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Department of Nuclear Sciences and Applications
IAEA Environment Laboratories**

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**(in cooperation with the US National Institute for Standards and
Technology (NIST))**

**REFERENCE SHEET FOR INTERNATIONAL
MEASUREMENT STANDARDS**

**VSMOW2 Vienna Standard Mean Ocean Water 2, water
($\delta^2\text{H}_{\text{VSMOW-SLAP}}$, $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$)**

**SLAP2 Standard Light Antarctic Precipitation 2, water
 $\delta^2\text{H}_{\text{VSMOW-SLAP}}$, $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$)**

Reference values for the relative difference in hydrogen and oxygen stable isotope-amount ratio for the international measurement standards [1]

Table 1: $\delta^2\text{H}$ and $\delta^{18}\text{O}$ reference values for the two international measurement standards VSMOW2 and SLAP2 and their associated combined standard uncertainties (1σ level) on the VSMOW-SLAP scale.

IAEA name	NIST code	Material	Reference value $10^3 \times$ $\delta^2\text{H}_{\text{VSMOW-SLAP}}$	Combined standard uncertainty $10^3 \times$ $\delta^2\text{H}_{\text{VSMOW-SLAP}}$	Reference value $10^3 \times$ $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$	Combined standard uncertainty $10^3 \times$ $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$
VSMOW2	RM 8535a	Water	0	0.3	0	0.02
SLAP2	RM 8537a	Water	-427.5	0.3	-55.50	0.02

Origin and preparation of the material

The two international measurement standards VSMOW2 and SLAP2 were prepared at the IAEA following a recommendation of a Consultants Group Meeting convened by the IAEA in December 1996.

VSMOW2 was prepared at the IAEA Isotope Hydrology Laboratory in 1999 from three selected fresh water samples, obtained from Lake Bracciano located near Rome, Italy (R. Gonfianini, G.-M. Zuppi), from Lake Galilea, Israel (E. Adar) and from a well located near Cairo, Egypt (F. Hussein). The raw water samples were selected to be sufficiently close to the isotopic composition of VSMOW and were mixed in appropriate proportions to obtain an isotopic composition of the mixture as close as possible to VSMOW. The $\delta^2\text{H}$ value of one of these raw materials had to be initially adjusted isotopically by about 6 ‰ to allow the production of about 300 litres of VSMOW2. This adjustment was performed by a modified platinum catalytic exchange reaction through diffusive exchange of hydrogen gas between two membrane separated compartments containing the raw water and deuterated water to avoid any change of the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values. The raw water isotopic compositions were carefully calibrated in five selected laboratories: IAEA Isotope Hydrology Laboratory, Vienna, Austria (M. Gröning); USGS Reston Stable Isotope Laboratory, Reston, Virginia, USA (T.B. Coplen); Center for Isotope Research, Groningen, Netherlands (H.A.J. Meijer); GFZ Isotope Hydrology Laboratory, Neuherberg, Germany (W. Stichler); University of East Anglia Isotope Hydrology Laboratory, U.K. (P. Dennis). Based on the calculated isotopic compositions, the gravimetric final mixing of the three samples was performed at IAEA into an especially constructed large storage container to produce 300 litres of VSMOW2. After filling the container, the water was internally circulated in the container for several hours for complete mixing. From this container put under slight overpressure of Argon, initially 5000 glass ampoules were filled with 20 mL of VSMOW2 each using the slight gas overpressure and an attached dispenser. The remaining portion of about 200 litres was kept in the original container for further ampouling whenever needed. In 2016 additional 5000 ampoules containing 4 mL VSMOW2 each were filled from the original container in order to support applications needing only smaller amounts of this reference material per calibration measurement.

SLAP2 was prepared at the IAEA Isotope Hydrology Laboratory in 2006 from four selected Antarctic snow/ice samples obtained from the U.S. National Science Foundation's South Pole station (coordinated by T.B. Coplen), from an ice core of the Vostok drilling site (J.M. Petit), from the Dome F drilling site (O. Abe) and from the Dome C drilling site (O. Abe). The $\delta^2\text{H}$ composition of the last material had to be isotopically shifted by about 60 ‰ to allow the production of about 280 litres of SLAP2. This adjustment was performed by a modified platinum catalytic exchange reaction of deuterium enriched H_2 gas produced by a zinc reduction of deuterated water with the selected raw water. Its isotopic $\delta^2\text{H}$ value was thereby adjusted without affecting its $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values. The mixing was performed after a calibration of the four waters at the IAEA Isotope Hydrology Laboratory, Vienna, Austria. Altogether 280 litres of SLAP2 were mixed gravimetrically from the four water samples in a specially constructed 300 litres container. Following the same procedure as described above for VSMOW2, initially 5000 glass ampoules were filled with 20 mL of SLAP2 each. The remaining portion of about 180 litres was kept in the original container. In 2016 additional 5000 ampoules containing 4 mL SLAP2 each were filled from the original container in order to support applications needing only smaller amounts of this reference material per calibration measurement day.

Each material is issued in units of 20 mL water in flame sealed glass ampoules.

Homogeneity of the material

VSMOW2 and SLAP2 are filled in 20 mL sealed glass ampoules. The homogeneity of the initially produced 5000 ampoules of 20 mL for both standards and of the filling procedure has been investigated by analyses of 27 ampoules each by isotope mass spectrometry and using water-gas equilibration methods with the gases CO_2 (for $\delta^{18}\text{O}$ analysis) and H_2 (for $\delta^2\text{H}$). The isotopic data measured from subsamples of each ampoule within one

or two measurement days were compiled to derive the overall measurement reproducibility. The average of all reproducibility data was compared with the standard deviation of ampoule means to estimate the possible isotopic inhomogeneity between ampoules as a residual of their isotopic means differences. As an independent approach, the “between-bottle” inhomogeneity was calculated by single factor ANOVA analysis [13, 14]. The uncertainty contribution of possible inhomogeneity between ampoules was found to be negligible at levels of below ± 0.004 ‰ for $\delta^{18}\text{O}$ and of below ± 0.07 ‰ for $\delta^2\text{H}$. The largest uncertainty component was due to the limited number of only six measurements which could be performed from water of one ampoule, as three mL were used for each subsample measurement. This limited the overall precision of the realization of the reference value.

Characterization study

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ reference values for VSMOW2 and SLAP2 in Table 1 were derived from a characterization study in direct reference to measurement results of their predecessor materials VSMOW and SLAP under repeatability conditions using three dual inlet isotope mass spectrometry systems. This minimized the resulting uncertainty of the measurement process due to direct comparison of the new international measurement standards with their predecessors.

The characterization was carried out in three isotope hydrology laboratories, namely the U.S. Geological Survey (USGS) laboratory in Reston, Virginia, USA; the Center for Isotope Research, University of Groningen, Netherlands; and the IAEA Isotope Hydrology Laboratory, Vienna, Austria. All three laboratories used dual inlet isotope ratio mass spectrometry combined with sample preparation using a water-gas equilibration method. For both $\delta^2\text{H}$ and $\delta^{18}\text{O}$, the calculated mean value and the calculated combined standard uncertainty are combining all measurements performed in the three laboratories. Combined standard uncertainties were calculated from results of measurements performed under repeatability conditions in direct comparison with the predecessor materials. They include contributions from evaluated upper limits for the inhomogeneity between bottled glass ampoules and the residual bias of the evaluated mean values. The results can be stated as follows in the paragraph assignment of values.

Assignment of values - Certification procedure

The $\delta^{18}\text{O}$ value of VSMOW2 is identical to that of VSMOW within the uncertainty of the measurements performed. The $\delta^2\text{H}$ value of VSMOW2 is identical to that of VSMOW within the uncertainty of measurements performed. The $\delta^{18}\text{O}$ value of SLAP2 is identical to that of SLAP within the uncertainty of measurements performed. The $\delta^2\text{H}$ value of SLAP2 is -427.5 ± 0.3 ‰. There is sufficient confidence in the performed $\delta^2\text{H}$ measurements of SLAP2 by the three laboratories to conclude the presence of a significant deviation from the $\delta^2\text{H}$ value of SLAP. The combined standard uncertainty associated to $\delta^2\text{H}$ and $\delta^{18}\text{O}$ reference values of VSMOW2 and SLAP2 as provided in Table 1 (rounded to two significant digits for $\delta^{18}\text{O}$) has to be included in any derivation of combined standard uncertainties of measurements performed in laboratories using VSMOW2 and SLAP2 as calibrators.

The details concerning all reported results as well as the criteria for certification may be found in the references as cited. These documents are available free of charge upon request.

Statement on metrological traceability and uncertainty of assigned values

The δ -values of the predecessor materials VSMOW and SLAP had borne no associated uncertainty due to their use in initially defining the VSMOW–SLAP $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ and $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$ scales. The δ -values for VSMOW were defined; the δ -values for SLAP were fixed by convention as the best possible assignment from measurements using independent techniques [2-7]. For analytical results of SLAP see results of two interlaboratory comparisons [8, 9].

The traceability chain for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ measurement results performed in testing laboratories, using VSMOW2 and SLAP2 as calibration standards, ends with the δ -values of these two materials calibrated in reference to

their successor materials VSMOW and SLAP, which serve as new international measurement standards. The use of VSMOW2 and SLAP2 for calibration of isotopic measurements is still done on the originally established respective $\delta^2\text{H}_{\text{VSMOW-SLAP}}$ and $\delta^{18}\text{O}_{\text{VSMOW-SLAP}}$ scales.

Intended use

The international measurement standards VSMOW2 and SLAP2 are intended for calibration purpose and provide water standards with reference values of the relative difference in $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ isotope-amount ratios expressed in the VSMOW–SLAP δ -scales. These two materials are distributed in 20 mL ampoules by the International Atomic Energy Agency (IAEA), Vienna, Austria. The 20 mL ampoules are further distributed by the National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, USA, with the following NIST material codes: RM 8535a for VSMOW2 and RM 8537a for SLAP2.

Instructions for use

It is recommended that these materials be used to calibrate/check internal laboratory standards immediately upon opening. The use of VSMOW2 and SLAP2 in different laboratories allows investigators to obtain $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data which are comparable worldwide [11, 12] on the respective VSMOW–SLAP δ -scales. Users are strongly advised to prepare their own internal standards for daily use and calibrate those standards against these international standards and reference materials.

Handling and storage

The original unopened ampoules should be stored at ambient temperature in the dark. It is not recommended to store unused fractions of the materials after opening ampoules due to the strong possibility of evaporation losses with possible significant isotope fractionation. Therefore, the reference values in this reference sheet do not apply for such retained portions. Under no circumstances may any portion of the material be used for repeated calibrations by repeated stable isotope measurements using water/ CO_2 equilibration devices on subsequent days, due to the isotopic exchange with the applied gas and corresponding shift of the isotopic composition of the material during the preparation process.

Issue and expiry date

The issue year of these Reference materials was 2006. The first version of the reference sheet was issued on 5 May 2009. The reference values for the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of VSMOW2 and SLAP2 are valid until 31 December 2026, provided the original ampoules are handled and stored in accordance with the instructions given in this reference sheet (see “Handling and Storage”). This certification is nullified if the glass ampoule container is damaged.

Normalization

The δ -values are stated in this reference sheet as parts per thousand difference (per mill; ‰) from the VSMOW δ -value normalized with the defined SLAP δ -value. The adoption of VSMOW as zero point of the δ -scale and of a fixed SLAP δ -value by convention corresponds to the normalization of δ -values on the VSMOW – SLAP scale [2]. A general formula can be expressed with two laboratory standards LS1 and LS2, which would correspond to VSMOW2 and SLAP2 in a calibration exercise, to calibrate an unknown sample. For hydrogen, the formula is:

$$\delta^2\text{H}_{\text{sample,cal}} = \delta^2\text{H}_{\text{LS1,cal}} + (\delta^2\text{H}_{\text{sample,WS}} - \delta^2\text{H}_{\text{LS1,WS}}) \times f \quad (1)$$

with the normalization factor f being

$$f = (\delta^2\text{H}_{\text{LS2,cal}} - \delta^2\text{H}_{\text{LS1,cal}}) / (\delta^2\text{H}_{\text{LS2,WS}} - \delta^2\text{H}_{\text{LS1,WS}}) \quad (2)$$

where

the subscript _{WS} denotes measurements performed versus an isotope mass spectrometer transfer gas (working standard), the subscript _{cal} denotes calibrated measurements performed versus the VSMOW–SLAP δ -scale, and $\delta^2\text{H}_{\text{LS1,cal}}$ and $\delta^2\text{H}_{\text{LS2,cal}}$ are the calibrated isotopic values of reference materials or calibrated internal laboratory standards LS1 and LS2 used for calibration, in this case the conventionally fixed $\delta^2\text{H}$ values for VSMOW2 and SLAP2 (see Table 1).

This $\delta^2\text{H}$ -value definition in Eq. (1) coincides with the classical one [11] only if $f = 1$, that means if no scale compression occurs and the δ -values measured with the used instrument correspond exactly to the recommended values $\delta^2\text{H}_{\text{VSMOW2}}$ and $\delta^2\text{H}_{\text{SLAP2}}$ (Table 1).

A corresponding formula is to be applied for $\delta^{18}\text{O}$.

Please note that the reporting scales for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are still denoted and referred to as VSMOW–SLAP scales, despite the exhaustion of supply of VSMOW and SLAP and their replacement by the two new international measurement standards VSMOW2 and SLAP2 [15]. Therefore, in the above mentioned formulae (1) and (2), the measured values for the new international measurement standards VSMOW2 and SLAP2 have to be entered for LS1 and LS2 instead of those of VSMOW and SLAP as well as the corresponding calibrated $\delta^2\text{H}_{\text{SLAP2}}$ value for SLAP2 from Table 1 instead of that one for SLAP.

By using this procedure all data using VSMOW2 and SLAP2 for calibration are still reported on the VSMOW–SLAP scale. Of course the standard uncertainties of VSMOW2 and SLAP2 isotopic values in Table 1 have to be included in any uncertainty propagation together with uncertainties derived from measurements of the unknown sample and of measurements of the reference materials used, to calculate the combined standard uncertainty for the isotopic value of a sample.

Reporting of stable isotope δ -values

The following recommendations are provided for reporting of the relative difference of hydrogen and oxygen stable isotope amount ratios using the δ -notation modified from [16]. It is recommended that:

- $\delta^2\text{H}$ values of all hydrogen-bearing substances be expressed relative to the VSMOW-SLAP scale so that $\delta^2\text{H}_{\text{SLAP2}} = -427.5 \text{ ‰}$;
- $\delta^{18}\text{O}$ values of all oxygen-bearing substances be expressed relative to VSMOW or relative to VPDB (mainly for carbonates, defined by $\delta^{18}\text{O}_{\text{NBS19-VPDB}} = -2.2 \text{ ‰}$), on a scale such that $\delta^{18}\text{O}_{\text{SLAP2}} = -55.5 \text{ ‰}$;
- reporting of the relative difference of stable isotope-amount ratios relative to SMOW and PDB be discontinued [17].

Limit of distribution

Both materials are distributed as single 20 mL sealed glass ampoules each denoted as one unit. Three such units of each reference material may be ordered per laboratory in a three-year period. This allows each laboratory to purchase sufficient amounts of the calibration materials once per year. This will enable more frequent calibration of laboratory standards than in the past, and it will still ensure that the supply of these materials will last as long as possible.

Isotope-amount ratios in VSMOW2 and SLAP2

No isotope-amount ratios have yet been determined on VSMOW2 and SLAP2. As their isotopic compositions are very close to those of their predecessors VSMOW and SLAP, those values provide a good estimate of the

isotope-amount ratios in VSMOW2 and SLAP2. Those values as determined by [5-7, 18, 19] are listed in Tables 2 and 3 of the reference sheet for VSMOW and SLAP dated 1 December 2006 (https://nucleus.iaea.org/rpst/documents/VSMOW_SLAP.pdf). These isotopic values are those as recommended by the Bureau International de Poids et Mesures (BIPM) in 2005 in its isotopic correction of the definition of the kelvin temperature scale [20].

Information Values

The $\delta^{17}\text{O}$ value of VSMOW is zero by consensus, just as its $\delta^{18}\text{O}$ value is zero by consensus. The $\delta^{17}\text{O}$ value of VSMOW2 was measured and compared with that of VSMOW [21]. It is identical with that of VSMOW within an uncertainty of about ± 0.03 ‰. Additional measurements of $\delta^{17}\text{O}$ values were conducted by Ying Lin at the University of Chicago (Chicago, Illinois, USA) in 2007 on comparing VSMOW2 with VSMOW and SLAP2 with SLAP, confirming their $\delta^{17}\text{O}$ equivalence within uncertainties of about ± 0.05 ‰ in both cases [22].

The tritium activity concentration of VSMOW2, determined at the IAEA by direct gas counting, was 3.5 ± 1.0 TU on 6 July 2007. The tritium activity concentration of SLAP2 was 27.6 ± 1.6 TU on 6 July 2007. Both values are reported with their 1- σ standard uncertainties.

Legal disclaimer

The IAEA makes no warranties, expressed or implied, with respect to the data contained in this reference sheet and shall not be liable for any damage that may result from the use of such data.

Compliance with ISO Guide 31:2015

The content of this IAEA Reference Sheet is in compliance with the ISO Guide 31:2015: Reference materials – Contents of certificates, labels and accompanying documentation [10].

Citation of this reference sheet

It is suggested to cite this reference sheet according to the following example, as appropriate to the citation format used: INTERNATIONAL ATOMIC ENERGY AGENCY, Reference Sheet for VSMOW2 and SLAP2 International Measurement Standards. IAEA, Vienna, 8 pp. (Rev 1 dated 2017-07-11). (The latest version published applies; see “Note” below).

Note

Certified values as stated in this reference sheet may be updated if more information becomes available. Users of this material should ensure that the reference sheet in their possession is current. The current version can be found in the IAEA’s Reference Materials online catalogue:

<http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials>

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Reference Sheet Revision History:

- Original version: 2009-05-09
- Rev. 1: 2017-07-11: Update of weblinks and addresses; deletion of old information in regard to GISP