content of the last injections in the sequence, k is a sample and j is the previous sample with respect to k. However, instead of using the value of the last injection as the true value (as in Gröning, 2011), the mean of the last three was computed to avoid possible influences of random fluctuations or the occurrence of "bad injections" (Penna et al., 2010). In the following, the isotopic difference (e) between the average of the last three injections of the second sample and its first injection was computed as

$$e = \left(\overline{i_{18}, i_{17}, i_{16}}\right)_k - (i_1)_k \quad (2)$$

where i_1 represents the isotopic content of the first injection of sample k. The computation of (e) was repeated for all injections of samples k. The ratio f:

$$f = \frac{e}{d} \quad (3)$$

constituted an approximation of ME. The final value of ME was determined considering an exponential decline with time and multiplying, for each injection of the series, the f-value times a reduction factor (RF) defined as follows:

$$\mathrm{RF} = \frac{f}{c} \quad (4)$$

where c was computed as:

$$c = f + f^2 + f^3 \quad (5)$$

to take into account the (most likely small) contribution of previous injections of the first sample to the total ME (Gröning, 2011).

3 Results and discussion

3.1 Measurement stabilisation and memory effect

The graphs in Fig. 1a, b display the δ^2H and δ^{18}O values of the second triplet of laboratory measurement standards for each instrument, as a function of the number of injections performed during the run (i.e., trend over time during the run). For the first injections, the curves referring to the second and the third standards (STD2 and STD3) showed a deviation from the δ-values obtained during the central and final part of the run. On average, at least seven or eight injections were required in order to obtain stable values (i.e., to observe variations between successive injections within the range of the instrumental precision). Conversely, the first measurement standard (STD1) exhibited more stable behaviour over time. STD2 and STD3 represented waters most affected by high inter-vial isotopic difference, whereas STD1, in the second triplet, was characterised by a relatively small isotopic difference with respect to the composition of the antecedent vial (Table 2). In addition, the same plots were drawn for other samples (not shown), featuring much smaller isotopic difference compared to the previous vial, but almost no variations after the first two or three injections were observed. Therefore, we related this behaviour to the tendency of each laser spectroscope to buffer the influence of the isotopic content of the previous sample during the run. This effect was observed for both isotopes, even though the trend for δ^{18}O was generally more variable than for δ^2H. The effect was observable on all spectroscopes, but slightly less evident on CRDS instruments. However, for both laser technologies and particularly for OA-ICOS instruments, the newest generations of instruments showed a marked performance improvement in the stabilisation effect (i.e., smaller difference between the values at the beginning and in the central-final part

Table 2. Sequence of samples and standards in the analysis run and absolute isotopic differences (IRMS values) between each vial and the previous. DW: deionised water. STD: laboratory measurement standard. Number: sample ID. All values are rounded to improve the readability.

	DW	STD 1	STD 3	STD 2	5	4	3	2	1	STD 1	STD 2	STD 3	6	7	8	9	10	STD 1	STD 3	STD 2
δ^2H difference (‰)	–	166	201	109	2	8	26	19	27	10	201	109	21	4	35	17	31	199	201	109
δ^{18}O difference (‰)	–	21	25	14	1	1	3	2	3	1	25	14	2	1	4	2	3	24	25	14

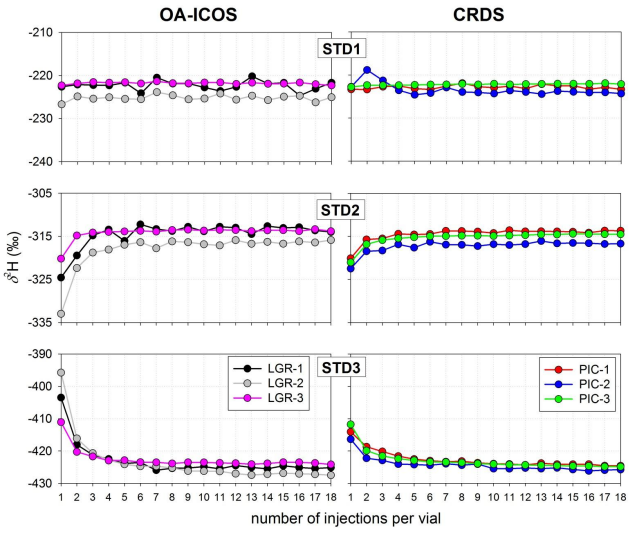

Fig. 1a. Measurement stabilisation by sequential injection number for three laboratory measurement standards (second triplet in an analysis run) for hydrogen. Left column: OA-ICOS instruments. Right column: CRDS instruments.

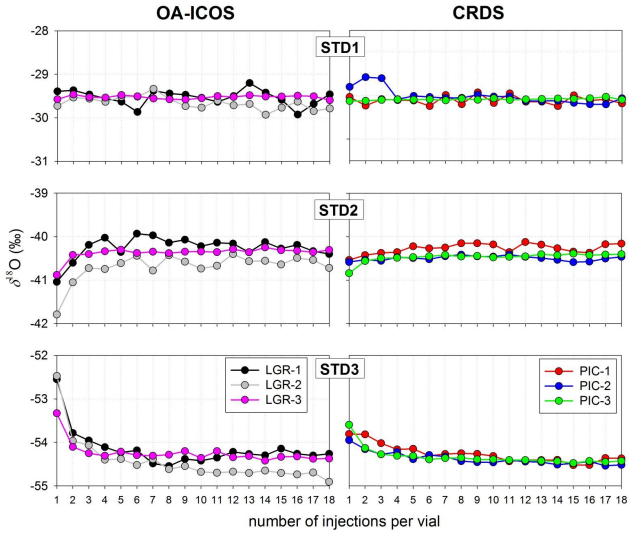

Fig. 1b. Measurement stabilisation by sequential injection number for three laboratory measurement standards (second triplet in an analysis run) for oxygen. Left column: OA-ICOS instruments. Right column: CRDS instruments.

of the run compared to earlier models) and in the overall low variability (i.e., precision) of the measurements.

Figure 2 shows the ME for the transition between STD1 and STD3 (third triplet in the run), the situation when the highest isotopic difference between adjacent vials occurred. The ME was greater for hydrogen than for oxygen, as observed elsewhere (Gupta et al., 2009). For OA-ICOS instruments the maximum ME ranged approximately from 6 % to 14 % for δ^2H measurements and from 4 % to 9 % for δ^{18}O measurements. For CRDS instruments, the maximum ME ranged approximately from 4 % to 6 % and from 2 % to 4 % for δ^2H and δ^{18}O, respectively. The analysis revealed that the first eight–ten injections were most affected by MEs for all instruments, whereas the final six–eight injections exhibited negligible MEs. This was confirmed by observing the average and standard deviation of MEs computed separately for the first ten and the last eight injections (Table 3a, b). The dataset in this Table was formed by the 18 injections performed during each of the three transitions in an analysis run (considered together) between STD1 and STD3. Analysis of Table 3a, b clearly confirmed, for both isotopes and for all spectroscopes, the smaller MEs for the last eight injections out of 18 compared to the first ten injections. Overall, the average and the standard deviation of MEs ranged between 0.8 % and 3.0 % and between 0.8 % and 3.9 %, respectively, when considering the first ten injections. However, average values ranged from 0.1 % to 0.3 % for both hydrogen and oxygen isotope species and standard deviation values ranged from 0.1 % to 0.6 % when the last eight injections were considered. This suggests that, even for very high differences in isotopic composition of subsequent samples, discarding the first ten injections and averaging the remaining ones prevents the final δ-value from being affected by MEs. Furthermore, Table 3a, b reveals that, on average, ME values were similar for both OA-ICOS and CRDS instruments, the only appreciable difference being the higher percentages of OA-ICOS spectroscopes for the first two or three injections (Fig. 2).

It is worth noticing that ME values were, on average, slightly lower for the most recent spectroscope models, compared to early ones. Improvement in the reduction of MEs, reflected also in lower standard deviations of ME, was particularly evident in third generation OA-ICOS instruments (LGR-3), for which discarding six injections would provide an effective solution. Conversely, LGR-2 showed the highest

Table 3a. Average and standard deviations of memory effects (hydrogen) considering the first ten and the last eight injections out of 18 for three transitions in an analysis run (considered together) between STD1 and STD3.

	First 10 out of 18 injections						Last 8 out of 18 injections					
	LGR-1	LGR-2	LGR-3	PIC-1	PIC-2	PIC-3	LGR-1	LGR-2	LGR-3	PIC-1	PIC-2	PIC-3
Number of samples	30	30	30	30	30	30	24	24	24	24	24	24
Average (%)	1.9	3.0	1.1	1.4	1.3	1.5	0.3	0.2	0.1	0.2	0.2	0.1
Std. deviation (%)	2.9	3.9	1.7	1.3	1.7	1.7	0.3	0.6	0.1	0.1	0.2	0.1

Table 3b. Average and standard deviations of memory effects (oxygen) considering the first ten and the last eight injections out of 18 for three transitions in an analysis run (considered together) between STD1 and STD3.

	First 10 out of 18 injections						Last 8 out of 18 injections					
	LGR-1	LGR-2	LGR-3	PIC-1	PIC-2	PIC-3	LGR-1	LGR-2	LGR-3	PIC-1	PIC-2	PIC-3
Number of samples	30	30	30	30	30	30	24	24	24	24	24	24
Average (%)	1.4	2.4	0.8	1.0	1.0	1.1	0.3	0.2	0.2	0.1	0.2	0.1
Std. deviation (%)	2.0	2.5	1.1	0.8	1.2	1.0	0.4	0.5	0.1	0.1	0.1	0.1

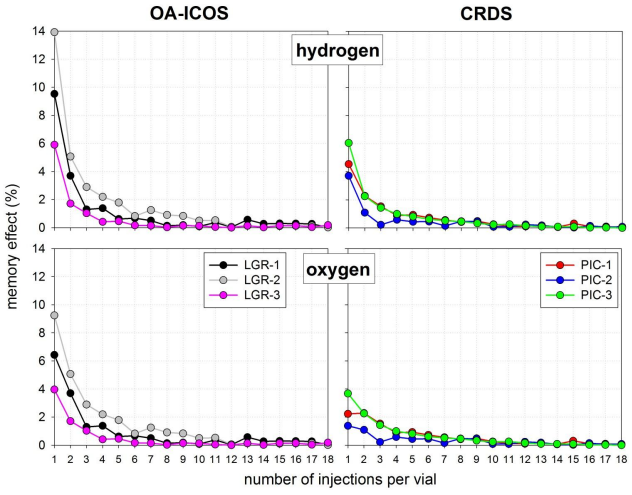

Fig. 2. MEs as a function of the number of sequential injections of the same vial for the transition between STD1 and STD3 (third triplet in an analysis run). Upper row: hydrogen. Lower row: oxygen. Left column: OA-ICOS instruments. Right column: CRDS instruments.

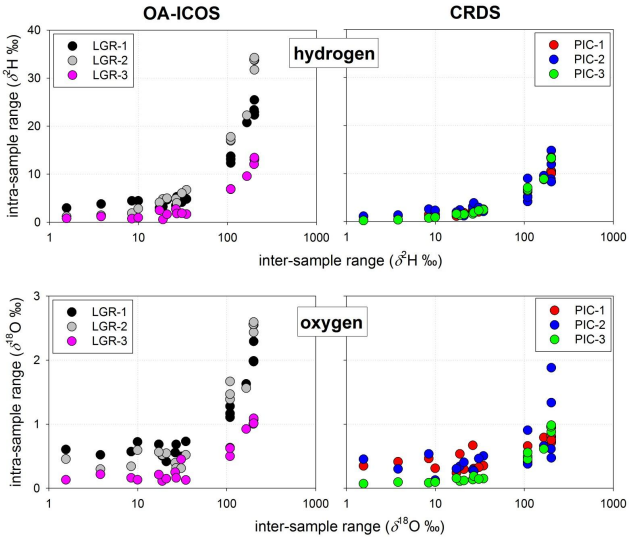

Fig. 3. Relation between the isotopic range (maximum–minimum of 18 injections) within each vial (either sample or measurement standard) and the absolute isotopic difference between adjacent vials in the tray. Upper row: hydrogen. Lower row: oxygen. Left column: OA-ICOS instruments. Right column: CRDS instruments.

percentage of ME (Fig. 2 and Table 3a, b), even higher than the first generation machine (LGR-1). This difference did not seem to be related to any specific variable, since all machines were routinely cleaned and maintained and the sampling conditions were the same for all instruments. An intrinsic variability for one specific instrument could be assumed, but further analyses are necessary to verify such behaviour.

Theoretically, the difference in MEs between OA-ICOS and CRDS devices (Fig. 2) or the different amount of ME between instruments of various generations (Table 3a, b, especially for LGR machines) might be related to the different analysis times for each injected water sample. In fact, long analysis times (including longer between-sample cavity vacuum pumping) could facilitate the removal of water molecules of the previous sample from the system. Conversely, short analysis times could allow for the persistence of residual water molecules in the vacuum chamber. However, based on our analyses, a dependency on analysis time was not found. In general, LGR-1 (first generation) took 245 s to inject and measure a sample, LGR-2 (second generation) took 140 s and LGR-3 (third generation) took only 77 s. Nevertheless, the highest values of ME were not observed for the "slowest" first generation machine, as might have been

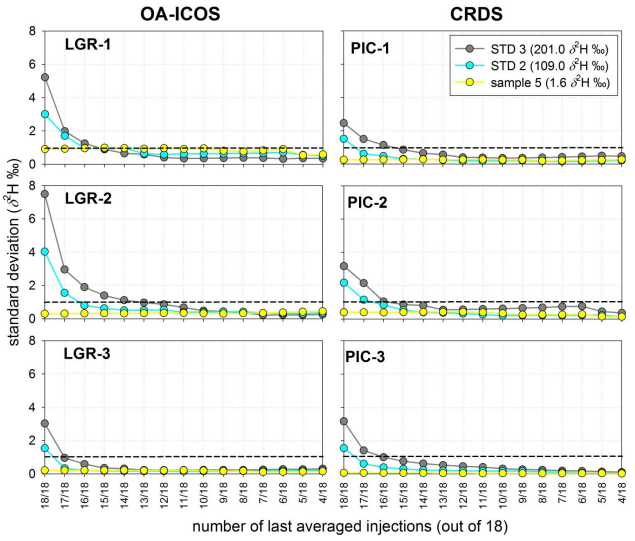

Fig. 4a. Standard deviation for δ^2H for two laboratory measurement standards and one sample as a function of number of averaged injections. 18/18 indicates that all 18 injections of the same vial (either standard or sample) were averaged, whereas 17/18, 16/18, 15/18... indicates that only the last 17, 16, 15... injections were averaged (and the remaining discarded). The dotted horizontal line indicates currently acceptable reference precision for δ^2H (1 ‰). The legend depicts the difference between the isotopic composition of the standard/sample displayed and the isotopic composition of the previous vial analysed in the tray.

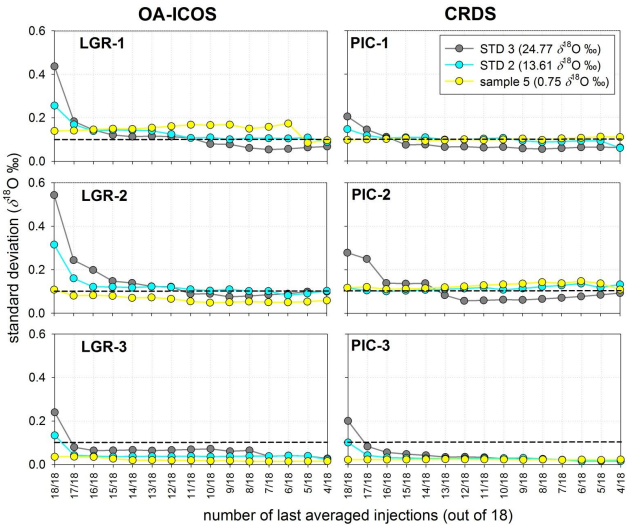

Fig. 4b. Standard deviation for δ^{18}O for two laboratory measurement standards and one sample as a function of number of averaged injections. 18/18 indicates that all 18 injections of the same vial (either standard or sample) were averaged, whereas 17/18, 16/18, 15/18... indicates that only the last 17, 16, 15... injections were averaged (and the remaining discarded). The dotted horizontal line indicates an acceptable reference precision for δ^{18}O (0.1 ‰). The legend depicts the difference between the isotopic composition of the standard/sample displayed and the isotopic composition of the previous vial analysed in the tray.

expected, and the "fastest" third generation spectroscope was not the one most affected by MEs (on the contrary, it had the lowest ME). Furthermore, CRDS lasers, that on average showed similar values of ME compared to OA-ICOS instruments, took 540 s (9 min) to perform a measurement, being more than two times, almost four times and more than six times slower than LGR-1, LGR-2 and LGR-3, respectively. Therefore, other influencing factors must explain the differences in ME between the three OA-ICOS generations and for the initial injections between the two technologies. For instance, the length of the transfer line (the longer the line, the higher are supposed the MEs), the heating of the transfer line and of the cavity (higher temperature helps the sample vaporization and likely reduces MEs), the amount of water per unit surface area of the laser cavity, the injection speed (the rate at which the water is injected into the instrument), the pump-out rate, the syringe deterioration, and the variations in vaporiser temperature might all affect the MEs. We do not have the appropriate technical insights and means to fully assess these aspects without involving the manufacturers, which is beyond the scope of this Technical Note.

Furthermore, we analysed and quantified (data are not reported here) the occurrence of MEs when changing from a very isotopically depleted to a significantly more enriched sample (e.g., from sample 10 to STD1) and vice versa (e.g., from STD1 to STD3). No significant differences in MEs were found.

The four panels of Fig. 3 show, for hydrogen and oxygen and for the six test instruments, the intra-vial range of isotopic δ-values (i.e., maximum minus minimum, when all 18 injections were considered) as a function of the inter-vial range (i.e., the isotopic difference between waters analysed during the run). The strong linear relation (x-axis is logarithmic scale to better display low values of inter-sample difference) observed for all machines revealed that the high measurement variability, obtained when averaging all injections, was related to the isotopic differences between adjacent vials which, in turn, was related to high percentages of ME. The correlation between intra-vial and inter-vial isotopic range declined noticeably when discarding the first four injections (from 18 to 15) and averaging only the last 14, ten or six injections, as indicated by the decreasing values of the determination coefficient (not reported here). The dependency of the 18 injection-averaged intra-vial variability on the inter-vial isotopic differences was more pronounced for the first and second generation OA-ICOS instruments compared to first generation CRDS instruments. However, the performance of the latest generation instruments of both manufacturers (LGR-3 and PIC-3) was almost identical.

3.2 Practical implications on measurement precision

Accepting all injections for a given analysis run, even the ones most affected by MEs, had some practical negative consequence on the measurement precision when evaluating the final reportable δ-values. Figure 4a, b shows the values of standard deviation for two measurement standards and one sample obtained by averaging a different number of injections (starting from all 18 injections down to four). The standard deviation of the two measurement standards (STD2 and STD3 of the first triplet), characterised by a high isotopic difference with respect to the previous vial in the tray, were compared with that of sample 5, featuring the lowest isotopic difference with respect to the previous vial in the whole run. For all instruments, the values of standard deviation for the two standards were markedly high (up to 7.5 ‰ for δ^2H and 0.54 ‰ for δ^{18}O) when all 18 injections were accepted and averaged, whereas the standard deviations decreased (i.e., measurement precision increased) with decreasing the number of averaged injections. However, when rejecting the first six or eight injections the measurements were stable. The highest standard deviations during the first injections were reached by STD3 (the one with the greatest isotopic difference compared to the previous vial, 201.0 ‰ for δ^2H and 24.77 ‰ for δ^{18}O) followed by STD2 (109.0 ‰ difference for δ^2H and 13.61 ‰ for δ^{18}O). Conversely, sample 5, characterised by a small isotopic difference with respect to the previous vial (1.6 ‰ for δ^2H and 0.75 ‰ for δ^{18}O) generally displayed stable values of standard deviations (in the range 0.1 ‰–1.0 ‰ for δ^2H and 0.05 ‰–0.17 ‰ for δ^{18}O) that indicated the instrumental precision. As mentioned in Sect. 3.1, standard deviations of the first injections were higher for LGR-1 and LGR-2 compared to PIC-1 and PIC-2, but a very similar precision was achieved by the latest instruments from both manufacturers, revealing the rapid evolution and improvement of laser spectroscopy technology.

4 Conclusions and outlook

In this work, we determined the isotopic composition (δ^2H and δ^{18}O) of ten isotopically depleted water samples, characterised by a wide range of δ-values, using three OA-ICOS and CRDS instruments. We assessed the practical implications on the instrumental performance deriving from the inclusion of injections affected by memory effects (MEs). In summary, we found

1. Measurement stabilisation was reached following seven–eight injections when water samples characterised by a high inter-vial isotopic difference were measured. This behaviour, evident for both isotopes and all instruments, was attributed to the ME that directly influenced the measurement variability.

2. Overall, the maximum MEs ranged from 4 % to 14 % for δ^2H and from 2 % to 9 % for δ^{18}O measurements. The first ten injections out of the 18 were most affected by MEs, with average MEs ranging between 1.1 % and 3.0 % for hydrogen and between 0.8 % and 2.4 % for oxygen. However, when discarding the first ten injections and considering only the last eight, MEs were negligible for all instruments (average MEs ranged between 0.1 % and 0.3 % for both hydrogen and oxygen). On average, ME values were similar for both OA-ICOS and CRDS instruments, with a significant improvement in the reduction of ME for the most recent generation of spectroscopes (especially OA-ICOS).

3. A strong correlation between the intra-vial range of isotopic values and inter-vial range was found for both technologies when considering all injections, indicating the dependency of the measurement variability on the size of the isotopic difference between adjacent vials. The correlation disappeared when the injections affected by MEs were discarded.

4. Standard deviations for the final reportable δ-values were unsatisfactorily high (up to 7.5 ‰ for δ^2H and 0.54 ‰ for δ^{18}O measurements for extreme cases) when all measurement injections were used, including those affected by MEs. However, for samples characterised by only small isotopic differences with respect to the previous vial in the tray or when rejecting the first six or eight injections, a marked precision increase was noted, with standard deviations in the range of 0.1 ‰–1.0 ‰ for δ^2H and 0.05 ‰–0.17 ‰ for δ^{18}O.

In this test we assessed the MEs of different laser spectroscopy instruments under standard operating conditions. Specifically, we quantified the MEs and assessed the impact of MEs on measurement precision. Given the practical perspective of this Technical Note and our experience as users of laser spectroscopes for hydrological and environmental applications, we can outline some operational solutions (a–c in the list below) or post-processing data analysis (d–e) that might be adopted by other users of laser spectroscopy in order to avoid the occurrence of MEs or to reduce their influence on the final reportable δ-values. Most of these suggestions consist of practical and basic laboratory procedures and, as such, they do not claim to eliminate the problems derived by the influence of ME. However, given a simple application, these approaches can be easily followed by users of laser spectroscopy.

a. Samples for laser spectroscopy analysis should be ordered or grouped in order of isotopic compositions, as this can often be estimated ahead of time, with the aim to analyse samples with similar isotopic ratios in the same analysis run. Furthermore, if possible, laboratory measurement standards should closely bracket

the expected range of sample isotopic composition. Additionally, ordering samples according to expected increasing or decreasing isotopic ratios might help to avoid high differences between adjacent unknown sample vials.

b. If samples are truly unknown, group them according to the same water source, sampling location and region of origin. However, keep in mind that, even at the small spatial scale, different water sources (e.g., liquid precipitation, solid precipitation, surface waters, groundwater, soil water etc.) might have significantly different isotopic ratios. Moreover, some physical processes such as seasonal effects and altitudinal effects might result in markedly different isotopic compositions of the same water sources.

c. If a broad range of isotopic composition of unknown samples is suspected, a preliminary run with a wide range of reference standards (very depleted and very enriched) could be carried out. This would allow to analyse samples exhibiting very high differences in isotopic ratios separately. The disadvantage of this approach is additional screening time and analysis cost.

d. It is often advisable to adopt an analysis scheme (e.g. the one suggested in IAEA, 2009b or similar) so that six or more injections are performed and the first two or more are discarded. However, as demonstrated and reported elsewhere (Gröning, 2011), there are cases when rejecting two or three injections might be insufficient to eliminate ME. Thus, as a quick and preliminary assessment of possible occurrence of ME, check for increasing or decreasing variations (according to the value of the previous sample) in δ-values of subsequent samples that exceed the typical instrumental precision by two or more times. If necessary, run a few samples and apply the procedure presented here in order to decide a proper number of injections to perform and a threshold number of injections to reject.

e. If it is not possible to employ the solutions listed above, post-analysis memory correction calculations, as the ones reported in Gupta et al. (2009) and Gröning (2011), can be applied.

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References

Brand W. A., Geilmann, H., Crosson, E. R., and Rella, C. W.: Cavity ring-down spectroscopy versus high-temperature conversion isotope ratio mass spectrometry; a case study on δ^2H and δ^{18}O of pure water samples and alcohol/water mixtures, Rapid Commun. Mass Sp., 23, 1879–1884, doi:10.1002/rcm.4083, 2009.

Chesson, L. A., Bowen, G. J., and Ehleringer, J. R.: Analysis of the hydrogen and oxygen stable isotopes ratios of beverage waters without prior water extraction using isotope ratio infrared spectroscopy, Rapid Commun. Mass Sp., 24, 3205–3213, 2010.

Epstein, S. and Mayeda, T. K.: Variations of δ^{18}O of waters from natural sources, Geochim. Cosmochim. Ac., 4, 213–224, 1953.

Gkinis, V., Popp, J. T., Johnsen, S. J., and Blunier, T.: A continuous stream flash evaporator for the calibration of an IR cavity ring-down spectrometer for the isotopic analysis of water, Isot. Environ. Healt. S., 46, 463–475, 2010.

Gonfiantini, R.: Standards for stable isotope measurements in natural compounds, Nature, 271, 534–536, 1978.

Gröning, M.: Improved water δ^2H and δ^{18}O calibration and calculation of measurement uncertainty using a simple software tool, Rapid Commun. Mass Sp., 25, 2711–2720, doi:10.1002/rcm.5074, 2011.

Gupta, P., Noone, D., Galewsky, J., Sweeney, C., and Vaughn, B. H.: Demonstration of high-precision continuous measurements of water vapor isotopologues in laboratory and remote field deployments using wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) technology, Rapid Commun. Mass Sp., 23, 2534–2542, 2009.

Horita, J., Ueda, A., Mizukami, K., and Takatori, I.: Automatic δD and δ^{18}O analyses of multi-water samples using H_2- and CO_2-water equilibration methods with a common equilibration set-up, Appl. Radiat. Isotopes, 40, 801–805, 1989.

IAEA: Reference Sheet for VSMOW2 and SLAP2 international measurement standards, issued 13 February 2009, International Atomic Energy Agency, Vienna, 5 pp., http://nucleus.iaea.org/rpst/Documents/VSMOW2_SLAP2.pdf, 2009a.

IAEA: Laser Spectroscopy Analysis of Liquid Water Samples for Stable Hydrogen and Oxygen Isotopes, Performance Testing and Procedures for Installing and Operating the LGR DT-100 Liquid Water Isotope Analyzer. International Atomic Energy Agency, Vienna, 2009, ISSN 1018-5518, 2009b.

Lis, G., Wassenaar, L. I., and Hendry, M. J.: High precision laser spectroscopy D/H and ^{18}O/^{16}O measurements of microliter natural water samples, Anal. Chem., 80, 287–293, 2008.

Los Gatos Research, Inc.: Liquid-Water Isotope Analyser, Automated Injection, 2008.

Olsen, J., Seierstad, I., Vinther, B., Johnsen, S., and Heinemeier, J.: Memory effect in deuterium analysis by continuous flow isotope ratio measurement, Int. J. Mass Spectrom., 254, 44–52, 2006.

Penna, D., Stenni, B., Šanda, M., Wrede, S., Bogaard, T. A., Gobbi, A., Borga, M., Fischer, B. M. C., Bonazza, M., and Chárová, Z.: On the reproducibility and repeatability of laser absorption spectroscopy measurements for δ^2H and δ^{18}O isotopic analysis, Hydrol. Earth Syst. Sci., 14, 1551–1566, doi:10.5194/hess-14-1551-2010, 2010.

Picarro, Inc.: Picarro L1102- i Isotopic Water Liquid Analyzer, 2008.

Sayres, D. S., Moyer, E. J., Hanisco, T. F., St. Clair, J. M., Keutsch, F. N., O'Brien, A., Allen, N. T., Lapson, L., Demusz, J. N., Rivero, M., Martin, T., Greenberg, M., Tuozzolo, C., Engel, G. S., Kroll, J. H., Paul, J. B., and Anderson, J. G.: A new cavity based absorption instrument for detection of water isotopologues in the upper troposphere and lower stratosphere, Rev. Sci. Instrum., 80, 044102, doi:10.1063/1.3117349, 2009.

Schultz, N. M., Griffis, T. J., Lee, X., and Baker, J. M.: Identification and correction of spectral contamination in ^{2}H/^{1}H and ^{18}O/^{16}O measured in leaf, stem and soil water, Rapid Commun. Mass Sp., 25, 3360–3368, 2011.

Wang, L., Caylor, K. K., and Dragoni, D.: On the calibration of continuous, high-precision δ^{18}O and δ^2H measurements using an off-axis integrated cavity output spectrometer, Rapid Commun. Mass Sp., 23, 530–536, 2009.

Wassenaar, L. I., Hendry, M. J., Chosten, V. L., and Lis, G. P.: High resolution pore water δ^2H and δ^{18}O measurements by $H_2O_{(liquid)}$-$H_2O_{(vapor)}$ equilibration laser spectroscopy, Environ. Sci. Technol., 42, 9262–9267, 2008.

West, A. G., Goldsmith, G. R., Brooks, P. D., and Dawson, T. E.: Discrepancies between isotope ratio infrared spectroscopy and isotope ratio mass spectrometry for the stable isotope analysis of plant and soil waters, Rapid Commun. Mass Sp., 24, 1948–1954, 2010.