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

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Abstract

This study focuses on the assessment of the practical implications of memory effects on the isotopic measurements of δ^2H and δ^{18}O in water samples analysed by means of laser spectroscopy. A set of ten depleted stable isotope samples featuring a broad range of isotopic compositions was measured by two Off-Axis Integrated Cavity Output Spectroscopy and two Cavity Ring-Down Spectroscopy instruments. The analysis scheme was set up to encompass both small (less than 2 ‰ for δ^2H and 1 ‰ for δ^{18}O) and large differences (up to 201 ‰ for δ^2H and 25 ‰ for δ^{18}O) in isotopic compositions between adjacent vials. All samples were injected 18 times for each analysis and the memory effect was computed for the entire run. Results showed that samples most affected by high inter-vial isotopic difference exhibited a tendency to stabilize after the first 7 or 8 injections, most likely as a result of memory effects during the run. These memory effects were quantified amounting to 14 % and 9 % of δ^2H and δ^{18}O measurements, respectively, with a decline to negligible values when first injections were discarded. The lowest percentages of memory effects were found for those instruments employing a long analysis time per injection, which most likely facilitated the removal of residual water molecules from the cavity. The measurement variability (range and standard deviation) for each sample was found to be strongly dependent on the isotopic differences between adjacent vials. A significant increase in measurement precision was obtained when injections most affected by memory effects were discarded from the computation of the reportable delta value. In conclusion, this study provides practical solutions to avoid or reduce the consequences of memory effects.

1 Introduction

Nowadays, the use of laser absorption spectroscopy for the determination of water stable isotopes (δ^2H and δ^{18}O, VSMOW-SLAP scale) in liquid samples is becoming increasingly common in several laboratories worldwide. The availability of the first

Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) instruments, approximately ten years ago, and more recently of Cavity Ring-Down Spectroscopy (CRDS) devices, has allowed many researchers to take full advantage of water stable isotopes as tracers in hydrological applications. Lately, a few studies have 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 liquid samples, revealing, in general, a very good comparability with classical mass spectrometric techniques. However, given the relative novelty of laser spectroscopy in hydrological laboratories and despite the available literature, some practical potential of laser machines in the field of water research is still unexplored and shortcomings about their operational limitations remain. Particularly, our group recently conducted a comparative study of four OA-ICOS spectroscopes tested against a mass spectrometer in order to evaluate the reproducibility and repeatability of laser-based measurements (Penna et al., 2010). One of the issues mentioned in the paper was the poor accuracy of laser spectroscopy results for very depleted water samples. Such poor accuracy had been possibly related to memory effects (ME), defined as the contamination of the sample being measured by reminiscences of the previous sample(s) (Olsen et al., 2006). In this Technical Note, we aim to assess the practical implications of the analysis of water samples characterized by a wide range of isotopic values and different conditions (under which the occurrence of ME might significantly influence the final isotopic measurement) on the performance of different laser spectroscopes. For this "stress experiment" we tested two OA-ICOS and two CRDS instruments on a set of ten isotopically depleted water samples.

2 Materials and methods

2.1 Laser spectroscopes and mass spectrometer

The water samples were analyzed by four laser spectroscopes (two OA-ICOS: Delft University of Technology, The Netherlands and Czech Technical University in Prague, Czech Republic; two CRDS instruments: University of Trieste, Italy and University of Zürich, Switzerland) and one mass spectrometer (University of Trieste), used as reference. The equipment included:

1. OA-ICOS: one Liquid Water Isotope Analyser, model DLT-100 version 908-0008 and one version 908-0008-2000, manufactured by Los Gatos Research Inc. (LGR, Mountain View, California, USA). These two instruments are referred to as "LGR-1" and "LGR-2", respectively. 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, manufactured by Picarro (Picarro, Mountain View, California, USA), named "PIC-1" and "PIC-2". 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 using the CO_2/H_2 water equilibration technique (Epstein and Mayeda, 1953; Horita et al., 1989). The 1-σ precision of the instrument was ±0.7 ‰ and ±0.05 ‰ for δ^2H and δ^{18}O measurements, respectively.

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 a dataset of 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 proper reference standards that bracketed the isotopic composition of the samples were used. These standards were calibrated against IAEA (International Atomic Energy Agency) water standards (Gonfiantini, 1978) in relation to the VSMOW-SLAP scale and normalized adopting the procedure described in IAEA (2009a). All samples and standards were injected into ND8 32 × 11.6 mm screw neck 1.5 ml vials with PTFE/silicone/PTFE septa, filled with 1 ml of water. Operations of vial filling were executed in the same laboratory to ensure consistency throughout the comparison. 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 calibration 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 scheme, sampling each vial 18 times instead of 6 times in order to monitor the trend of resulting ME. The waters were grouped in two sets of five samples interposed by three triplets of reference standards. Each run started with a dummy sample to prime the transfer line and stabilize the machine and ended with deionized water to clean the syringe (IAEA, 2009b).

Since the isotopic composition range of the selected samples and reference standards was very broad, we tried to minimize the differences between the isotopic content of subsequent vials, designing the analysis sequence presented in Table 2. Still, marked differences remained during the analysis. This allowed us to test the machine

performances 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 heaviest and lightest water was approximately 201 ‰ for δ^2H and 25 ‰ for δ^{18}O, see Table 2).

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

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

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. Instead of simply using the value of the last injection as the true value (as in Gröning, 2011), the average 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:

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

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 a preliminary 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 stabilization and memory effect

The graphs in Fig. 1 display δ^2H and δ^{18}O values of the second triplet of reference standards for each instrument, as a function of the 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 delta values obtained during the central and final part of the run. On average, at least 7 or 8 injections were necessary in order to stabilize the measurement (i.e. to observe variations between successive injections within the range of the instrumental precision). Conversely, the first standard (STD1) exhibited a more stable behaviour over time. STD2 and STD3 represented the waters most affected by high inter-vial isotopic difference whereas STD1, in the second triplet, was characterized 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 here), featuring much smaller isotopic difference compared to the previous vial, but almost no variations after the first 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 visible for all lasers and both isotopes, even though the trend for δ^{18}O was generally more variable than for δ^2H.

Figure 2 presents the ME for the transition between STD1 and STD3 (third triplet in the run), the situation when the highest difference between the isotopic composition

of adjacent vials occurred. The ME was greater for hydrogen than for oxygen, as also observed elsewhere (Gupta et al., 2009). For OA-ICOS instruments the maximum ME ranged approximately from 10 % to 14 % δ^2H and from 6 % to 9 % for δ^{18}O measurements. For CRDS instruments the maximum ME was smaller, approximately around 4 % and 2 % for δ^2H and δ^{18}O measurements, respectively. However, a direct comparison between the two types of laser analysers was not possible since the analysis time for each injection was different. While the LGR-1 machine needed 4.2 min to inject and measure a sample, the LGR-2 machine (upgraded model) took only 2.3 min. In contrast, both CRDS lasers took approximately 9 min for each injection. This time difference is most likely related to the different proportion of the observed ME: the highest percentage of ME was observed for the "faster" machines (LGR-2 and LGR-1) whereas PIC-1 and PIC-2, the "slower" machines, were generally characterized by the smallest values of the ME. This could be due to the easier removal of water molecules of the previous sample from the system for relatively long analysis times (including cavity flushing) and, on the contrary, to a persistence of residual water molecules in the system when the analysis times were reduced. In all cases, the influence of ME tended to become negligible (i.e. close to 0 %) after the first 8 or 10 injections for δ^2H measurements and after 4 or 6 injections for δ^{18}O measurements (less prone to be influenced by ME but more variable in time).

The two panels of Fig. 3 show, for hydrogen and oxygen and for the four test instruments, the intra-vial range of isotopic delta 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 consequently analysed during the run). The strong linear relation (x-axis is in 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 marked isotopic differences between adjacent vials which, in turn, was associated 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, 10 or

6 injections, as demonstrated by the decreasing values of the determination coefficient (Table 3a, b). On average, the dependency of the 18 injection-averaged intra-vial variability on the inter-vial isotopic differences was less marked for CRDS instruments, as also evident in Fig. 2.

3.2 Practical implications on measurement precision

Accepting all injections of a given analysis run, even the ones most affected by ME, had some practical effect on the measurement precision when evaluating the final delta reportable values. Figure 4 shows the values of standard deviation for two standards and one sample obtained by averaging a different number of injections (starting from all 18 injections down to 4). The standard deviation of the two standards (STD2 and STD3 of the first triplet), characterized 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. the measurement precision increased) with decreasing the number of averaged injections. However, when rejecting approximately the first 4 or 6 injections the measurements became 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, characterized 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. Finally, the range of standard deviation values was generally lower for CRDS instruments than for OA-ICOS instruments, reflecting the variability of ME percentages.

4 Conclusions and outlook

In this work, we determined the isotopic composition (δ^2H and δ^{18}O) of ten depleted water samples, characterized by a wide range of delta values, by means of two Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) and two Cavity Ring-Down Spectroscopy (CRDS) instruments. We aimed to assess the practical implications on the instrumental performance deriving from the inclusion of injections affected by memory effects (ME). In summary, we found that:

1. A clear tendency to measurement stabilization after the first 7 or 8 injections was observed during the analysis run when the waters characterized by a high inter-vial isotopic difference were analysed. We related this behaviour, evident for both isotopes and all machines, to the ME that influenced the measurement variability during the run.

2. Overall, the ME ranged from 4 % to 14 % for δ^2H and from 1 % to 9 % for δ^{18}O measurements. On average, CRDS devices showed lower percentages of ME compared to OA-ICOS instruments, most likely due to the longer analysis time (including cavity flushing) per injection, which facilitated the removal of the residual water molecules from the system.

3. A strong linear relation between the intra-vial range of isotopic values and inter-vial range was found for all devices when considering all injections, indicating a dependency of the measurement variability on the marked isotopic difference between adjacent vials. The relation strongly declined when the first injections (the ones most affected by ME) were discarded.

4. Standard deviations were unsatisfactorily high when the injections affected by ME were averaged for the final reportable value whereas a precision increase was clearly noted when the first injections were discarded.

In this comparative test, we assessed the influence of ME on laser spectroscopy measurements without investigating physical mechanisms such as the role of syringe deterioration, variations in vaporizer temperature, injection volumes and length of the transfer line tube. Instead, we adopted practical and basic laboratory procedures. In this context, we can outline some operational solutions to avoid, reduce or mitigate the consequences of ME. The unknown stable isotope samples to be determined by laser spectroscopes should be grouped properly, trying to analyse in the same run waters with similar or not too different isotopic compositions (maybe by distinguishing them on the basis of their origin and sampling location). In addition, ordering samples in expected increasing or decreasing isotopic ratios might also avoid high differences between adjacent vials. If necessary, a preliminary run with a wide range of reference standards (very depleted and very enriched) could be carried out. Alternatively, in case of evidence of ME, post-analysis correction calculations should be applied (Gupta et al., 2009; Gröning, 2011).

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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 ^{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 $\delta^{18}O$ 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 $\delta^{18}O$ 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 2009-02-13, International Atomic Energy Agency, Vienna, 5 p., available at: http://nucleus.iaea.org/rpst/Documents/VSMOW2_SLAP2.pdf (last access: 25 November 2011), 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 $\delta^{18}O$ 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 $^2H/^1H$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ 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.

Table 1. Isotopic compositions of samples and reference standards used in this study. 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

Table 2. Sequence of samples and standards in the analysis run and absolute isotopic differences (IRMS values) between each vial and the previous one. DW: deionized water. STD: 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 3	STD 2	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

Table 3a. Determination coefficient (R^2) for hydrogen for the relation between the isotopic range (maximum-minimum) within each vial (either sample or standard) and the absolute isotopic difference between each vial and the previous one, when considering all 18 injections or the last 14, 10 or 6.

	18 injs.	14 injs.	10 injs.	6 injs.
LGR-1	.98	.03	.11	.39
LGR-2	.99	.62	.11	.03
PIC-1	.99	.59	.10	.00
PIC-2	.85	.30	.05	.00

Table 3b. Determination coefficient (R^2) for oxygen for the relation between the isotopic range (maximum-minimum) within each vial (either sample or standard) and the absolute isotopic difference between each vial and the previous one, when considering all 18 injections or the last 14, 10 or 6.

	18 injs.	14 injs.	10 injs.	6 injs.
LGR-1	.96	.00	.02	.18
LGR-2	.95	.13	.10	.01
PIC-1	.71	.09	.01	.06
PIC-2	.46	.11	.10	.01

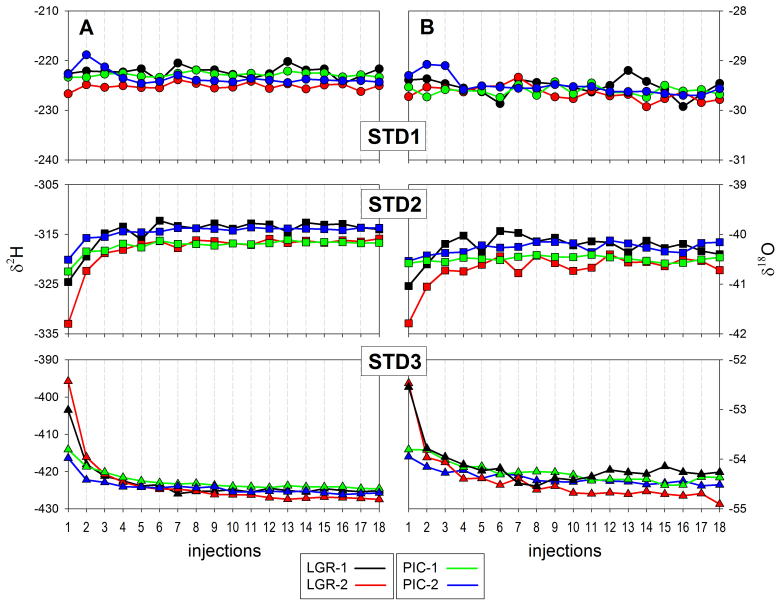

Fig. 1. Measurement stabilization over time for the three standards (second triplet in the run). Column **(A)**: hydrogen. Column **(B)**: oxygen.

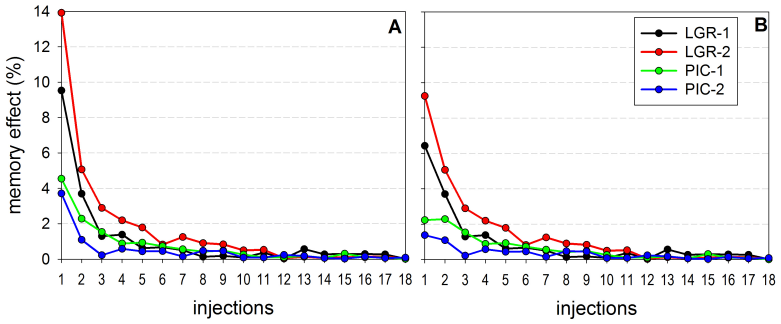

Fig. 2. ME as a function of the number of injections for the transition between STD1 and STD3 (third triplet in the run). **(A)**: hydrogen. **(B)**: oxygen.

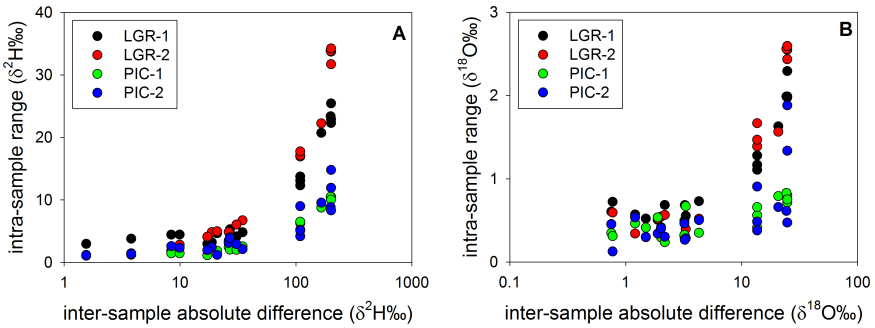

Fig. 3. Relation between the isotopic range (maximum-minimum) within each vial (either sample or standard) and the absolute isotopic difference between adjacent vials in the tray. **(A)**: hydrogen. **(B)**: oxygen.

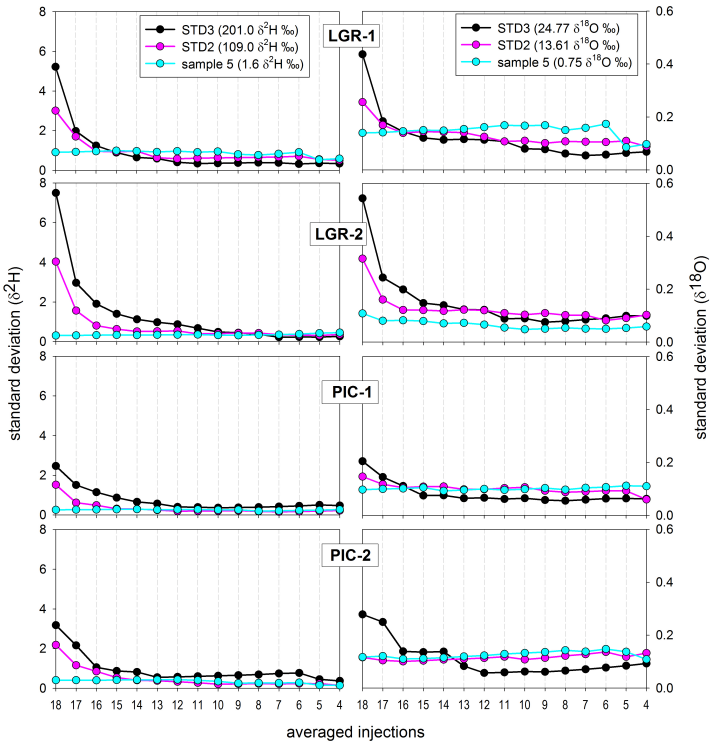

Fig. 4. Standard deviation values for two samples and one standard as a function of different numbers of averaged injections. In brackets in the legend: difference between the isotopic composition of the standard/sample displayed and the isotopic composition of the previous vial analysed in the tray.