

Report on FARLAB lab standards calibration (201705)

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1 Introduction

This is the second report of the lab (water) standard calibration in FARLAB. General introduction and description of the water standards and the calibration principle can be found in the first report (*Report on lab standard calibration (July 2016)*, hereafter referred as *the 1st report*). Only the specific changes regarding to the second calibration is documented in this report.

The calibration has been carried out on May 18th, 2017 (hereafter referred as Cal201705). The purpose of this calibration is to evaluate the possible (if any) change in the isotope compositions for the water standards that have been used in FARLAB since 2016 Summer.

2 Standards description

2.1 IAEA standards

IAEA now only delivers two water standards: VSMOW2 and SLAP2. Table 1 shows the δ values of the IAEA standards.

Table 1: δ values of IAEA standards (IAEA 2009). The $\delta^{18}\text{O}$ and δD values of VSMOW2 are zero by consensus. d -excess values are calculated from $\delta^{18}\text{O}$ and δD values according to its definition (Craig 1961; Dansgaard 1964).

	Picarro L2140- <i>i</i> , FARLAB					
	$\delta^{18}\text{O}$ [‰]	CSD* [‰]	δD [‰]	CSD* [‰]	d -excess [‰]	CSD* [‰]
VSMOW2	0	± 0.02	0	± 0.3	0	± 0.34
SLAP2	-55.5	± 0.02	-427.5	± 0.3	16.50	± 0.34

* Combined Standard Deviation (Root Mean Square)

2.2 FARLAB internal standards

The same lab standards (except sea water standard SEA2) as calibrated in 2016 summer have been calibrated in Cal201705. SEA2 is excluded due to the intention of keeping the new spectrometer (Picarro L2140-*i* HKDS2038) a salt-free instrument.

A new lab standard, named EVAP, has been created on December 16, 2016 by evaporating tap water. Evaporation is based on two approaches, with ~ 200 mL from a beaker of crashed ice (originally tap water) undergone sublimation in freeze dryer, and ~ 1000 mL from two beakers of DI tap water evaporated under ventilation opening at room temperature. The evaporated water was filtered and then stored in inert foil gas sampling bag¹ in fridge. EVAP is here for the first time to be calibrated against IAEA standards.

¹Supel™ inert foil 1L SCV (Screw Cap Valve) gas sampling bag with Thermogreen® LB-2 (Low Bleed) septa.

Therefore, this calibration includes 5 fresh water standards that have been used as lab standards since 2016 summer² and the new generated enriched standard, i.e., **GSM1**, **VATS**, **SVAL**, **BRE**, **DI**, and **EVAP**.

3 Lab standard calibration

The IAEA standards used in Cal201705 are the pre-reserved portion from the last calibration in May, 2016³. Right before the calibration, the water was merged from three half-full 1.5 mL vials into two nearly-full 1.5 mL vials. In this way, the water had occupied most of the volume in the vial so we could expect the evaporation within the vial can be negligible.

The calibration was still carried out on the same WS-CRDS module, Picarro L2140-*i* (Picarro Inc., Sunnyvale, CA, USA). But the instrument is a recently-launched one (serial number: HKDS2038). As the same as the last calibration in May 2016, each vial of water standard was injected 20 times and all of the reported δ values are normalised on the VSMOW-SLAP scale as described in IAEA (2009).

3.1 Calibration 201705

The calibration was carried out on May 18, 2017 (hereafter referred as *Cal201705*). The IAEA standards were ordered in April, 2016, and was distributed and stored in 1.5 mL vials upon opening. The same measuring method was applied on CRDS (two times wet flushes with double-peaked water concentration (~ 50000 ppm) is a promising measure to reduce the memory effect). The calibration scheme is described as below:

Sequence: VSMOW2, SLAP2 \rightarrow GSM1, VATS, BRE, SVAL, DI, EVAP \rightarrow VSMOW2, SLAP2
Job Method: sample volume 1.80 ul, 1 pre sample rinse ("rinse between vials" not working)
Coordinator Mode: High Prec double wet peak
Duration: ~ 36 h

Before data processing, the isotopic dependency on water concentration was calibrated for the water concentration between 15000-24000 ppm with the new version of calibration function (see *Report of humidity dependency calibration (Version 2)*).⁴

The δ value reported here is the mean of those from the last 6 injections. The precision reported here is referred to the standard deviation of the mean delta values of the last 6 injections. The instrument drift is assumed to be linear during the 36 hour measurement. A linear drift correction is applied through the IAEA standards measured at the beginning and end of the batch. Table 2 shows the calibration results.

4 Calibration results comparison

Figure 1 shows the comparison between the calibration results on May 11, 2016 (Cal201605, Cal201605_new)⁵ and May 18, 2017 (Cal201705).

The humidity dependency in Cal201605 and Cal201605_new have been calibrated according to two versions of function. The new version has brought the $\delta^{18}\text{O}$ values more positive (0.01‰, 0.05‰, 0.10‰,

²Actually only GSM1, VATS, and DI are actively used.

³(see the 1st report) The ordered IAEA standards (20 mL each) were redistributed into 1.5 mL vials immediately upon opening. The vial cap was sealed with laboratory film and then stored in fridge bottom up to best prevent evaporation. Though, according to IAEA (2007, 2009), it is actually not recommended to store unused fractions of the material for further use due to the strong possibility of evaporation losses with significant isotope fractionation.

⁴Here, the water concentration measured from Picarro was not calibrated against Dew Point Generator (DPG) LI-610. This calibration, referred as *absolute water concentration calibration* in the 1st report, in fact does not affect the final results. The point is to provide all the raw measurement (both the standards and samples) in the same batch at a same reference level regarding to water concentration, so that we can calibrate the measured samples with the measured standards. It does not matter whether the reference level is raw value measured by Picarro or *absolute value* after calibration against to DPG.

⁵See appendix for the report of Cal201605_new.

Table 2: δ values of lab standards, calibrated against IAEA standards on May 18, 2017. Isotopic dependency on water concentration is corrected (according to the second version of humidity dependency function).

	Picarro L2140- <i>i</i> (HKDS2038), FARLAB					
	$\delta^{18}\text{O}$ [‰]	σ^* [‰]	δD [‰]	σ^* [‰]	<i>d</i> -excess [‰]	σ^* [‰]
GSM1	-33.07	± 0.02	-262.95	± 0.04	1.63	± 0.17
VATS	-16.47	± 0.02	-127.88	± 0.09	3.89	± 0.18
SVAL	-14.72	± 0.01	-105.51	± 0.04	12.29	± 0.08
BRE	-12.68	± 0.02	-91.01	± 0.05	10.44	± 0.15
DI	-7.78	± 0.01	-50.38	± 0.02	11.83	± 0.10
EVAP	5.03	± 0.02	4.75	± 0.11	-35.47	± 0.16

* Standard deviation of the means

0.08‰, 0.12‰) and δD values slightly more negative (0‰, -0.04‰, -0.10‰, -0.07‰, -0.11‰) compared to that from the first version. Since the new version of calibration function is based on a more reliable method via liquid injections, the results from Cal201605_new would be more recommended here.

With the same new version of humidity dependency calibration function applied, Cal201705 provided generally more negative values for both $\delta^{18}\text{O}$ (-0.10‰, -0.07‰, -0.02‰, -0.03‰, -0.19‰) and δD (-0.33‰, -0.32‰, -0.40‰, 0.01‰, -0.56‰) values compared to those of Cal201605_new. This systematic discrepancy between the two calibrations could be due to the instrument properties, since a new spectrometer (HKDS2038) was used for the Cal201705. It could also be due to the discrepancy of the applied primary standards, in which case it means some very small evaporation has occurred for the IAEA standards used for Cal201705.

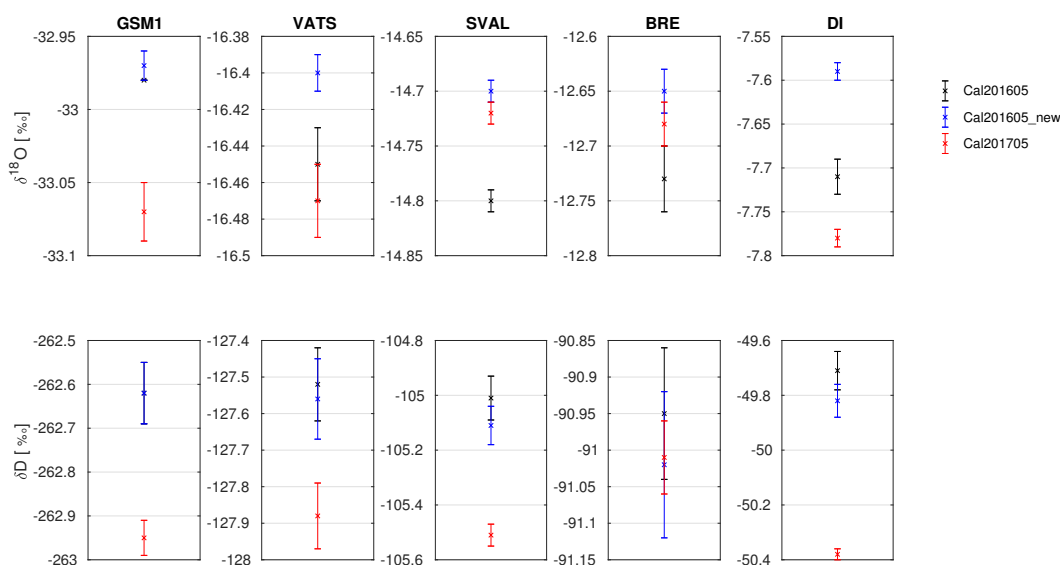


Figure 1: Comparison of $\delta^{18}\text{O}$ and δD results from calibration 2016-05-11 (Cal201605) and 2017-05-18 (Cal201705). Cal201605_new and Cal201705 were calibrated based on the second version of humidity dependency function.

A Second version of Cal201602 and Cal201605

Calibration 201602 (Cal201602) and calibration 201605 (Cal201605) have been carried out on February 23, 2016 and May 11, 2016, respectively. Details can be found in the first report: *Report on lab standard calibration (201602, 201605)*. With the update of the humidity dependency calibration function (version 2), these two lab standard calibrations have also obtained a second version, which are here referred as *Cal201602_new* and *Cal201605_new*. The results are shown in Table 3 and Table 4 respectively (Cal201605_new also in Figure 1).

The comparison between Cal201602 and Cal201602_new shows that the results are almost identical, i.e., the difference (if any) is well below the measurement precision. This is due to the advantage that the water concentration has been quite stable throughout the measurement, which will naturally introduce a very small effect from humidity dependency calibration⁶. The comparison between Cal201605 and Cal201605_new have already been discussed in Section 4.

Table 3: δ values of lab standards, calibrated against IAEA standards on February 23, 2016 (Cal201602_new). Linear drift assumed and corrected during the measurement and isotopic dependency on water concentration is corrected according to the second version of humidity dependency calibration function (version 2).

	Picarro L2140- <i>i</i> (HKDS2039), FARLAB					
	$\delta^{18}\text{O}$ [‰]	σ^* [‰]	δD [‰]	σ^* [‰]	<i>d</i> -excess [‰]	σ^* [‰]
VATS	-16.44	± 0.02	-128.34	± 0.17	3.16	± 0.22
SVAL	-14.79	± 0.02	-106.00	± 0.07	12.29	± 0.17
BRE	-12.63	± 0.01	-91.14	± 0.08	9.86	± 0.14
DI	-7.74	± 0.01	-50.47	± 0.08	11.48	± 0.11
SEA	0.85	± 0.02	4.99	± 0.13	-1.80	± 0.22

* Standard deviation of the means

Table 4: δ values of lab standards, calibrated against IAEA standards on May 18, 2017 (Cal201605_new). Linear drift assumed and corrected during the measurement and isotopic dependency on water concentration is corrected according to the second version of humidity dependency calibration function (version 2).

	Picarro L2140- <i>i</i> (HKDS2039), FARLAB					
	$\delta^{18}\text{O}$ [‰]	σ^* [‰]	δD [‰]	σ^* [‰]	<i>d</i> -excess [‰]	σ^* [‰]
GSM1	-32.97	± 0.01	-262.62	± 0.07	1.18	± 0.11
VATS	-16.40	± 0.01	-127.56	± 0.11	3.67	± 0.13
SVAL	-14.70	± 0.01	-105.11	± 0.07	12.48	± 0.12
BRE	-12.65	± 0.02	-91.02	± 0.10	10.18	± 0.18
DI	-7.59	± 0.01	-49.82	± 0.06	10.94	± 0.10
SEAI	0.23	± 0.03	1.26	± 0.11	-0.62	± 0.24

* Standard deviation of the means

⁶Though, for the daily sample measurements where the water concentrations have varied over a certain range (e.g., ± 1000 ppmv), the effect of applying different humidity dependency calibration function will be notable.

References

Craig, H. (1961). Isotopic variations in meteoric waters. *Science*, 133(3465):1702–1703.

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