Reference Sheet
for
International Measurement Standards

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

VSMOW	Vienna Standard Mean Ocean Water	(δ^2H_{VSMOW}, $\delta^{18}O_{VSMOW}$)
SLAP	Standard Light Antarctic Precipitation, water	(δ^2H_{VSMOW}, $\delta^{18}O_{VSMOW}$)

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

Table 1: δ^2H and $\delta^{18}O$ reference values for the two international measurement standards VSMOW and SLAP.

IAEA name	NIST code	Material	1000 × δ^2H_{VSMOW}	1000 × $\delta^{18}O_{VSMOW}$	Reference
VSMOW	RM 8535	Water	0	0	[2, 3] Definition
SLAP	RM 8537	Water	– 428.0	– 55.5	[4-6] Convention

VSMOW and SLAP δ-values bear no associated uncertainty due to their use in defining the δ^2H and $\delta^{18}O$ scales. The δ-values for VSMOW are defined, the δ-values for SLAP are fixed by convention as the best possible assignment from measurements using independent techniques [4-9]. For analytical results of SLAP see results of two intercomparison exercises [10, 11].
The traceability chain for δ^2H and $\delta^{18}O$ measurement results performed in testing laboratories, using VSMOW and SLAP as calibration standards, ends with the δ-values of these two materials, serving as international measurement standards.
The contents of this reference sheet comply with the requirements of ISO Guide 31 [12].

Intended use

The international measurement standards VSMOW and SLAP are intended for calibration purpose and provide water standards with fixed values of relative difference in $^2H/^1H$ and $^{18}O/^{16}O$ isotope-amount ratios. Both materials are not more distributed since November 2006 due to exhaustion of stocks. However, due to the importance of these international measurement standards, this last updated version of the reference sheet is made available. Successor materials VSMOW2 and SLAP2 are produced and available from 2007 onwards. VSMOW and SLAP define the VSMOW-SLAP δ-scales for δ^2H and $\delta^{18}O$ measurements. A third certified reference material GISP is used in addition to check the successful calibration of internal laboratory standards by the use of VSMOW and SLAP. These materials were distributed by the International Atomic Energy Agency (IAEA), Vienna, Austria, and by the National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, USA, with the following NIST material codes: RM 8535 for VSMOW, RM 8536 for GISP and RM 8537 for SLAP.

It is recommended that these materials are used to calibrate/check internal laboratory standards immediately upon opening. The use of VSMOW and SLAP in different laboratories allows investigators to obtain δ^2H and $\delta^{18}O$ data which are comparable worldwide [2, 3]. Users are strongly advised to prepare their own internal standards for daily use and calibrate those standards against these international standards and certified reference materials. From 2007 onwards, the successor materials VSMOW2 and SLAP2 are distributed together with GISP as a set.

Sample preparation

VSMOW was prepared by H. Craig [2-4] by mixing distilled ocean water with small amounts of other water in order to adjust its δ^2H and $\delta^{18}O$ values as close as possible to that of the calculated reference point Standard Mean Ocean Water (SMOW) [3]. SLAP was obtained from a South Pole snow sample collected by E. Picciotto, Université Libre de Bruxelles, at Plateau Station, Antarctica, in 1967 [4]. Each material is issued in units of 20 mL water in a sealed glass ampoule.

Homogeneity

The two international measurement standards VSMOW and SLAP were prepared following a recommendation of an Advisory Group Meeting convened by the IAEA in 1966 [4]. VSMOW has been distributed by the IAEA since 1968. According to control analyses made by Craig, VSMOW has the same $^{18}O/^{16}O$ ratio as the defined SMOW, but a slightly lower $^2H/^1H$ ratio (0.2 ‰), which lies within the analytical measurement uncertainty of virtually all laboratories. About 30 L of VSMOW were stored in 10 L storage flasks in the Agency's Laboratories, Vienna, and an additional 20 L at NIST (formerly NBS), Gaithersburg, USA. Both supplies are exhausted since end of 2006.

VSMOW and SLAP are filled in 20 mL sealed glass ampoules. The homogeneity of the different charges and of the filling procedure has been cross-checked before their distribution. These checks revealed identical values within the experimental error.

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 for further use due to the strong possibility of evaporation losses with significant isotope fractionation. Therefore, the reference values in this reference sheet **do not apply** any more for such retained portions. Under no circumstances may any portion of the material be used for repeated stable isotope measurements (e.g. using it in water/CO_2 equilibration devices on subsequent days) due to the isotopic exchange and corresponding shift of the isotopic composition of the material during the preparation process.

Expiration of reference values

The reference values for the δ^2H and $\delta^{18}O$ values of VSMOW and SLAP are valid until 31 December 2022, provided the original ampoules are handled and stored in accordance with the instructions given in this reference sheet (see "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 re-definition of δ-values as normalized on the VSMOW – SLAP scale [4]:

$$\delta = ((R_{sample} / R_{VSMOW}) - 1) \cdot f \qquad (1)$$

$$f = \delta_{SLAP} / ((R_{SLAP} - R_{VSMOW}) / R_{VSMOW})$$

where R_A is the hydrogen or oxygen stable isotope-amount ratio in substance A, $n_A(^2H)/n_A(^1H)$ or $n_A(^{18}O)/n_A(^{16}O)$,
and δ_{SLAP} is the conventionally fixed δ^2H or $\delta^{18}O$ value for SLAP (see Table 1).

This δ-definition of Eq. (1) coincides with the classical one [2] only if $f = 1$, that is if the δ-value derived from the measured ratio R_{SLAP} corresponds exactly to the recommended value δ_{SLAP}.

Please note that the reporting scales for δ^2H and $\delta^{18}O$ 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[13].

Limit of distribution

Both materials are not more available for distribution. Only small portions are kept at the IAEA. Successor materials with isotopic amount-ratios as close as possible to the original materials were produced and are made available under the names VSMOW2 and SLAP2. Each set of these new reference materials may be ordered only once per laboratory in a three-year period. This should ensure that the materials are kept available as long as possible for international use.

Isotope-amount ratios in VSMOW

VSMOW is the international isotopic measurement standard to which GISP, SLAP and most other oxygen-bearing substances are compared [6]. The δ-values of VSMOW are equal to zero exactly due to the definition of the δ^2H and $\delta^{18}O$ scales. Table 2 lists the absolute hydrogen and oxygen isotope-amount ratio of VSMOW and the calculated atom per cent of ^2H, ^{17}O and ^{18}O, respectively:

Table 2: Absolute isotope abundance ratios and atom per cent abundance of hydrogen and oxygen isotopes in VSMOW. The quoted uncertainties include the measurement component and the uncertainty associated with the absolute isotope abundance of the calibration mixtures. Atom fraction data are calculated from the isotope ratio data. "mass spec." stands for mass spectrometric measurement, FT-NMR stands for Fourier-Transform Nuclear Magnetic Resonance.

Isotope-amount ratio	$10^6 \times$ isotope-amount ratio	$10^6 \times$ isotope-amount ratio standard uncertainty	100 × atom fraction of ^2H, $^{18}O^{(a)}$ and $^{17}O^{(b)}$	100 × atom fraction standard uncertainty	Method	Reference
$^2H/^1H$	155.76	± 0.05	0.015574	±0.000005	mass spec.	[7]
$^2H/^1H$	155.75	± 0.08	0.015573	±0.000008	mass spec.	[8]
$^2H/^1H$	155.60	± 0.12	0.015558	±0.000012	FT-NMR	[9]
$^{18}O/^{16}O$	2005.20	± 0.45	0.20004 (a)	±0.00005	mass spec.	[14]
$^{17}O/^{16}O$	379.9	± 0.8	0.03790 (b)	±0.00009	mass spec.	[15]

Isotope-amount ratios in SLAP

The oxygen and hydrogen δ-scales are defined in such a way, that the δ^2H and $\delta^{18}O$ values of SLAP relative to VSMOW are exactly -428 ‰ and -55.5 ‰, respectively. These δ-values for SLAP were conventionally fixed at an IAEA Consultants Meeting on Stable Isotope Standards in 1976, in Vienna, on the basis of a data set achieved in an interlaboratory comparison [4]. Participating scientists and laboratories included in the measurement of SLAP and their reported δ-values are given in Ref. [11]. Table 3 gives values for the absolute hydrogen and oxygen isotope-amount ratios of SLAP, the calculated atom per cent of ^2H and the calculated δ-values, respectively.

Table 3: Absolute isotope-amount ratios, atom per cent abundance, and δ-values for hydrogen and oxygen in SLAP. The quoted uncertainties include the measurement uncertainty and those of the absolute isotope-amount ratios of the calibration mixtures. Atom fraction data for ^2H and δ^2H values are calculated from the isotope-amount ratio data.

Isotope-amount ratio	$10^6 \times$ isotope-amount ratio	$10^6 \times$ isotope-amount ratio standard uncertainty	100 × atom fraction of ^2H	100 × atom fraction standard uncertainty	1000 × δ^2H value	1000 × δ^2H standard uncertainty	Method	Reference
$^2H/^1H$	89.02	± 0.05	0.008901	±0.000005	-428.5	± 0.4	mass spec.	[7]
$^2H/^1H$	89.12	± 0.07	0.008911	±0.000007	-427.8	± 0.5	mass spec.	[8]
$^2H/^1H$	88.88	± 0.18	0.008887	±0.000018	-428.8	± 1.2	FT-NMR	[9]
$^{18}O/^{16}O$	1893.91 (a)	± 0.45 (a)						

(a) Back-computed from VSMOW isotope-amount ratio using SLAP-$\delta^{18}O$ = -55.5 ‰.

Uncertified Values

The absolute maximum density of VSMOW is 999.975 kg·m^{-3} [16]. The tritium activity concentration of VSMOW, determined at the IAEA by direct gas counting, was 18.5 ± 3.6 TU on 16t September 1976. The tritium activity concentration of SLAP was 374 ± 9 TU on 16 September 1976. Both values are reported with their 1-σ standard uncertainties.

The $^{17}O/^{16}O$ isotope-amount ratio of SLAP has been determined in six individual measurements each [17]. The reported $\delta^{17}O$ value on the VSMOW scale (with $\delta^{17}O$ = 0 relative to VSMOW) is -28.86 ± (0.03 to 0.12) ‰ for SLAP. The numbers in brackets give the range of the standard deviation of the individual measurements. The extended standard uncertainty is reported to be 0.1 ‰.

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.

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Further information

Users of these reference materials should ensure that the reference sheet in their possession is current. This can be accomplished by contacting the IAEA reference material site at:
http://www.iaea.org/programmes/aqcs/
or the Isotope Hydrology Laboratory website at:
http://www-naweb.iaea.org/NAALIHL/reference_materials.shtml

For further information, please contact:
Head of the Isotope Hydrology Laboratory
International Atomic Energy Agency
P.O. Box 100
A-1400 Vienna
Austria

Tel:. + 43–1–2600–21740
Fax + 43–1–2600–7
e-mail: stabiso.refmat@iaea.org

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Manfred Gröning, Unit Head,
IAEA Isotope Hydrology Laboratory

REFERENCES

[1] VIM, International Vocabulary of Metrology - Basic and General Concepts and Associated Terms (VIM) (draft version for voting). 3rd ed. (2006) p. 1-127.

[2] CRAIG, H., Isotopic variations in meteoric waters. Science **133** (1961) 1702-1703.

[3] CRAIG, H., Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. Science **133** (1961) 1833-1834.

[4] GONFIANTINI, R., Standards for stable isotope measurements in natural compounds. Nature **271** (1978) 534-536.

[5] HUT, G., Stable Isotope Reference Samples for Geochemical and Hydrological Investigations (Rep. Consultants Group Meeting, Vienna, 1985). International Atomic Energy Agency, Vienna (1987) p. 1-42. http://www-naweb.iaea.org/NAALIHL/publications3.shtml

[6] COPLEN, T.B., Normalization of oxygen and hydrogen data. Chemical Geology **72** (1988) 293-297.

[7] HAGEMANN, R., NIEF, G., ROTH, E., Absolute isotopic scale for deuterium analysis of natural waters. Absolute D/H ratio for SMOW. Tellus **22** (1970) 712-715.

[8] DE WIT, J.C., VAN DER STRAATEN, C.M., MOOK, W.G., Determination of the absolute hydrogen isotopic ratio of VSMOW and SLAP. Geostandards Newsletter **4**(1) (1980) 33-36.

[9] TSE, R.S., WONG, S.C., YUEN, C.P., Determination of deuterium/hydrogen ratios in natural waters by Fourier transform nuclear magnetic resonance spectrometry. Analytical Chemistry **52** (1980) 2445-2448.

[10] GONFIANTINI, R., Stable Isotope Reference Samples for Geochemical and Hydrochemical Investigations (Rep. Advisory Group Meeting, Vienna, 1983). International Atomic Energy Agency, Vienna (1984) p. 1-77. http://www-naweb.iaea.org/NAALIHL/publications3.shtml

[11] GONFIANTINI, R., Stable Isotope Standards and Intercalibration in Hydrology and in Geochemistry (Rep. Consultants Group Meeting, Vienna, 1976). International Atomic Energy Agency, Vienna (1977) p. 1-29. http://www-naweb.iaea.org/NAALIHL/publications3.shtml

[12] ISO, Reference materials - Contents of Certificates and Labels (ISO-Guide 31). 2nd ed. Geneva, Switzerland, International Organization for Standardization. (2000) p. 1-7.

[13] GRÖNING, M., International stable isotope reference materials. In: *Handbook of stable isotope analytical techniques*, De Groot, P.A., Editor. Elsevier, Amsterdam (2004) p. 874-906.

[14] BAERTSCHI, P., Absolute ^{18}O content of Standard Mean Ocean Water. Earth and Planetary Science Letters **31** (1976) 341-344.

[15] LI, W., NI, B., JIN, D., ZHANG, Q., Measurement of the absolute abundance of oxygen-17 in V-SMOW. KEXUE TONGBAO (Chinese Sciene Bulletin) **33**(19) (1988) 1610-1613.

[16] GIRARD, G., MENACHÉ, M., Sur le calcul de la masse volumique de l'eau. C.R. Acad. Sci.Paris **274** (1972) 377-379.

[17] JABEEN, I., KUSAKABE, M., Determination of $\delta^{17}O$ values of reference water samples VSMOW and SLAP. Chemical Geology **143** (1997) 115-119.