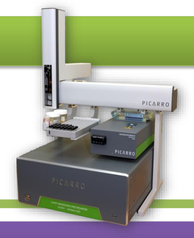
TRIPLE ISOTOPE ANALYSES OF WATER (δ^2H, $\delta^{18}O$, $\delta^{17}O$) WITH THE AID OF LASER SPECTROSCOPY:

Analytical performance of Picarro L2140-*i* spectrometer

A. PIERCHALA, K. ROZANSKI, M. DULINSKI, Z. GORCZYCA, M. MARZEC, R. CZUB

AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, al. Mickiewicza 30, 30-059 Krakow, Poland | pierchala@fis.agh.edu.pl

INTRODUCTION



Thorough evaluation of measurement uncertainty, together with the control of short- and long-term precision of the analyses should be the basis of any successful Quality Assurance/Quality Control (QA/QC) strategy aimed at maintaining high quality of the analytical process. A comprehensive assessment of the analytical performance of Picarro L2140-*i* CRDS laser spectrometer in routine analyses of δ^2H, $\delta^{18}O$ and $\delta^{17}O$ in water samples of various nature is presented here. The assessment is based on the data obtained during 27 months of continuous operation of this instrument. Impact of various factors affecting the measurement uncertainty was carefully examined and combined uncertainties of single analysis for the expected range of δ values were evaluated. Both short- and long-term precision was evaluated and compared with the precision guaranteed by the manufacturer of the instrument.

METHOD

Samples are typically analysed in batches. Each batch, apart from unknown samples being analysed, contains several QA/QC samples used to correct measurement results for various instrumental effects (memory effects, drift), to calibrate them, and to assess repeatability and reproducibility of the analyses (Table 2).

Various measurement protocols addressing QA/QC issues related to isotope analyses of water using laser spectrometers were proposed in the literature. In our study, we used measurement protocol proposed by van Geldern and Barth [1], supplemented by a segment related to $\delta^{17}O$ analysis.

TABLE 1. ISOTOPE VALUES OF STANDARDS USED

	δ^2H [‰]	$\delta^{18}O$ [‰]	$\delta^{17}O$* [‰]
USGS47	-150.2 ±0.5	-19.8 ±0.02	-10.47 ±0.02
USGS48	-2.0 ±0.4	-2.224 ±0.012	-1.15 ±0.01
DI	-66.07 ±0.02	-9.37 ±0.01	-4.93 ±0.01
KWK3	-77.30 ±0.10	-11.17 ±0.03	-5.89 ±0.02

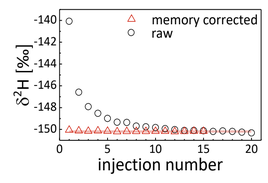
**Published in [3].*

TABLE 2. STRUCTURE OF TYPICAL MEASUREMENT RUN

Vial	Type of the sample	Function	No. of injections
1	Deionised water (DI)	Stabilisation of instrument parameters Drift correction Memory correction	15
2	High water standard (USGS48)	Calibration Memory correction	15
3	Low water standard (USGS47)	Calibration Memory correction	15
4	Deionised water (DI)	Memory correction Drift correction	15
5	Laboratory water standard KWK3 (control)	Control of long-term precision	4
6-10	Unknown samples	Measurement	4
11	Deionised water (DI)	Drift correction	4
12-18	Unknown samples	Measurement	4
19	Deionised water (DI)	Drift correction	4
20-25	Unknown samples	Measurement	4
26	Deionised water (DI)	Drift correction	4

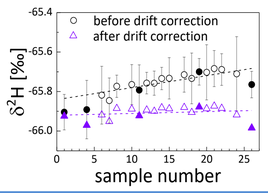
MEMORY CORRECTION

The major drawback of isotope analyses of water using laser spectrometers is a strong memory effect between consecutive samples being analysed. To reduce the memory effect a correction algorithm was applied [1]. This approach determines the memory correction coefficients on the basis of measurements of samples 1-4 with large number of injections (cf. Table 2).



DRIFT CORRECTION

The in-the-run drift is quantified using five samples of DI water distributed uniformly within the measured sequence of samples (vials 1,4,11,19,26; Table 2). When DI values scatter randomly, no drift correction is possible using this method. In such cases, the observed scatter of DI values can be used as a measure of the standard uncertainty of δ values measured in this run.



TWO-POINT CALIBRATION

$$c = \alpha \cdot m + \beta \quad (1)$$

$$\alpha = \frac{H - L}{h - l} \qquad \beta = L - \alpha \cdot l$$

c – calibrated δ value of the analysed sample;
m – measured δ value of the analysed sample (mean of 4 injections)
H, L – assigned δ value for 'high' ('low') calibration standard
h, l – measured δ value of 'high' ('low') standard (mean of 15 injections)

RESULTS

MEASUREMENT UNCERTAINTY

The combined uncertainty of calibrated measurement results (see Eq. 1) can be assessed using the uncertainty propagation law:

$$u(c) = \sqrt{\left(\frac{\partial c}{\partial m}u(m)\right)^2 + \left(\frac{\partial c}{\partial H}u(H)\right)^2 + \left(\frac{\partial c}{\partial L}u(L)\right)^2 + \left(\frac{\partial c}{\partial h}u(h)\right)^2 + \left(\frac{\partial c}{\partial l}u(l)\right)^2} \quad (2)$$

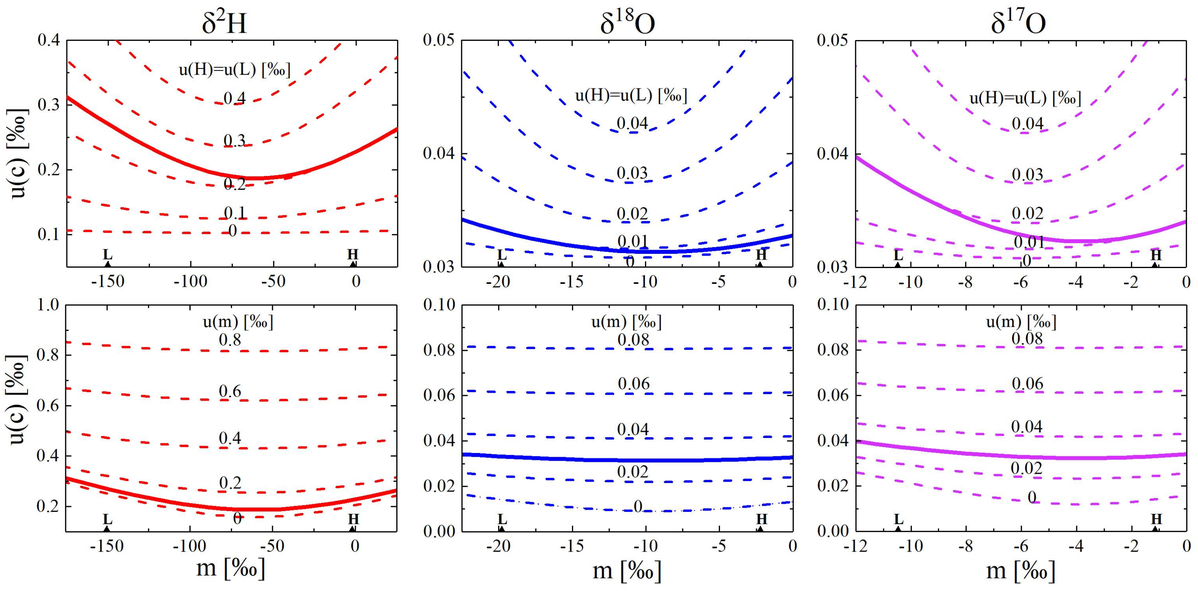
u(m) **– standard uncertainty of the mean of consecutive analyses (4 injections) of a sample, corrected for memory effects and instrumental drift, multiplied by an appropriate correction factor derived from Student t-distribution and accounting for the low number of repeated injections,**
u(h),u(l) **– standard uncertainties of the mean values of consecutive analyses (15 injections) of the calibration standards, corrected for memory effects and instrumental drift,**
u(H),u(L) **– uncertainties assigned to the calibration standards in use.**

TABLE 3. TYPICAL UNCERTAINTIES OF MEASUREMENT VARIABLES

	δ^2H (‰)	$\delta^{18}O$ (‰)	$\delta^{17}O$ (‰)
u(m)	0.1	0.03	0.03
u(h)	0.03	0.01	0.01
u(l)	0.03	0.01	0.01
u(H)	0.2	0.006	0.01
u(L)	0.25	0.01	0.02
m	(-150.20…-76.10…-2.00)	(-19.80…-11.01…-2.22)	(-10.47…-5.81…-1.15)
u(c)	(0.27 … 0.19 … 0.23)	(0.033…0.031…0.033)	(0.037…0.032…0.033)

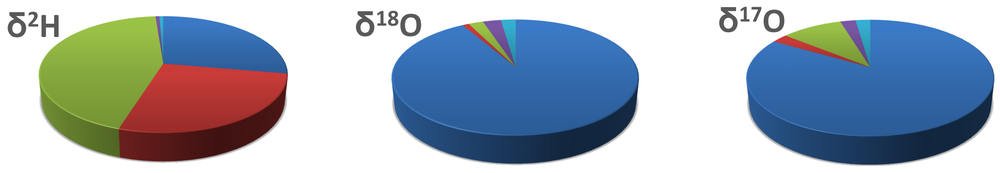
In the midpoint of the range defined by δ values of 'high' and 'low' standard, where most of the samples analysed in our laboratory are located, partial derivatives related to the standards are two times lower compared to the one representing the measured δ value of the analysed sample and they increase while moving away from the midpoint. Consequently, when the δ value of the analysed sample is moving away from the midpoint, the combined uncertainty increases, as it is more affected by the uncertainty of one of the calibration standards in use.

CONTRIBUTION OF *u(H), u(L) & u(m)* TO *u(c)*



The sample measurement uncertainty (*u(m)*) for $\delta^{18}O$ and $\delta^{17}O$ analyses is significantly higher than other uncertainty components (cf. Table 3.). Consequently, it dominates the uncertainty budget. It does not change much when the measured δ value approaches the assigned δ values of the calibration standards in use. Hence, the *u(m)* is in this case a good approximation of the combined uncertainty of single measurement result *u(c)*. On the contrary, for δ^2H analyses *u(c)* is dominated by assigned uncertainties of the calibration standards.

UNCERTAINTY BUDGET



$$\left(\frac{\partial c}{\partial m}u(m)\right)^2 \quad \left(\frac{\partial c}{\partial H}u(H)\right)^2 \quad \left(\frac{\partial c}{\partial L}u(L)\right)^2 \quad \left(\frac{\partial c}{\partial h}u(h)\right)^2 \quad \left(\frac{\partial c}{\partial l}u(l)\right)^2$$

SHORT- & LONG-TERM PRECISION

Figures below summarise 252 repeated analyses of KWK3 control standard over the period of 27 months (from February 2017 to April 2019). The linear fit of the data revealed that slopes of best fit lines are indistinguishable from zero, thus indicating absence of significant, long-term drift. Statistical distributions of all measured and derived parameters of KWK control standard were approximated by a normal distribution. Standard uncertainties obtained from those distributions can be viewed as good approximation of long-term precision of the analytical system in use. Closer examination of time series presented below revealed that the period February 2019 – April 2019 can be split into two distinct periods. The first one comprises initial 11 months of instrument operation when, apart from measurements of freshwater samples, there were also numerous analyses of highly mineralised samples done. Although salt liner was used to avoid contamination of inner surfaces of the vaporizer, experiments with brines affected the precision of the instrument. After a thorough cleaning of the vaporizer unit, the long-term precision improved significantly.

TIME SERIES OF CONTROL STANDARD KWK

DISTRIBUTION OF THE RESULTS

BEFORE VAP. CLEANING **AFTER VAP. CLEANING**

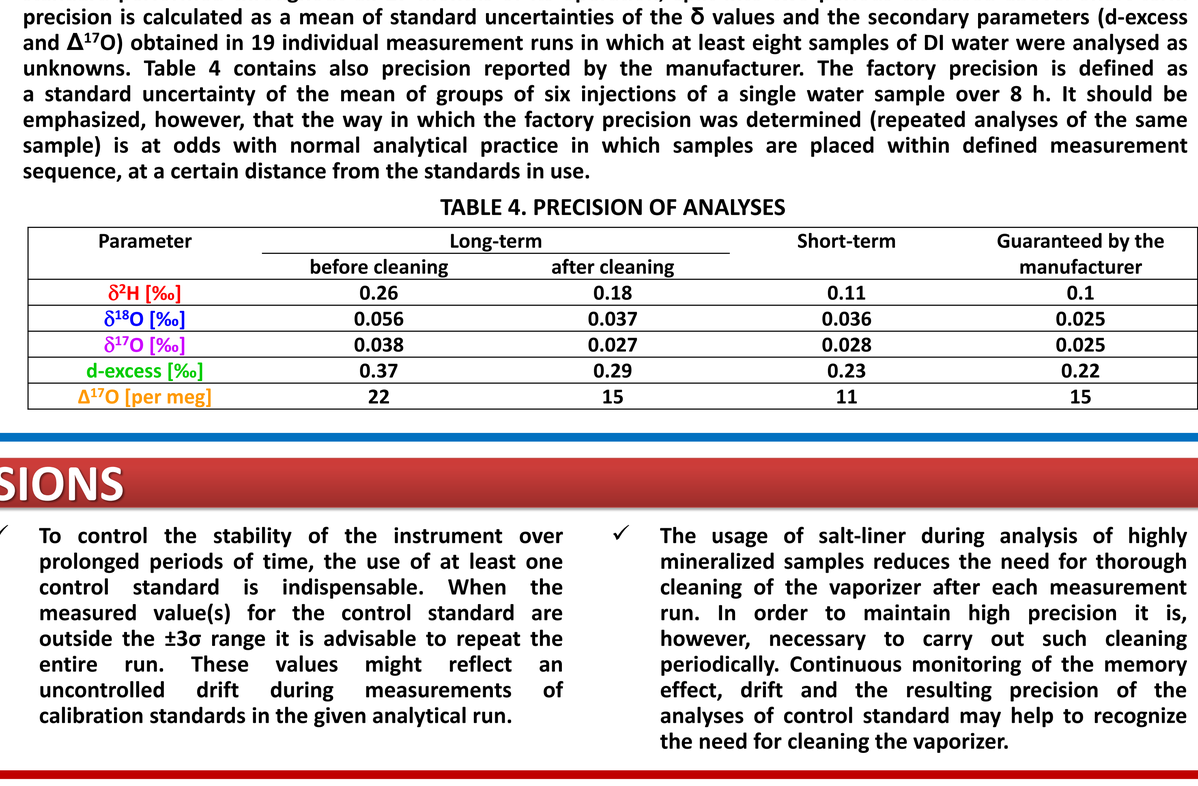


Table 4 summarizes precision of isotope analyses derived for the L2140-*i* spectrometer. The long-term precision is represented here by the standard uncertainty of single measurement results of repeated analyses of KWK3 control standard performed throughout all 27 months of its operation, split into two periods discussed above. Short-term precision is calculated as a mean of standard uncertainties of the δ values and the secondary parameters (d-excess and $\Delta^{17}O$) obtained in 19 individual measurement runs in which at least eight samples of DI water were analysed as unknowns. Table 4 contains also precision reported by the manufacturer. The factory precision is defined as a standard uncertainty of the mean of groups of six injections of a single water sample over 8 h. It should be emphasized, however, that the way in which the factory precision was determined (repeated analyses of the same sample) is at odds with normal analytical practice in which samples are placed within defined measurement sequence, at a certain distance from the standards in use.

TABLE 4. PRECISION OF ANALYSES

Parameter	Long-term		Short-term	Guaranteed by the manufacturer
	before cleaning	after cleaning		
δ^2H [‰]	0.26	0.18	0.11	0.1
$\delta^{18}O$ [‰]	0.056	0.037	0.036	0.025
$\delta^{17}O$ [‰]	0.038	0.027	0.028	0.025
d-excess [‰]	0.37	0.29	0.23	0.22
$\Delta^{17}O$ [per meg]	22	15	11	15

CONCLUSIONS

- ✓ **The adopted mode of analyses of unknown water samples with only four injections per sample allowed us to achieve short-term precision comparable to that guaranteed by the manufacturer of the spectrometer. Performing only four injections per sample increases sample throughput and reduces the risk of unexpected interruptions of the measurement sequence due to syringe failure, especially when analyzing highly mineralized waters.**
- ✓ **Analysis of combined uncertainty of single measurement results revealed that neglecting the assigned uncertainty of the calibration standards might lead to underestimation of measurement uncertainty, especially in the case of δ^2H analyses. The uncertainty budget presented here suggests that there is a need for calibration standards having δ values (especially δ^2H values) with lower assigned uncertainties than currently offered.**
- ✓ **To control the stability of the instrument over prolonged periods of time, the use of at least one control standard is indispensable. When the measured value(s) for the control standard are outside the ±3σ range it is advisable to repeat the entire run. These values might reflect an uncontrolled drift during measurements of calibration standards in the given analytical run.**
- ✓ **The usage of salt-liner during analysis of highly mineralized samples reduces the need for thorough cleaning of the vaporizer after each measurement run. In order to maintain high precision it is, however, necessary to carry out such cleaning periodically. Continuous monitoring of the memory effect, drift and the resulting precision of the analyses of control standard may help to recognize the need for cleaning the vaporizer.**

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[3] BERMAN ES, LEVIN NE, LANDAIS A, et al. Measurement of $\delta^{18}O$, $\delta^{17}O$ and ^{17}O-excess in water by off-axis integrated cavity output spectroscopy and isotope ratio mass spectrometry. Anal. Chem. 85, 2013.

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IAEA International Atomic Energy Agency

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