

Report on lab standard calibration

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1 Introduction

The measured isotopic composition (δ values) is different for each individual instrument. To obtain a reliable inter-comparison of results measured in different laboratories, two water standards have been distributed worldwide by the International Atomic Energy Agency (IAEA). The principle is to link the measured δ values to the true δ values by calibration with water of known isotopic composition.

IAEA standards are often referred as the primary standards. Due to the limit amount of the primary standards, laboratories are recommended to prepare their own internal standards (also called working/local/secondary standards) for daily use. The primary standards will be only used to calibrate the isotopic compositions of the internal standards. This report presents the results of such kind of calibration for the internal standards in FARLAB, UiB.

The calibration has been carried out two times with different measuring schemes. The results from the second calibration (Calibration 201605) will be used. An inter-comparison between the laboratories has also been carried out by measuring the internal standards in use at ETH Zürich.

2 Standards description

2.1 IAEA standards

The two water standards that have been distributed by IAEA since 1968 (Gonfiantini 1978) are known as VSMOW (Vienna Standard Mean Ocean Water) and SLAP (Standard Light Antarctic Precipitation). GISP (Greenland Ice Sheet Precipitation) is a third reference water with isotopic composition approximately midway between VSMOW and SLAP and is used to verify the successful two point calibration with VSMOW and SLAP (IAEA 2009). GISP had been distributed by IAEA since 1977 (Hut 1987) and has been exhausted in 2015.

Supplies of both VSMOW and SLAP were exhausted at the end of 2006 (Lin et al. 2010). Meanwhile VSMOW2 and SLAP2 had been produced by IAEA to replace VSMOW and SLAP, respectively. The isotopic compositions of VSMOW2 and SLAP2 had been adjusted to be as close as possible to those of VSMOW and SLAP. They were found by Lin et al. (2010) to be indistinguishable in their $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values within measurement uncertainties. Table 1 shows the δ values of the IAEA standards that are currently in use.

2.2 FARLAB internal standards

The internal standards in FARLAB were collected from different locations in Norway. Based on the original environment they were collected, the standards are named:

VATS snow collected in Vats, Hallingdal in winter 2015

SVAL snow collected in Svalbard in summer 2015 (by Eva Falck at UNIS)

Table 1: δ values of IAEA standards (IAEA 2009). The $\delta^{18}\text{O}$ and δD values of VSMOW 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
GISP	-24.76	± 0.09	-189.5	± 1.2	8.58	± 1.40
SLAP2	-55.5	± 0.02	-427.5	± 0.3	16.50	± 0.34

* Combined Standard Deviation (Root Mean Square)

BRE ice collected from a glacier in Svalbard in 2015 ("bre" means "glacier" in Norwegian)

DI deionized tap water collected at UiB in 2016

SEA sea water collected from sea water tap at UiB in 2012

SEAI sea water collected from sea water tap at UiB in 2016

GSM1 Greenland melted water provided by the Alfred Wegener Institute (AWI) in Bremerhaven, Germany in 2016.

All the standards have been filtered and then stored in inert foil gas sampling bag¹ in fridge. The collapsible bag shrinks as standard is used, thus eliminating free air space and ensuring an entire standard can be used without data degradation due to evaporation and re-condensation.

3 Lab standard calibration

The two calibrations have been carried out in February and May of 2016, respectively (hereafter referred as Calibration 201602 and Calibration 201605). Both calibrations were carried out on a Wavelength-Scanned Cavity Ring-Down Spectrometer (WS-CRDS), Picarro L2140-*i* (Picarro Inc., Sunnyvale, CA, USA). 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 up². The standards in vial were measured on Picarro during the calibration and each vial was injected 20 times. All of the reported δ values are normalised on the VSMOW-SLAP scale as described in IAEA (2009).

In Calibration 201602, the IAEA standards were from the retained portion of a previous order around 2013 and the default measuring scheme on CRDS was used. In Calibration 201605, the newly-ordered IAEA standards in 2016 as well as a modified measuring scheme on CRDS was applied. The results from the two calibrations are pretty close (Sec. 3.3). It is decided to adopt the δ values from Calibration 201605 for the future daily calibration in FARLAB, in order to keep consistence with the newly-ordered IAEA standards. In addition, the IAEA standards here are used immediately upon opening.

3.1 Calibration 201602

3.1.1 Calibration on Picarro L2140-*i*

Calibration 201602 was carried out on February 23, 2016. The IAEA standards were the last retained portion of an order around 2013, which composed of VSMOW2, GISP, and SLAP2. Regarding to the measuring method on CRDS, the Picarro default setup was applied. The calibration scheme is described as below:

Sequence: VSMOW2, GISP, SLAP2 \rightarrow VATS, SVAL, BRE, DI, SEA \rightarrow VSMOW2, GISP, SLAP2

Job Method: 1 pre rinse, 1 pre sample rinse, 0 fill strokes (Picarro default setup)

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

²According 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.

Coordinator Mode: High Precision

Duration: ~37 h

VSMOW2 and GISP were used when normalizing the δ values on VSMOW-SLAP scale, since the isotopic compositions of the lab standards are already well covered by these two standards. This way is believed to be more favourable with respect to the accuracy. The reported δ value is the mean of those from the last 7 injections. The reported precision is the combined standard deviation (root mean square) of the standard deviations of the last 7 injections.

3.1.2 Calibration on IRMS

The $\delta^{18}\text{O}$ values of lab standards had also been independently calibrated against IAEA standards on an Isotope-Ratio Mass Spectrometer (IRMS). For this calibration, VSMOW2, GISP, and SLAP2 are measured in triplicate in the start of the sequence and used for calibration. A sea water house standard (SEA) is measured up to 12 times (4 triplicates with regular intervals) throughout the sequence to control for drift and to verify the calibration. The samples are also run in triplicate to verify that standard deviation does not change during the run.

Samples are pipetted (0.5 ml) into 12 ml exetainers, and flushed with 0.3% CO_2 in He. Samples are then allowed to equilibrate for 18 h or more at 24 °C. CO_2 in headspace is then analysed for $\delta^{18}\text{O}$ on a Gasbench and Delta V+ IRMS.

Table 2: δ values of lab standards, calibrated against IAEA standards on February 23, 2016.

	Picarro L2140- <i>i</i> , FARLAB						IRMS, FARLAB	
	$\delta^{18}\text{O}$ [‰]	CSD* [‰]	δD [‰]	CSD* [‰]	<i>d</i> -excess [‰]	CSD* [‰]	$\delta^{18}\text{O}$ [‰]	σ^{**} [‰]
VATS	-16.44	± 0.09	-128.34	± 0.68	3.16	± 0.98	-16.31	± 0.05
SVAL	-14.79	± 0.09	-106.00	± 0.70	12.28	± 1.00	-14.58	± 0.03
BRE	-12.63	± 0.09	-91.15	± 0.70	9.86	± 0.99	-12.59	± 0.04
DI	-7.74	± 0.09	-50.47	± 0.70	11.49	± 0.98	-7.60	± 0.06
SEA	0.85	± 0.09	4.98	± 0.72	-1.79	± 1.02	1.11	± 0.05

* Combined Standard Deviation (Root Mean Square)

** Standard deviation of the means

3.2 Calibration 201605

3.2.1 Calibration on Picarro L2140-*i*

Calibration 201605 was carried out on May 11, 2016. The IAEA standards were ordered in April, 2016, which composed of VSMOW2 and SLAP2 only. A modified measuring method was applied on CRDS (according to the memory tests, 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 → GSM1, VATS, BRE, SVAL, DI → VSMOW2, SLAP2 → WS3, PS3, LCS2, PS1, LCS1, PS2 → VSMOW2, SLAP2 → SLAP2_{old}, GISP_{old}, VSMOW2_{old}, SEAI, SEA_{old} → VSMOW2, SLAP2

Job Method: 0 pre-rinse, 3 sample rinse between vials (rinse volume: 3 mL)

Coordinator Mode: Peaked Wet Flush x2

Duration: ~97 h

Before data processing: a) water concentration measured from Picarro was calibrated against dew point generator (LI-610); b) the isotopic dependency on water concentration was calibrated for the range of 15000-21000 ppm³.

³The δ values of lab standards with calibration a) & b) is rather close to those without calibration a) & b) (see Figure 1 and Figure 2), though the measured values of water concentration and isotopic compositions have changed after calibration.

The reported δ value is the mean of those from the last 6 injections. The reported precision is referred to the standard deviation of the mean delta values of the last 6 injections. Table 3 shows the calibration results.

3.2.2 Calibration on IRMS

The $\delta^{18}\text{O}$ values of lab standards had also been independently calibrated against IAEA standards on an Isotope-Ratio Mass Spectrometer (IRMS). The procedure is the same as described in Sec. 3.1.2, except that the newly-ordered VSMOW2 and SLAP2 are used for calibration.

Table 3: δ values of lab standards, calibrated against IAEA standards on May 11, 2016. Water concentration is calibrated and isotopic dependency on water concentration is corrected.

	Picarro L2140- <i>i</i> , FARLAB						IRMS, FARLAB	
	$\delta^{18}\text{O}$ [‰]	σ^* [‰]	δD [‰]	σ^* [‰]	<i>d</i> -excess [‰]	σ^* [‰]	$\delta^{18}\text{O}$ [‰]	σ^* [‰]
GSM1	-32.98	± 0.00	-262.62	± 0.07	1.20	± 0.08	-33.14	± 0.04
VATS	-16.45	± 0.02	-127.52	± 0.10	4.09	± 0.16	-16.47	± 0.11
SVAL	-14.80	± 0.01	-105.01	± 0.08	13.41	± 0.13	-14.71	± 0.04
BRE	-12.73	± 0.03	-90.95	± 0.09	10.87	± 0.24	-12.75	± 0.07
DI	-7.71	± 0.02	-49.71	± 0.07	11.95	± 0.20	-7.71	± 0.15
SEAI	0.25	± 0.03	1.24	± 0.12	-0.80	± 0.27	0.49	± 0.10
SEA _{old} **	0.89	± 0.02	5.13	± 0.10	-2.02	± 0.22	1.00	± 0.14
VSMOW2 _{old} **	-0.08	± 0.01	-1.22	± 0.13	-0.57	± 0.16	-0.04	± 0.02
GISP _{old} **	-24.72	± 0.03	-190.84	± 0.13	6.93	± 0.24	–	–
SLAP2 _{old} **	-55.51	± 0.02	-429.12	± 0.08	14.99	± 0.18	-55.54	± 0.03

* Standard deviation of the means

** Standards (IAEA standards and lab standards) used in Calibration 201602 were measured against newly-ordered IAEA standards in Calibration 201605.

3.3 Calibration results comparison

Comparison of the results from both calibrations on Picarro and the calibration from IRMS are shown in Figure 1 and Figure 2 for each standard. The IAEA standards (VSMOW2, SLAP2, GISP) which were used in Calibration 201602 were measured again as samples in Calibration 201605, where the newly-ordered IAEA standards (VSMOW2, SLAP2) were used. One purpose was to identify the "between bottle" inhomogeneity if any between the two sets of IAEA standards; another purpose was to check whether storage in an injected vial in room temperature would cause significant evaporation thus isotopic fractionation. Lab standards SEAI and GSM1 were calibrated only in Calibration 201605. Only $\delta^{18}\text{O}$ values of lab standards have been calibrated on IRMS.

Figure 1 and Figure 2 show that:

1. For the 5 lab standards (VATS, SVAL, BRE, DI, and SEA), the $\delta^{18}\text{O}$ values calibrated on IRMS in May, 2016 (IRMS05) are about 0.13‰ more negative than those calibrated on IRMS in February, 2016 (IRMS02). It indicates a systematic discrepancy between the two calibrations, due to either the instrument drift or more possibly the discrepancy of the applied primary standards.
2. For the 5 lab standards, the $\delta^{18}\text{O}$ values of Calibration 201602 (Cal02) are basically undistinguishable (except BRE) from those of Calibration 201605 (Cal05_Cor); while the δD values of Cal02 are generally more negative ($\sim 0.6\text{‰}$) than those of Cal05_Cor. The discrepancy might be explained by the difference of the IAEA standards that were used for calibration. Taking δD as an example, SLAP2 and VSMOW2 used for Cal02 are generally more depleted while measured in Cal05. This will cause an overall shift of calibration function. As a consequence, the δD values of the 5 lab standards calibrated in Cal05 are shifted towards higher values (Figure 2).

- For δD , there is no significant difference between the calibration with (Cal05_Cor) or without (Cal05) correction of water concentration and isotopic dependency on water concentration. This is due to, i) the water concentration during the measurements maintains well around the same level and, ii) the slope of the isotopic response function for δD is rather small (which is bigger in the case of $\delta^{18}O$, see the report of instrument characterization).
- There is a slight discrepancy between the two sets of IAEA standards. Specifically, the δD values calibrated in Cal05 are generally more negative than the certified values.

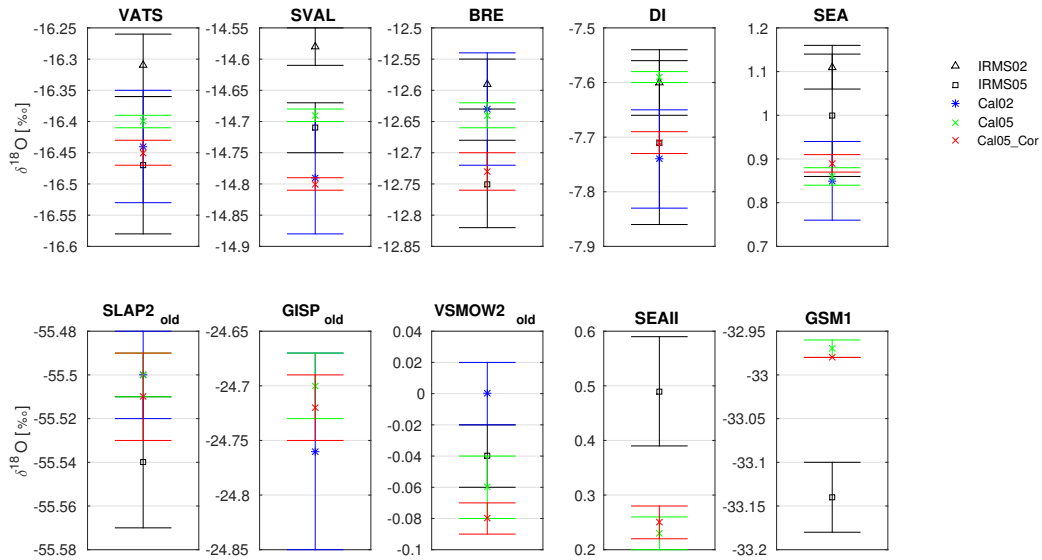


Figure 1: Comparison of $\delta^{18}O$ results from calibration 201602 and 201605. Cal05_Cor indicates the calibration with the correction of water concentration and isotopic dependency on water concentration.

3.4 Lab inter-comparison

Table 4: δ values of lab standards in use at ETH Zürich, calibrated against IAEA standards at FARLAB on February 23, 2016.

	Picarro L2140- <i>i</i> , FARLAB						ETH Zürich		
	$\delta^{18}O$ [‰]	σ^* [‰]	δD [‰]	σ^* [‰]	<i>d</i> -excess [‰]	σ^* [‰]	$\delta^{18}O$ [‰]	δD [‰]	<i>d</i> -excess [‰]
WS3	-43.72	± 0.01	-251.63	± 0.09	98.11	± 0.13	~-43	~-253	~91
PS3	-43.07	± 0.03	-248.90	± 0.09	95.69	± 0.25	-43.09	-248.93	95.79
LCS2	-23.89	± 0.02	-152.79	± 0.12	38.34	± 0.20	-24.11	-153.96	38.92
PS1	-10.89	± 0.02	-78.04	± 0.12	9.07	± 0.19	-10.64	-77.74	7.38
LCS1	-0.04	± 0.03	5.55	± 0.10	5.84	± 0.23	-0.10	5.88	6.68
PS2	4.72	± 0.04	42.67	± 0.13	4.89	± 0.37	4.73	42.69	4.85

* Standard deviation of the means

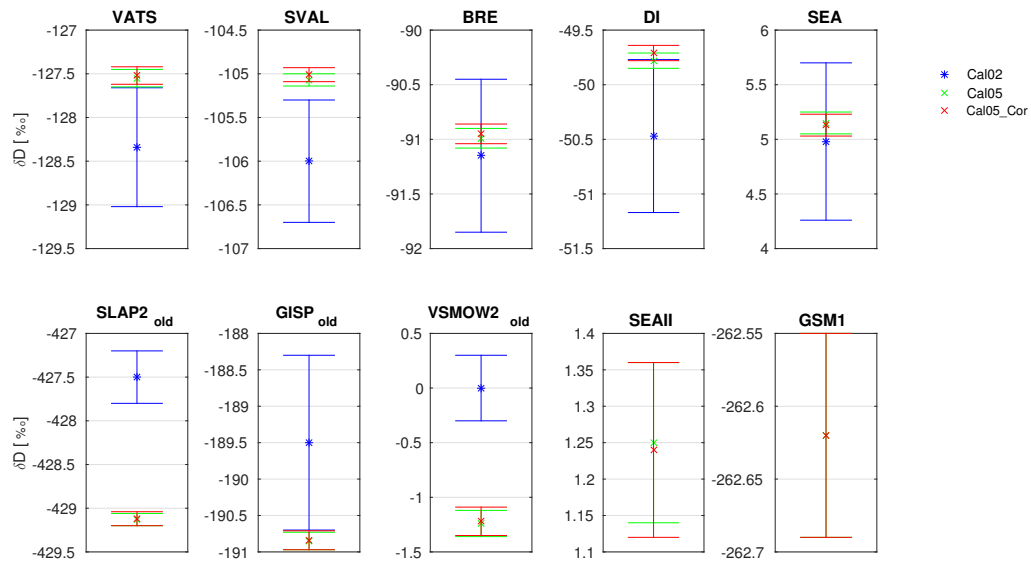


Figure 2: Comparison of δD results from calibration 201602 and 201605. Cal05_Cor indicates the calibration with the correction of water concentration and isotopic dependency on water concentration.

References

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