

TEL Technical Note No. 03

Stable Isotope Internal Laboratory Water Standards:

Preparation, Calibration and Storage

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Purpose:

The precision of a water stable isotope measurement is far better than its accuracy. Within a single stable isotope laboratory, very precise comparisons of isotopic compositions of materials can be carried out. For comparison of data produced in different laboratories, these data need to be calibrated to the same scale. For such purpose, internationally recognized reference materials (RMs) are needed which are available to all laboratories. If every analysis is calibrated by reference materials to the same scale, then the measured isotopic value for a substance should be the same in any analysing laboratory that is calibrated. However, internationally recognized isotope reference materials are expensive and are only available in limited quantities. Therefore, these materials should be used with great care and are often not appropriate for daily use. For example, water stable isotope standards supplied by the IAEA can only be requested once per year in maximum. Thus, the need arises to prepare internal laboratory standards for daily use in the laboratory for routine measurements. The purpose of this guidance is to describe how to prepare, calibrate, and store internal laboratory standards.

It is subdivided into several chapters covering relevant information on the following:

1. The term “Internal Laboratory Standard”.....	p.2
2. Selection and Preparation of Water Internal Laboratory Standards.....	p.2
3. Storage of Water Internal Laboratory Standards.....	p.3
4. Calibration of internal standards and samples.....	p.6
5. Example calibration scheme at IAEA.....	p.7
6. Uncertainty assessment.....	p.9
Recommended reading.....	p.9
Annex A: Stainless steel barrels for long term water storage.....	p.10
Annex B: Tool for water mixing calculation.....	p.11

1. The term “Internal Laboratory Standard”

An Internal Laboratory Standard (ILS) is a sample prepared at a laboratory locally for its use in routine calibration/quality control purposes. The ILS is calibrated by use of reference materials or International Measurement Standards (e.g. VSMOW2, SLAP2 for water) and has therefore assigned δ -values, in the case of water on the respective $\delta^2\text{H}$ and $\delta^{18}\text{O}$ VSMOW-SLAP scales. The uncertainty of its assigned δ -value includes the combined measurement uncertainty (from both the ILS and reference materials *measured* during their calibration) and the *assigned* uncertainty of the individual reference materials according to their certificates.

2. Selection and Preparation of Water Internal Laboratory Standards:

Each laboratory analysing the stable isotopic composition of water samples is advised to prepare several (at least two) internal laboratory water standards for routine use in the laboratory, for the purposes of calibration and of quality control. Their isotopic compositions need to be carefully calibrated using VSMOW2 and SLAP2 international measurement standards as references. Then these internal laboratory standards are used in routine analyses together with unknown samples to properly perform the sample calibration. The choice of these standards should be such that they cover the entire isotopic range of waters under investigation in the laboratory, or the total range of environmental waters i.e., from Antarctic snow melt to sea water. It is useful to prepare sufficient amounts of these internal laboratory standards to serve at least for a decade of measurements in the laboratory. The amount needed should be calculated by the frequency of measurements performed. Assuming that a single analysis by water-gas equilibration uses 4 mL water, and that four such standard measurements are performed each of 200 measurement days per year, it means a consumption of over 3 liters per year per ILS used. Therefore in such case it is recommended to produce amounts in the range of 30 liters or more per ILS. Similar calculations apply for infrared laser systems with generally lower amounts required.

As every year one set of VSMOW2/GRESP/SLAP2 IAEA reference waters can be ordered by any laboratory to recalibrate its existing internal laboratory water standards, with time the confidence in its ILS isotopic values should increase. Using this method and adding up such individual calibration data with time, a laboratory will continuously produce refined and improved means and lower uncertainties for its Internal Laboratory Standards used. This is another reason why ILS should be used for long time and a large amount of water should be prepared for each ILS.

For daily routine measurements laboratories should use at least two internal laboratory standards of different isotopic composition for calibration of the unknown samples. These ILS should be chosen to isotopically bracket the bulk of samples analyzed. In general, the isotopic composition of one laboratory standard should be close to that of sea water or VSMOW2 (zero per mill), which can be distilled sea water or precipitation from equatorial latitudes. The other one should be depleted in ^2H and ^{18}O at the lower end of δ -values of samples to be analysed. It could for example be obtained from high mountain snow. In some cases, melted Antarctic ice is available from ice core libraries or from Antarctic researchers. If applications are isotopically narrow ranged with only small isotopic variation, a suitable pair of ILS should be used. With such two ILS standards on a daily basis the scale normalization can be performed successfully. These waters should normally be of low salinity (not like sea water) in order to have a similar chemical composition as analyzed water samples. It is usually not recommended to use waters containing a lot of dissolved substances or even particles due to probable clogging effects in

various analytical methods and due to possible problems like growth of algae in the water during longer storage times. Selected samples should ideally be in a pH range between 5.5 and 8 to avoid analytical problems with usual instrumentation. The use of distilled water is possible [Fig.1], it provides no analytical problem, but is eventually not similar enough to normal samples. It is highly recommended for quality control purposes to use a third ILS with an isotopic composition intermediate to the two internal laboratory standards used for daily calibration. This third ILS should also be analysed on a daily basis as quality control standard and analyses compiled and stored for long term checks. Comparing its daily measured δ -value to its reference δ -value enables a continuous check of the quality of daily calibrations and measurements. The preparation of 2-3 more internal laboratory standards helps to keep a long term consistency even when one standard gets exhausted and replacements have to be prepared.

Restrictions on the kind of water samples to be used as ILS depend very much on the analytical method (mass spectrometry with online/offline sample preparation, laser spectroscopy) and kind of samples analysed (fresh water, sea water, leave leachates, juices, ...).



Fig.1: Modified commercial distillation unit for distillation from a closed tank (lower right side) into another tank at lower left side, to minimise any isotopic change of the water during distillation.



Fig.2: Sealed 20mL glass ampoules as used by IAEA for long term storage of water reference materials.

3. Storage of Water Internal Laboratory Standards:

Containers selected for long term water storage need to prevent any change of the water isotopic composition with time due to water evaporation or isotopic exchange. The most reliable containers are hermetically sealed glass ampoules, like the ones in which VSMOW2 and SLAP2 reference materials are provided by the IAEA [Fig.2]. Such ampoules sealed with a gas torch are very reliable for long term storage of water samples.

Depending on analytical systems and necessary water amounts, 25mL glass ampoules with 20mL of water or 5ml ampoules with 4ml of water are usual sizes. The amount in the ampoule should be selected to provide sufficient aliquots for daily measurements (often 3-4 aliquots for

each ILS are a good choice). After filling and sealing, ampoules can be sterilized by using a food canning device or oven to heat the ampoules to about 105°C over a period of eight hours. This sterilization will eliminate the possibility of growth of algae or other unwanted biological activities. Ampoules should be put upside down when heated. In this manner, any non-tight ampoules will leak out and can be easily identified. For ampoule flame sealing, the cheapest commercial ampoule filling devices cost over 2000 Euros, and manual gas torches are available at prices below 100 Euros. Costs for glass ampoules are below one Euro per item. With use of two internal laboratory standards per day and a quality control sample, 200 measurement days correspond to a total of 600 ampoules needed per year.

At the IAEA, for a proper long term storage of water reference materials and internal laboratory standards, stainless steel tanks as used in food industry for storage of beverages (beer kegs) were adapted for stored amounts between 10 to 300 litres [Fig.3]. See annex A for details of the assembly and for some examples of supplier addresses. The tanks are water diffusion tight. The tanks were equipped with a special dispensing system consisting of an extraction valve attached to a tube reaching down to the bottom of the tank for extraction of water and a second valve with manometer and a tube connecting it to the headspace at top of the tank, to keep the tank under a slight overpressure of argon gas [Fig.4]. In this manner water can be dispensed just by opening the water extraction valve, with water being flushed out via the bottom tube by the headspace argon gas overpressure. Thus water can be extracted out of the tank without any exposure of the laboratory standard to the outside atmosphere. This it avoids any risk of isotopic change of stored water by evaporation or isotopic contamination with air moisture. Only in case the headspace gas pressure gets too low (less than 100 hPa overpressure), dry argon gas from a gas cylinder needs to be refilled into the headspace through the second valve and tube to reach a pressure of 250 hPa. Higher pressure is not necessary, avoids higher amounts of dissolved gas, and it avoids larger sample loss in the rare case of potential outlet valve leakage.

It would be not convenient to use the tanks to extract small millilitre amounts on daily basis, as after any water extraction the water remaining in the tubing between closing valve and atmosphere is subject to evaporation and associated isotopic change. Thus, that remaining water needs to be removed from the outlet (e.g. by blowing water out of the tube with pressurized air). For the same reason, the outside tubing needs to be rinsed with sufficient amount of water before taking a sample.

At the IAEA for routine work with ILS using mass spectrometry and water equilibration (3ml per sample), every week from each ISL tank a subsample in a 250ml glass bottle (with plastic stopcock and plastic insert) is filled to the top. For use by laser spectrometers, a 100 ml glass bottle is more appropriate. For daily use, after shaking the bottles, individual samples are taken out of these bottles via pipettes, thus exposing the water in the bottle for short time to atmospheric moisture. After one week each used bottle is filled up again to the top, without discarding the remaining portion of the precious ILS. This method keeps any net isotope change to the stored ILS negligible despite the unavoidable small evaporation and exposure to air during each opening for pipetting standards. Special care is necessary to use high quality glass bottles with minimal evaporation effects through their plastic stopcocks. The use of plastic bottles should obviously be avoided. More details can be found in a "TEL Technical Note 04" on water evaporation out of bottles. The use of small glass bottles with greased glass stopcocks avoids any possible evaporation during storage.

Alternative storage methods for large amounts include storage in glass bottles with greased glass stopcocks. However, such bottles are limited in size to one or two litres volume. Larger volume greased stopcock bottles are very expensive and not easy to handle due to their weight. Repeated decanting of water from those bottles exposes the headspace each time to air moisture

with a resulting gradual isotopic drift of the water, which should be taken into account. The use of glass bottles with plastic caps and additional plastic inserts is cheaper, and may be used in case the other methods are not available. The use of plastic bottles is generally not recommended due to ongoing water permeation through the plastic material, causing even for high quality products measurable isotopic drifts over longer storage periods.



Fig.3: Stainless steel tank for storage of water internal laboratory standards with water dispensing assembly.

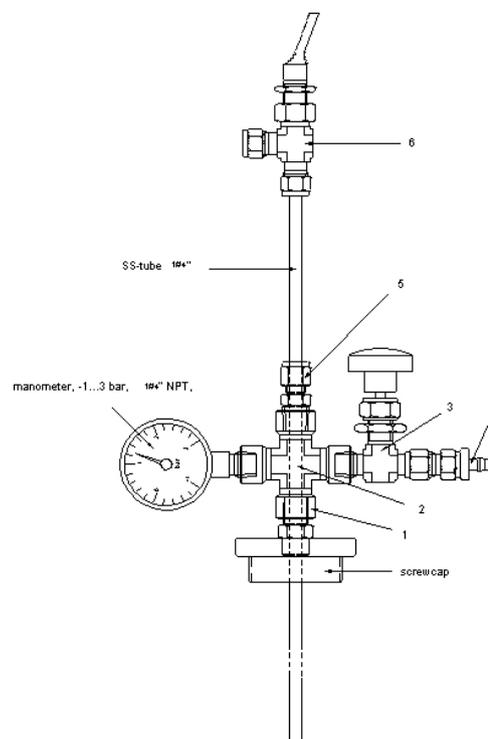


Fig.4: Sketch of water dispensing assembly for stainless steel tanks.

4. Calibration of internal standards and samples:

A prerequisite for an optimal calibration of ILS standards is achieving a satisfactory reproducibility of the sample preparation system and that of sample measurements on the used analytical system. Two main steps are necessary to calibrate sample results versus the internationally agreed VSMOW/SLAP scale.

First, the internal laboratory standards have to be calibrated directly versus VSMOW2 and SLAP2 to define their isotopic composition. This is performed by analyzing several aliquots of VSMOW2, SLAP2, GRESP and the internal laboratory standards to be calibrated on the same day. The obtained measurement results for the internal laboratory standards are thus calibrated in reference to known assigned isotopic values of VSMOW2 and SLAP2 on the VSMOW/SLAP scale (see equations below). The third calibrated standard GRESP is used as a control sample to monitor the successful calibration of the internal laboratory standards. Be aware that the calibration is performed on the VSMOW/SLAP scale, while the actual

international measurement standards used for the calibration are VSMOW2 and SLAP2. This is possible due to their isotopic δ -values having been carefully calibrated on the VSMOW/SLAP scale.

Secondly, for daily routine analysis, samples are then analyzed together with internal laboratory standards and calibrated on the VSMOW/SLAP scale using the previously determined reference values of the internal laboratory standards. A third internal standard should be used as known quality control sample to assess the daily performance of the system.

4.1 Calibration method:

Here two laboratory standards are used, denominated with LS1 and LS2. This could be any internal laboratory standard or the standards VSMOW2 and SLAP2 in case of an internal standard calibration. Raw data are expressed versus working standard (“WS”), the final calibrated and normalized data versus VSMOW/SLAP scale are also marked (“cal”).

Each sample is evaluated according to the following formula:

$$\delta^2 H_{cal}^{sample} = \delta^2 H_{cal}^{LS1} + \left(\delta^2 H_{WS}^{sample} - \delta^2 H_{WS}^{LS1} \right) \times \left(\frac{\left(\delta^2 H_{cal}^{LS2} - \delta^2 H_{cal}^{LS1} \right)}{\left(\delta^2 H_{WS}^{LS2} - \delta^2 H_{WS}^{LS1} \right)} \right)$$

All values marked with “WS” are obtained from current measurements. Those marked with “cal” on the right side of the equation are known reference values. In case of calibration of an internal laboratory standard, LS1 and LS2 would correspond to VSMOW2 and SLAP2, respectively. In case of normal sample measurements, they would be two of the calibrated and normalized internal laboratory standards. The factor in large brackets at the right side of the equation is the calibration/normalization factor and can be interpreted as measure of the scale compression of the performed measurement and of the analytical system. The same formula of course is valid for $\delta^{18}\text{O}$, too.

5. Example calibration scheme for internal laboratory standards used at the IAEA:

At the IAEA, special measurement evaluation schemes were developed for water stable isotopic measurements. The easiest to use is an Excel spreadsheet template, in which raw measurements data are inserted together with calibrated values of standards, and which evaluates all data from a measurement run, regardless whether it is a Dual Inlet Mass Spectrometer with water-gas equilibration or an infrared laser spectroscopy equipment. A much more sophisticated and automated method is the Excel based program SICalib, in which raw data are imported and corrected for memory, drift, and then calibrated with a complete uncertainty calculation, virtually for all kinds of measurement systems. For purely laser-based measurements, other evaluation schemes are also offered by other groups (LIMS for lasers).

In the following an example is given for the manual template, with a special measurement scheme applied for calibrations using a dual-inlet mass spectrometer and associated 48-port water equilibration device with 3 mL water sample size. Due to the of 20mL limitation of available water amount in glass ampoules for international measurement standards, for each standard ampoule six individual samples can be prepared for measurement. Therefore the equilibration device is filled with 6 samples each of the following standards: VSMOW2, SLAP2, GRESP, plus the samples of five internal laboratory standards to be calibrated. Sample

positions are interspersed to avoid masking of time related effects. In the following Table 2 results are given from an actual calibration in the year 2005 (at that time still using VSMOW, SLAP and GISP).

Table 1: Example of a $\delta^{18}\text{O}$ calibration performed at the IAEA.

$\delta^{18}\text{O}$		Calibration		MS: Delta+/EQ48				2005- Date: 04-12	
$\delta^{18}\text{O}$ values □ vs. WS in ‰									
	VSMOW	SLAP	Std7	Std8	GISP/Std9	Std10	Std11	Std12	
1	16.02	-40.53	15.96	4.48	-9.21	-35.80	16.12	3.76	
2	*15.57	*-40.27	15.95	4.52	-9.22	-35.85	16.11	3.68	
3	15.99	-40.55	15.96	4.48	-9.21	-35.84	*15.61	3.78	
4	16.02	-40.52	15.96	4.47	-9.20	-35.83	16.12	3.75	
5	15.99	-40.52	15.92	4.47	-9.24	-35.80	16.09	3.74	
6	16.05	-40.49	15.92	4.48	-9.20	-35.73	16.06	3.75	
7									
8									
Average	16.01	-40.52	15.95	4.48	-9.21	-35.81	16.10	3.74	
std.dev.	0.03	0.02	0.02	0.02	0.02	0.04	0.03	0.03	
Max	16.05	-40.49	15.96	4.52	-9.20	-35.73	16.12	3.78	
Min	15.99	-40.55	15.92	4.47	-9.24	-35.85	16.06	3.68	
N	5	5	6	6	6	6	5	6	
Reference values for calibration standards (on VSMOW-SLAP scale)									
	ref.value	± uncert.							
VSMOW	0.00	0							
SLAP	-55.50	0							
GISP	-24.76	± 0.09							
Correction factor for VSMOW-SLAP scale = 0.9816754									
$\delta^{18}\text{O}$ results vs VSMOW-SLAP in ‰ (calibrated & normalised on VSMOW-SLAP scale)									
	cal.value	± uncert.	ese comb.	ese statist.					
VSMOW	0.00	0							
SLAP	-55.50	0							
Std7	-0.07	0.02	0.017	0.020					
Std8	-11.32	0.02	0.017	0.020					
GISP/Std9	-24.77	0.02	0.016	0.020					
Std10	-50.87	0.02	0.023	0.020					
Std11	0.08	0.02	0.019	0.020					
Std12	-12.05	0.02	0.020	0.020					

Note for Table 1: On that day, one $\delta^{18}\text{O}$ measurement failed each for VSMOW, SLAP and Std11 at the calibration on 12 March 2005, and was marked in the list and excluded from further calculations. The final calibrated values were calculated from the average values for each sample against working standard. The calculated value for GISP (same water as Std9) corresponds nicely with its reference value, therefore assuring a proper calibration of the internal standards. Calculated uncertainties include standard errors of the mean (ese) of the measured sample and those of the standards VSMOW and SLAP. They do not include other terms like the uncertainty of the reference value or long term statistics on previous calibrations.

That manual calibration template including uncertainty calculations, or the Water Stable Isotope Calibration Program SICalib are available from the IAEA from this website

https://nucleus.iaea.org/rpst/ReferenceProducts/Analytical_Methods/Stable_Isotope_Reference_Laboratory/index.htm

or from the author (m.groening@iaea.org) on request.

As example of the calculation performed, Std7 is taken from Table 2. The average of six determinations for Std7 is:

$$\delta_{WS}^{sample} = \delta_{WS}^{Std7} = 15.95\text{‰}$$

Similarly

$$\delta_{WS}^{LS1} = \delta_{WS}^{VSMOW} = 16.01\text{‰}$$

$$\delta_{WS}^{LS2} = \delta_{WS}^{SLAP} = -40.52\text{‰}$$

Using the equation of section 4.1 and the reference values

$$\delta_{cal}^{LS1} = \delta_{cal}^{VSMOW} = 0\text{‰} \text{ (per definition !)}$$

$$\delta_{cal}^{LS2} = \delta_{cal}^{SLAP} = -55.5\text{‰}$$

one obtains finally

$$\delta_{cal}^{sample} = \delta_{cal}^{Std7} = -0.07 \pm 0.02\text{‰}$$

This is the calibrated value with reference to SMOW-SLAP scale used in our laboratory.

6. Uncertainty assessment:

First, the standard deviations of the sample measurements are compiled. These should be compared with the routine long term reproducibility of measurements in the laboratory. In case the samples show much smaller standard deviations (less than 40% of the long term reproducibility), then these standard deviations may underestimate the real variability. In this case it is recommended to use the long-term reproducibility instead.

From the standard deviation value the estimated standard error of the mean (ese) is calculated by dividing the standard deviation by the square root of the number of measurements. This value is squared and then added to the squares of ese-values compiled for VSMOW and SLAP measurements (and principally with their reference value uncertainties, which are zero in this special case). The square root of this term is then used as proxy of the uncertainty for each sample. This method is only a proxy for the uncertainty associated to each sample. In practice the spread between several calibrations carried out over the years may be still slightly higher. For example the reference $\delta^{18}\text{O}$ value for Std7 was set to -0.07‰ in 2003. The average of 16 calibrations performed over more than 10 years using two mass spectrometers provided a mean value of $-0.064 \text{‰} \pm 0.024 \text{‰}$.

Much more sophisticated uncertainty evaluation methods are used in the program SICalib.

Recommended reading:

1. GRÖNING, M., Improved water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ calibration and calculation of measurement uncertainty using a simple software tool. *Rapid Communications in Mass Spectrometry* 25 (2011) 2711-2720.
2. GRÖNING, M., SICalib User Manual (Stable Isotope Calibration for routine δ -scale measurements) Ver 2.16j. TEL Technical Note 01, International Atomic Energy Agency, May 2018, 37p.: [link to be included here](#)
3. FAGHIHI, V., MEIJER, H.A.J, GRÖNING, M: A thoroughly validated spreadsheet for calculating isotopic abundances (2H , 17O , 18O) for mixtures of waters with different isotopic compositions. *Rapid Communications in Mass Spectrometry* 29, 2015, 1351-1356.
4. GONFIANTINI, R.: Standard for stable isotope measurement in natural compounds. *Nature*, 217, 1978, 534 - 536.
5. GONFIANTINI, R.: Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations. Vienna 19 - 21 September 1983. Report to the Director General, IAEA Vienna 77p.
6. IAEA: Stable Isotope Hydrology: Deuterium and Oxygen-18 in the Water Cycle. Technical Reports Series No. 210. IAEA Vienna 1981 (Chapter 4 pp .35 - 84).
7. HUT, G.: Consultants' group meeting on stable isotopes reference samples for geochemical and hydrological investigations. Report to the Director General, IAEA Vienna. April 1987.
8. GRÖNING, M., VAN DUREN, M., PÖLTENSTEIN, L., TANWEER, A., JAKLITSCH, M., GATTIN, M.: Quality Assurance for Water Stable Isotope Analysis by Mass Spectrometry. IAEA internal report, Technical Procedure Note No. 41. IAEA Isotope Hydrology Laboratory, 2006, 1-13
9. HOEFS, J.: Stable Isotope Geochemistry, Springer - Verlag New York, 1973, 140 p.

€

Annex A: Stainless steel tanks with water extraction system for long term water storage

The principle of water extraction from stainless steel tanks is shown in the figure below. A slight overpressure of less than 500 hPa of suitable gas (nitrogen or argon) is maintained in the headspace of the tank, introduced from tube connector 4 via valve 3 and pressure controlled by the manometer. When opening the extraction valve 6, then the gas pressure forces water into the spear tube reaching down to the bottom of the tank and induces it to flow out through valve 6. As no air is pumped into the headspace, no atmospheric moisture can contaminate and alter the isotopic composition of the water in the tank. After stopping the valve 6, it has to be noted that some water remains in the external side of the valve and has to be removed (blown out by pressurized air and then waiting until completely dried), before using the extraction system again (or rinsing it sufficiently long).

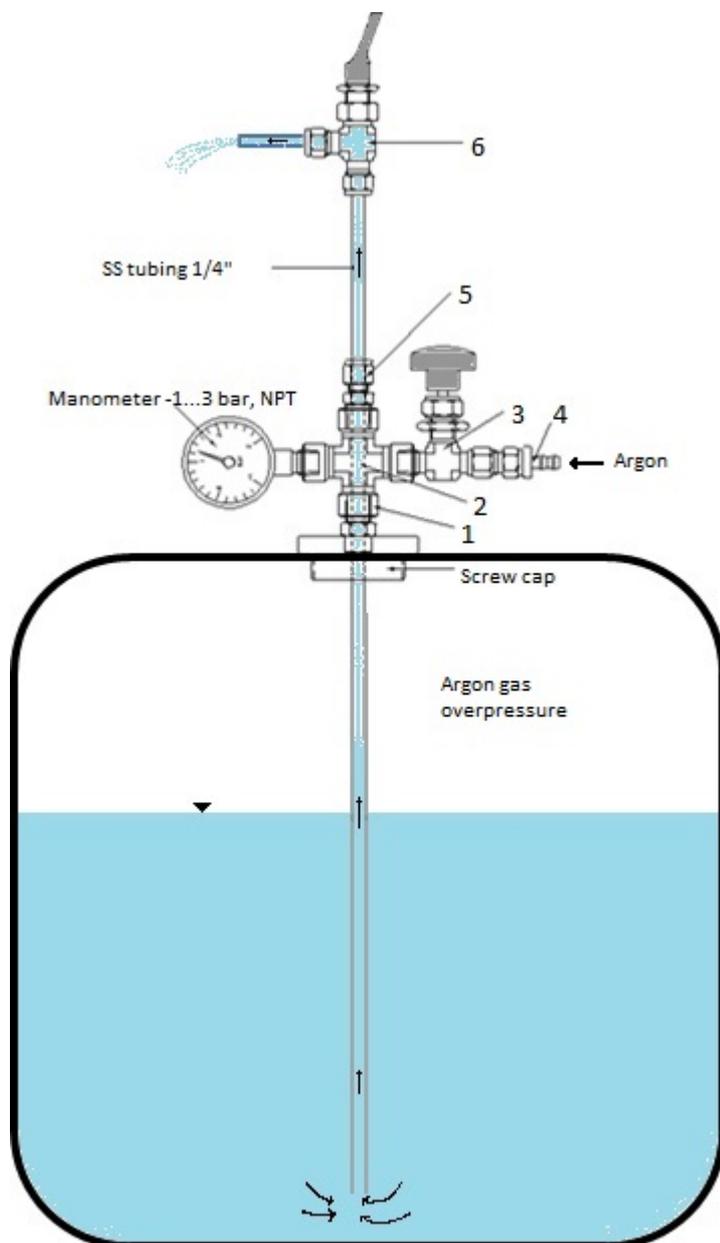


Fig.5: Complete assembly of storage tank with water extraction / gas fill system.

A complete order (for tank & water dispensing system) can be placed at the following company for the complete setup of a storage tank (e.g. 25 liters) and the water dispensing system, gas injection system and pressure gauge at a price around 500 € per set in the year 2013:

V&F HANDELS KG
 Dr. Friedrich Stöhrigasse 6
 2340 Mödling
 AUSTRIA
 Tel.: 0043/2236/908184
 Fax.: 0043/2236/908185
office@vundf.at
www.vundf.at

As separate parts, the stainless steel tanks can be ordered from suppliers for juice- and wine processing equipment:

Franke: http://www.franke.com/en/activities/beverage_systems/index.html

Schäfer: <https://www.schaefer-container-systems.de>

SuperMonte:

http://www.kegsmanufacturing.com/kegs_manufacturing_beer_keg_manufacturer_suppliers_made_italy.htm

Webpages of supply companies for extraction parts (see Table 2 below):

Swagelok: <http://www.swagelok.com/>

Parker: <http://www.parker.com>

Table 2: Part list for stainless steel barrel dispensing system (around 200 € in 2018)

		Part Number List		
Part	Description	V&F	Swagelok	Parker
1	Male connector for welding	IP68TS06H04	SS-6-TSW-1-4	6FW-316
2	Female cross	102H SS 1/4	SS-4CS	4FX-316
3	Needle valve	H-395U-SS-NL-R-1/4-RS	SS-1KM4-S4	4M4Z- V4LN-SS
4	Tube adapter	130LT SS 1/4 X 1/4	SS-4-HC-A-401	4B2TU4-316
5	Male connector	768L SS 1/4 X 1/4 TC	SS-400-1-4BT	4MTC4N-316
6	Toggle valve	H-1200-SS-L-1/4-A	SS-1GS4	4A-V4AQ-SS

For assembly, additionally a conventional manometer (range of 2000 hPa) is needed, and the necessary ¼ inch stainless steel tubing in appropriate length. A hole has to be drilled into the upper side cap of the tank and the male connector has to be welded to it.

Annex B: Tool for calculation of isotopic composition for gravimetric water mixing

The preparation of new internal laboratory standards can be performed easily by using spare amounts of already calibrated water samples in a laboratory. So it is possible to calibrate first larger amounts of two water samples with widely different isotopic composition (e.g. sea water and high mountain snow) and later on to prepare a whole suite of intermediate standards for use in the laboratory.

A publication on a spreadsheet tool for easy calculation of resulting isotopic properties of gravimetric mixing of water samples is available here:

<https://onlinelibrary.wiley.com/doi/abs/10.1002/rcm.7232>

and the spreadsheet itself can be downloaded here:

https://nucleus.iaea.org/rpst/ReferenceProducts/Analytical_Methods/Stable_Isotope_Reference_Laboratory/index.htm

This spreadsheet was developed and validated for general water mixture processes including those using also isotopically enriched waters with isotopic compositions provided as isotopic abundances instead of delta-values. The mixing can be done for up to five different water samples mixed together gravimetrically.