Calibration of laboratory standards at FARLAB

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This document summarizes the calibration of internal laboratory standards for stable water isotopes at FARLAB. Since the establishment of FARLAB as an NFR infrastructure project in 2016, primary standards (VSMOW2, SLAP2) have been obtained twice from IAEA. The original internal (secondary) standards, stored in aluminium/plastic storage bags, were nearly exhausted in 2019. Therefore, new waters were prepared for long-term storage in pressurized stainless steel kegs in 2020. This document describes the calibration runs performed in sequence between 2016 and 2021 for each of the secondary laboratory standards. A best-estimate of the final calibrated value with total uncertainty is given, that should be used for calibration of stable isotope measurements from FARLAB onto VSMOW-SLAP scale. Furthermore, the performance of FARLAB during the international WICO intercomparisons in 2016 and 2020 are briefly summarized.

Combined uncertainty is estimated from an error budget, involving the following components (Gröning, 2011, 2018; Pierchala et al., 2019):

- u(h): variance from the assigned uncertainty of calibration standard h wrt VSMOW2-SLAP2
- u(l): variance from the assigned uncertainty of calibration standard l wrt VSMOW2-SLAP2
- u(H): variance from uncertainty (SEM) of measured values of standard H (SD for a single measurement)
- u(L): variance from uncertainty (SEM) of measured values of standard L (SD for a single measurement)
- u(m): variance of sample (unknown). Approximated by repeated measurements or by long-term reproducibility (+ repeatability). Here estimated by the scaled SEM of the repeated sample measurements.

Each component also includes a ‘sensitivity’ term, which is given by the location of the sample along the calibration curve. In the centre of the calibration curve, samples can obtain a lower uncertainty than near the edges of the calibration curve.
The primary standard uncertainty is obtained from the specifications of the reference material. The combined uncertainty u(c) is then calculated from the square root of the squared sum of all error components in the budget.

1. Calibrations of first set of laboratory standards (2016-2020)

The first set of laboratory standards was produced from several waters from different sources. All waters were filtered through a 0.2 um Nylon filter and stored in plastic/aluminium bags in the fridge. Upon use, a small amount of water was discarded, before filling sample vials for redistribution. The waters were: GSM1, Greenland melt water, obtained from AWI. SVAL: water from a Svalbard glacier. BRE: water from Norwegian glacier melt water. DI: de-ionised tap water from Bergen. EVAP: de-ionised tap water, evaporated under a vent for several weeks. SEAII: sea water (with salt).

Calibration	Description and summary
2016-05	20 injections, 10 used, single vial per standard GSM1, SVAL, BRE, DI, SEAII, VATS
2016-09	20 injections, 10 used, two vials each for DI and GSM1
2017-05	20 injections, 10 used, two vials for DI, GSM1, EVAP, one for VATS, BRE, SVAL
2017-07	15 injections, 12 used, 3 vials each for DI, GSM1, EVAP, VATS, 1 run with 17-O
2017-08	15 injections, 15 used, 3 vials each for DI, GSM1, EVAP, VATS, 2 runs with 17-O
2020-02	20 injections, 10 used, 1 vial for first set of standards DI, GSM1, EVAP, VATS, SEAII, 3 runs. Only first two used because of 20 injections instead of 15 for run 3. Run 4 is for 17-O calibration.

In the following summary tables for each standard, the numbers on the left half are the final average of each set of calibration runs, indicated by year-month, including the average total uncertainty for the set of calibration runs. On the right side of the table, the average of all standard measurements from calibration runs up to that point in time is displayed, together with the standard error of the mean (SEM).

1.1 GSM1 calibrations

	dD	dD_u	d18O	d18O_u	dxs	dxs_u	dD	SEM	d18O	SEM	dxs	SEM
2016-05	-262.31	0.61	-32.9332	0.0592	1.16	0.77	-262.31		-32.9332		1.16	
2016-09	-262.69	0.61	-33.1231	0.0593	2.30	0.77	-262.56	0.26	-33.0598	0.0653	1.92	0.52
2017-05	-262.48	0.44	-33.0224	0.0519	1.71	0.60	-262.53	0.18	-33.0448	0.0388	1.83	0.29
2017-07	-261.33	0.61	-32.9468	0.0593	2.24	0.77	-262.08	0.24	-33.0080	0.0297	1.99	0.19
2017-08	-262.99	0.61	-32.9607	0.0592	0.70	0.77	-262.47	0.19	-32.9878	0.0238	1.43	0.27
2020-02	-261.89	0.53	-32.9576	0.0556	1.78	0.69	**-262.40**	**0.18**	**-32.9840**	**0.0209**	**1.48**	**0.23**

1.2 VATS calibrations

	dD	dD_u	d18O	d18O_u	dxs	dxs_u	dD	SEM	d18O	SEM	dxs	SEM
2016-05	-127.48	0.56	-16.3927	0.0574	3.66	0.73	-127.48		-16.3927		3.66	
2017-05	-127.82	0.37	-16.4743	0.0498	3.98	0.54	-127.65	0.17	-16.4335	0.0408	3.82	0.16
2017-07	-126.03	0.56	-16.3839	0.0574	5.04	0.73	-126.68	0.40	-16.4037	0.0199	4.55	0.32
2017-08	-126.45	0.56	-16.3584	0.0574	4.42	0.73	-126.55	0.20	-16.3790	0.0143	4.48	0.16
2020-02	-126.59	0.47	-16.3818	0.0536	4.47	0.64	**-126.56**	**0.17**	**-16.3794**	**0.0120**	**4.48**	**0.13**

1.3 DI calibrations

	dD	dD_u	d18O	d18O_u	dxs	dxs_u	dD	SEM	d18O	SEM	dxs	SEM
2016-05	-49.81	0.55	-7.5959	0.0569	10.96	0.72	-49.81		-7.5959		10.96	
2016-09	-50.89	0.55	-7.8531	0.0569	11.94	0.72	-50.53	0.36	-7.7673	0.0933	11.61	0.46
2017-05	-50.38	0.35	-7.7730	0.0492	11.81	0.53	-50.47	0.20	-7.7696	0.0511	11.69	0.26
2017-07	-49.10	0.55	-7.6737	0.0569	12.29	0.72	-49.96	0.28	-7.7337	0.0353	11.92	0.19
2017-08	-50.81	0.55	-7.6328	0.0569	10.25	0.72	-50.32	0.21	-7.6904	0.0260	11.20	0.26
2020-02	-49.99	0.45	-7.7367	0.0531	11.91	0.63	**-50.28**	**0.18**	**-7.6962**	**0.0230**	**11.29**	**0.24**

1.4 EVAP calibrations

	dD	dD_u	d18O	d18O_u	dxs	dxs_u	dD	SEM	d18O	SEM	dxs	SEM
2017-05	4.34	0.35	4.9990	0.0491	-35.66	0.53	4.34		4.9990		-35.66	
2017-07	5.70	0.55	5.1973	0.0568	-35.88	0.71	5.16	0.36	5.1180	0.0503	-35.79	0.16
2017-08	5.28	0.55	5.0604	0.0568	-35.21	0.71	5.22	0.21	5.0865	0.0264	-35.47	0.14
2020-02	5.24	0.45	5.0926	0.0530	-35.51	0.62	**5.22**	**0.18**	**5.0875**	**0.0222**	**-35.48**	**0.12**

1.5 SEAII calibrations

	dD	dD_u	d18O	d18O_u	dxs	dxs_u	dD	SEM	d18O	SEM	dxs	SEM
2017-05	1.36	0.55	0.2622	0.0567	-0.73	0.71	1.36		0.2622		-0.73	
2017-08	1.27	0.55	0.2804	0.0567	-0.97	0.71	1.30	0.06	0.2758	0.0050	-0.91	0.07
2020-02	1.30	0.45	0.2396	0.0529	-0.61	0.62	**1.30**	**0.05**	**0.2638**	**0.0084**	**-0.81**	**0.09**

1.6 BRE calibrations

	dD	dD_u	d18O	d18O_u	dxs	dxs_u	dD	SEM	d18O	SEM	dxs	SEM
2016-05	-91.02	0.56	-12.6485	0.0571	10.16	0.72	-91.02		-12.6485		10.16	
2017-05	-91.01	0.36	-12.6868	0.0495	10.49	0.54	-91.02	0.01	-12.6677	0.0192	10.33	0.17
2020-02	-90.64	0.46	-12.7290	0.0533	11.19	0.63	**-90.83**	**0.12**	**-12.6983**	**0.0195**	**10.76**	**0.26**

2. Calibrations of second set of laboratory standards (since 2020)

The second set of laboratory standards was extended by waters obtained through HCSL from Greenland, and Bermuda. Stainless steel kegs were prepared according to instructions from IAEA, holding up to 60L of standard water. Standard water was filtered into the kegs, and pressurized with N2 to 1 bar above ambient. Water can be tapped from a riser. Thereby, a nozzle is screwed onto the tap, a small squirt discarded, and the liquid trapped in the nozzle collected when unscrewing it. It is expected that the standards last for about 10 years with conservative use. The waters are: GLW: Greenland winter snow. FIN: Finse tap water. DI2: De-ionised tap water from Bergen. BERM: De-ionised tap water from Bermuda. EVAP2: Evaporated tap-water from Bergen, kept in a heated, ventilated cabin for several weeks.

Persisten, but small offsets detected in δ18O during the WICO2020 intercomparison prompted a sequence of re-evaluations of the handling and storage of the laboratory standards. By running triplicates of each sample, the latest calibration run takes an extra step to reduce memory effects between vials. This run setup is now also used routinely for sample analysis. The memory effect reduces specifically for δD measurements. In the latest calibration, the assigned δD value of the secondary standards is thus about 0.8 to 1.0 permil different than before. We use the δD value from the 2022-05 calibration, and the long-term average from all available calibrations for the δ18O value in calibration set 2022.

Calibration	Description and summary
2020-02	20 injections, 10 used, 1 vial for first set of standards DI2, GLW, EVAP2, BERM, FIN, 3 runs. Only first two used because of 20 injections instead of 15 for run 3. Run 4 is for 17-O calibration.
2021-05	20 injections, all used. 4 vials for each standard from set2, and 2 vials from the standard stored within the fridge door. Second run discarded because of very variable humidity during measurements.
2021-06	12 injections, all used. 17-O mode. 6 vials of each standard from set 2 only. GRESP for calibration standard control. Variable drift (FIN or DI2).
2022-05	16 injections, all used. 3 vials of each standard in sequence. WICO2 as control. 2 triplicates of each standard. First sample of each set only used for memory correction.

2.1 GLW calibrations

	dD	dD_u	d18O	d18O_u	dxs	dxs_u	dD	SEM	d18O	SEM	dxs	SEM
2020-02	-308.02	0.27	-40.0587	0.0209	12.45	0.11	-308.02		-40.0587		12.45	
2021-05	-308.89	0.46	-40.1067	0.0294	11.96	0.30	-308.46	0.22	-40.0827	0.0141	12.21	0.11
2021-06	-307.60	0.75	-40.0243	0.1233	12.59	0.45	-308.14	0.20	-40.0608	0.0211	12.35	0.11
2022-05	-308.8	0.1	-40.23	0.01	13.2	0.1	**-308.8**	**0.1**	**-40.0951**	**0.0225**	**12.5**	**0.1**

2.2 FIN calibrations

	dD	dD_u	d18O	d18O_u	dxs	dxs_u	dD	SEM	d18O	SEM	dxs	SEM
2020-02	-81.06	0.46	-11.6687	0.0533	12.29	0.63	-81.06		-11.6687		12.29	
2021-05	-81.34	0.64	-11.6861	0.0461	12.15	0.41	-81.21	0.15	-11.6781	0.0107	12.21	0.10
2021-06	-80.97	0.49	-11.5786	0.0443	11.66	0.48	-81.10	0.13	-11.6468	0.0150	12.07	0.12
2022-05	-80.8	0.4	-11.74	0.05	13.1	0.0	**-80.8**	**0.4**	**-11.6619**	**0.0148**	**12.2**	**0.1**

2.3 DI2 calibrations

	dD	dD_u	d18O	d18O_u	dxs	dxs_u	dD	SEM	d18O	SEM	dxs	SEM
2020-02	-50.95	0.47	-7.6609	0.0538	10.34	0.64	-50.95		-7.6609		10.34	
2021-05	-49.89	0.13	-7.5532	0.0112	10.54	0.04	-50.65	0.31	-7.6301	0.0258	10.39	0.12
2021-06	-50.97	0.84	-7.6437	0.0686	10.18	0.39	-50.80	0.22	-7.6364	0.0176	10.29	0.10
2022-05	-49.8	0.3	-7.66	0.03	11.5	0.1	**-49.8**	**0.3**	**-7.6419**	**0.0148**	**10.6**	**0.1**

2.4 BERM calibrations

	dD	dD_u	d18O	d18O_u	dxs	dxs_u	dD	SEM	d18O	SEM	dxs	SEM
2020-02	6.64	0.47	0.5711	0.0536	2.08	0.64	6.64		0.5711		2.08	
2021-05	6.64	0.54	0.5733	0.0341	2.05	0.29	6.64	0.13	0.5722	0.0115	2.06	0.07
2021-06	6.17	0.33	0.5796	0.0686	1.53	0.53	6.47	0.11	0.5750	0.0122	1.87	0.11
2022-05	7.3	0.2	0.54	0.04	2.95	0.16	**7.3**	**0.2**	**0.5675**	**0.0123**	**2.1**	**0.1**

2.5 EVAP2 calibrations

	dD	dD_u	d18O	d18O_u	dxs	dxs_u	dD	SEM	d18O	SEM	dxs	SEM
2020-02	9.22	0.45	1.7466	0.0529	-4.76	0.62	9.22		1.7466		-4.76	
2021-05	9.52	0.60	1.8035	0.0769	-4.91	0.10	9.35	0.17	1.7724	0.0199	-4.83	0.09
2021-06	8.95	0.44	1.7725	0.0816	-5.23	0.72	9.21	0.14	1.7724	0.0173	-4.97	0.13
2022-05	10.0	0.1	1.7800	0.0339	-4.25	0.18	**10.0**	**0.1**	**1.7739**	**0.0147**	**-4.8**	**0.1**

3. Participation in WICO laboratory intercomparisons 2016 and 2020.

FARLAB has so far two times participated in the WICO laboratory intercomparisons, organised by the IAEA. A set of unknown waters is sent to participating laboratories. Each lab analyses these samples according to standard operating procedures. Results are then returned to IAEA, who calculates z-scores, bias and reproducibility for each lab. Results of WICO are published anonymously, and laboratories chose individually if they want to make the outcome public or not.

3.1 WICO2016 participation

In 2016, FARLAB participated for the first time after instrument setup and establishment of measurement routines in WICO. The 8 samples, including a salty sample, a very depleted sample, and one with organic contamination, were processed using standard procedures at that time. A comparison with reference values by IAEA yielded overall satisfying results at the time of submission, except for the contaminated sample. The most depleted sample was questionable for δ18O, due to the limited range of FARLAB standards. Reprocessing with FLIIMP 1.8 (including memory and drift correction) resulted in slightly better, but overall similar results.

WICO-1	Danube River Water, Austria, filtered
WICO-2	Neusiedler See (Lake Water), Austria, filtered
WICO-3	Bow River Water*, Canada, filtered
WICO-4	Ground Water Mix, Egypt, Austria, filtered
WICO-5	WICO-5 Vienna Tap water and WICO-6 Mix, research grade methanol was added gravimetrically to produce a 0.05 % methanol/water volumetric ratio of contaminated water sample
WICO-6	Depleted Greenland Ice Sheet fern melt**, unfiltered
WICO-7	Enriched Vienna groundwater with 99 % D O and 99.9 % H ^{18}O mixed to ensure a normal d-excess and isotopically enriched result, unfiltered
WICO-8	Synthetic seawater to 30 g/L (commercial Red Sea salt), mixed with WICO-6 to produce a slightly depleted result with a normal d-excess, unfiltered.

	Reference values			**FARLAB 2016**					**FLIIMP V1.8**				
	δ18O	**δD**	**dxs**	**δ18O**	**δD**	**dxs**	**z-δ18O**	**z-δD**	**δ18O**	**δD**	**dxs**	**z-δ18O**	**z-δD**
WICO-1	-10.80	-77.4	9	-10.87	-78.4	8.6	0.35	0.65	-10.87	-78.3	8.6	0.35	0.60
WICO-2	-5.11	-41.7	-0.8	-5.07	-42.1	-1.5	0.20	0.27	-5.17	-42.7	-1.4	0.30	0.67
WICO-3	-22.01	-168.3	7.8	-22.24	-170.3	7.6	1.15	1.31	-22.06	-169.0	7.5	0.25	0.47
WICO-4	-0.50	0.5	4.5	-0.38	1.0	4	0.60	0.33	-0.57	-0.6	4.1	0.35	0.73
WICO-5	-15.68	-114.3	11.1	-9.70	-106.0	-28.4	>3.00	>3.00	-9.73	-105.8	-28.0	>3.00	>3.00
WICO-6	-41.41	-323.7	7.6	-41.84	-326.6	8.1	2.15	1.94	-41.40	-323.7	7.5	0.05	0.00
WICO-7	5.61	55.7	10.8	5.71	55.2	9.6	0.50	0.31	5.50	53.7	9.8	0.55	1.33
WICO-8	-3.45	-17.6	10	-3.34	-18.3	8.5	0.55	0.45	-3.50	-19.3	8.6	0.25	1.13

3.2 WICO2020 participation

In 2020, FARLAB participated in the next round of intercomparison organised by the IAEA (WICO2020). The 6 water samples did not contain salt or contaminations, but included for the first time the option to intercompare 17O measurements. Sample OH-30 and OH-26 were identical, allowing for assessment of internal reproducibility. FARLAB has so far not used the 17O information contained in the WICO2020 samples. A comparison with the reference values revealed acceptable results, but with a consistent bias in δ18O. This promptet and investigation and re-calibration effort of the in-house standards in May/June 2021. After recalibrationof standards and reprocessing with FLIIMP V1.8, results have improved slightly, but overall giving a mixed picture. Drift standards of run01 and run01 indicate an offset in δ18O that would have lead to rejecting the run, had procedures to that effect been in place. Run03 and run04 did not show such an offset and would have produced a consistently better z-score also in δ18O (not shown). Corresponding quality control procedures leading to rejection of a run are now being implemented at FARLAB. Part of the offset may be due to the set-up of the run, in combination with a bug in the drift correction of FLIIMP V1.8 that occured in some cases.

OH-25	Arctic Mix
OH-26	Vienna TW
OH-27	Halley Bay
OH-28	Spiked TW
OH-29	Tropical Mix
OH-30	OH-26

	Reference values			**FARLAB 2016**					**FLIIMP V1.8**				
	δ18O	**δD**	**dxs**	**δ18O**	**δD**	**dxs**	**z-δ18O**	**z-δD**	**δ18O**	**δD**	**dxs**	**z-δ18O**	**z-δD**
OH-25	-16.98	-129.5	6.34	-17.11	-129.9	6.98	1.30	0.50	-16.95	-129.3	6.3	0.29	0.21
OH-26	-11.20	-78.1	11.5	-11.32	-78.2	12.36	1.20	0.13	-11.17	-78.0	11.3	0.28	0.07
OH-27	-24.89	-190.8	8.32	-25.04	-191.4	8.92	1.50	0.75	-25.08	-191.7	8.9	1.89	1.15
OH-28	-7.95	-49.0	14.6	-8.04	-49.4	14.92	0.90	0.50	-8.06	-49.6	15.0	1.15	0.70
OH-29	-1.05	1.8	10.2	-1.21	1.1	10.78	1.60	0.88	-1.21	1.1	10.8	1.63	0.86
OH-30	-11.21	-77.9	11.78	-11.32	-78.3	12.26	1.10	0.50	-11.35	-78.6	12.2	1.40	0.83

4. Intercomparison to other laboratories and lab standards

In addition to the WICO intercomparisons, FARLAB occasionally measured internal laboratory standards from other labs for intercomparison purposes. These include an intercomparison with samples measured at University of Iceland in Reykjavik, with samples from the Institute for Atmospheric and Climate Sciences, ETH Zürich, with standards from INSTAAR, Boulder, USA, with standards from LOCEAN, France, and with samples measured at GFZ, Potsdam, Germany.

5. Calibration of standards for 17-O analysis

Calibration of secondary laboratory standards for 17-O analysis, and the calculation of the 17-O excess requires separate calibration runs in 17-O mode with either HKDS2038 or HKDS2039. Calibration runs have been started early in 2016, and then continued in 2017, and 2019-2022. From consultations with the community, the randomisation of samples and a large number of repeats seems necessary to obtain meaningful results. Drift is a particular problem for 17-O analysis, and needs to be constrained by frequent and precise measurements of a drift standard, ideally with known (assigned) value and uncertainty.

5.1 Calibration of secondary standards for 2016-2020

The first set of laboratory standards at FARLAB in use until 2020 was calibrated several times for 17-O analysis. A sequence of 3 runs against primary waters was done in 2017. The runs repeated a fixed sequence, rather than randomizing samples. The runs are therefore consistent among each other, but may include fixed biases. Standard SEAII was only analyzed during one of the runs. Since no additional drift/control standard was available, the drift was solely determined from the (repeated) measurement of the calibration standards VSMOW2 and SLAP2.

Standard	d17O	d17O_u	e17	e17_u
DI	-4.0032	0.0441	35	16
EVAP	2.6437	0.0456	-54	9
GSM1	-17.5123	0.0304	24	18
VATS	-8.6287	0.0334	39	10
SEAII	0.1476	0.0102	2	5

5.2 Calibration of secondary standards from 2020-2021

A specific run with randomized samples was set up during the 2020 calibrations for 17-O analysis. The sequence consisted of 10 injections each of primary standards, and the new calibration standards, using VATS as drift standard. In 2021, one run (run03) was set up with 12 injections of the secondary standards, using GRESP as a drift. Randomisation of 4 samples was performed during both calibration runs. The two runs appear however from a different distribution, with consistent offsets in all isotopes of almost 0.1 permil with regard to d17O. Results for e17 are consistent across the runs, giving some confidence in the analysis results. In order to proceed working with the secondary standards, we calculate the average across both calibration runs. A new calibration run for 17-O, using the protocol adopted in early 2022 (with duplicates/triplicates of standards) will be performed in 2022.

Cal run	Standard	δ18O	δ18O_u	d17O	d17O_u	e17	e17_u
2020-02	BERM	0.38	0.01	0.2059	0.0082	5	3
2021-05	BERM	0.53	0.08	0.2859	0.0456	7	10
2020-02	DI2	-7.89	0.02	-4.1448	0.0110	28	4
2021-05	DI2	-7.64	0.07	-4.0189	0.0410	48	15
2020-02	EVAP2	1.55	0.04	0.8116	0.0231	-6	4
2021-05	EVAP2	1.73	0.06	0.9015	0.0376	-8	11
2020-02	FIN	-11.92	0.03	-6.2802	0.0141	30	2
2021-05	FIN	-11.64	0.02	-6.1294	0.0157	35	6
2020-02	GLW	-40.38	0.16	-21.4977	0.0832	30	4
2021-05	GLW	-40.07	0.12	-21.3301	0.0774	35	14

The currently (18 July 2022) adopted values for δ17O for the secondary laboratory standards at FARLAB are listed in the table below. The combined uncertainty has been approximated from the standard error of the mean of all valid, calibrated sample results.

Standard	d17O	d17O_SEM	e17	e17_u
BERM	0.2539	0.0170	6	2
DI2	-4.0693	0.0228	37	4
EVAP2	0.8655	0.0177	-8	3
FIN	-6.1897	0.0250	33	2
GLW	-21.3971	0.0362	33	4
GRESP	-17.7232	0.0052	31	3

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