

Reference Material 8537

SLAP Standard Light Antarctic Precipitation

(Hydrogen and Oxygen Isotopes in Water)

REFERENCE MATERIAL INFORMATION SHEET

Purpose: This Reference Material (RM) is a primary international measurement standard [1,2] that defines the depleted end of the VSMOW – SLAP (Vienna Standard Mean Ocean Water – Standard Light Antarctic Precipitation) δ -scales for isotope ratios of hydrogen (H) and oxygen (O). The equivalent name for this RM, as used by the International Atomic Energy Agency (IAEA) and the U.S. Geological Survey (USGS), is SLAP.

Description: A unit of RM 8537 consists of one ampoule containing approximately 20 mL of water.

Non-Certified Values: The assigned values for this RM are at present the best estimate of the true values. The assigned isotope-delta values for this RM are provided in Table 1 below.

Table 1. Non-Certified Values for the Hydrogen and Oxygen Stable Isotopes of RM 8537 (SLAP)

NIST RM Number	IAEA Name	Non-Certified Value $\delta^2\text{H}_{\text{VSMOW}}^{(a)}$	Combined Uncertainty $\delta^2\text{H}_{\text{VSMOW}}^{(a)}$	Expanded Uncertainty $\delta^2\text{H}_{\text{VSMOW}}^{(a)}$	Non-Certified Value $\delta^{18}\text{O}_{\text{VSMOW}}^{(a)}$	Combined Uncertainty $\delta^{18}\text{O}_{\text{VSMOW}}^{(a)}$	Expanded Uncertainty $\delta^{18}\text{O}_{\text{VSMOW}}^{(a)}$
8537	SLAP	-428.0 ‰	0 ‰	0 ‰	-55.5 ‰	0 ‰	0 ‰

^(a) The $\delta^2\text{H}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ are the anchors for the VSMOW – SLAP scales for both hydrogen and oxygen isotopes. This material, by definition, has no uncertainty; it has a value of zero for combined standard uncertainty and expanded uncertainty value, $k = 2$. Each expanded uncertainty is equal to $U = ku_c$, where u_c is the combined standard uncertainty and k is the coverage factor, as defined in the ISO/JCGM Guide [3]. Non-certified values and uncertainties are given in units of per mil (‰), which is equivalent to per thousand.

Metrological Traceability: SLAP is the accepted depleted anchor of the oxygen and hydrogen stable isotope ratio measurement scales and provides the traceability link for the oxygen and hydrogen isotope-delta (δ) measurements [2]. SLAP is realized primarily and explicitly through the water RM 8537, where:

$$\text{RM 8537 water: } \delta^2\text{H}_{\text{VSMOW}} = -428.0 \text{ ‰}$$

$$\text{RM 8537 water: } \delta^{18}\text{O}_{\text{VSMOW}} = -55.50 \text{ ‰}$$

Isotope values for hydrogen and oxygen are not traceable to the International System of Units (SI) or other higher-order reference system [3,4]; however, a *Traceability Exception* has been approved by the Bureau International des Poids et Mesures (BIPM) International Committee for Weights and Measures (CIPM), which states non-SI traceable isotope values “should be made traceable to materials recognized as International Standards” [4,5].

Period of Validity: The non-certified values are valid within the measurement uncertainty specified until **31 December 2030**. The value assignments are nullified if the material is stored or used improperly, damaged, contaminated, or otherwise modified.

Maintenance of Non-Certified Values: NIST will monitor this material to the end of its period of validity. If substantive technical changes occur that affect the non-certified values during this period, NIST will update this Reference Material Information Sheet and notify registered users. RM users can register online from a link available on the NIST SRM website or fill out the user registration form that is supplied with the RM. Registration will facilitate notification. Before making use of any of the values delivered by this material, users should verify they have the most recent version of this documentation, available through the NIST SRM website (<https://www.nist.gov/srm>).

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Storage: The original unopened ampoules of RM 8537 should be stored at ambient temperature in the dark. The unused fractions of this RM should be discarded immediately after opening due to the strong possibility of evaporative losses causing significant isotope fractionation. Furthermore, aliquots of this RM should not be used for repeated stable isotope calibrations using water/CO₂ equilibration devices over multiple days due to isotopic exchange with the applied gas and resulting shift of the isotopic composition of the material during the preparation process. The non-certified values in this Reference Material Information Sheet apply only to freshly opened ampoules.

Non-Certified Absolute Isotope-Number Ratios in SLAP: The absolute isotope-number ratios of RM 8537 have been evaluated in several different exercises [6–8]. Table 2 provides a summary of absolute hydrogen and oxygen isotopic abundances for SLAP.

Table 2: RM 8537 SLAP Absolute Isotopic Abundances

Isotope Ratio	Isotope Ratio ^(a)	Standard Deviation ^(a)	Atom Percent of ¹ H ^(a) (%)	Standard Deviation (%)	δ Value (‰)	Standard Deviation (%)	Method	Reference
² H / ¹ H	0.00008902	0.00000005	(99.991099)	0.000005	−428.5	0.1	Mass spec.	6
² H / ¹ H	0.00008912	0.00000007	(99.991089)	0.000007	−427.8	0.5	Mass spec.	7
² H / ¹ H	0.00008888	0.00000018	(99.991113)	0.000018	−428.8	1.2	FT-NMR ^(b)	8
¹⁸ O / ¹⁶ O	(0.00189391)	(0.00000045)	Computed from VSMOW using δ ¹⁸ O = −55.5 ‰					

^(a) Values in parenthesis are calculated

^(b) Fourier-Transform Nuclear Magnetic Resonance

Additional Non-Certified Values: The ¹⁷O/¹⁶O ratio SLAP was determined in six individual measurements [9]. The reported δ¹⁷O value (‰) on the VSMOW/SLAP scale is −28.86 ‰ ± (0.03 to 0.12) ‰ for SLAP. The numbers in parentheses give the range of the standard deviation of the individual measurements. The uncertainty is reported to be ± 0.1 ‰. The tritium activity concentration of SLAP, determined at the IAEA by direct gas counting, was 374 ± 9 TU on 16 September 1976. The reported uncertainty is one standard deviation [10].

Additional Information: The distribution of RM 8537 is limited to one unit per three-year period. Users are encouraged to prepare their own standards for daily use and calibrate those standards against international reference materials. Preparation, analysis, and reporting information can be found in Appendix A.

REFERENCES

- [1] JCGM 200:2012; *International Vocabulary of Metrology – Basic and General Concepts and Associated Terms (VIM)*, 3rd ed.; Joint Committee for Guides in Metrology (JCGM) (2012); available at <https://www.bipm.org/en/publications/guides> (accessed Jul 2022).
- [2] Brand, W.A.; Coplen, T.B.; Vogl, J.; Rosner, M.; Prohaska, T.; *Assessment of International Reference Materials for Isotope Ratio Analysis (IUPAC Technical Report)*; Pure and Appl. Chem., Vol. 86, pp. 425–467 (2014).
- [3] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement (GUM 1995 with Minor Corrections)*; Joint Committee for Guides in Metrology (2008); available at <https://www.bipm.org/en/publications/guides> (accessed Jul 2022).
- [4] Beauchamp, C.R.; Camara, J.E.; Carney, J.; Choquette, S.J.; Cole, K.D.; DeRose, P.C.; Duewer, D.L.; Epstein, M.S.; Kline, M.C.; Lippa, K.A.; Lucon, E.; Molloy, J.; Nelson, M.A.; Phinney, K.W.; Polakoski, M.; Possolo, A.; Sander, L.C.; Schiel, J.E.; Sharpless, K.E.; Toman, B.; Winchester, M.R.; Windover, D.; *Metrological Tools for the Reference Materials and Reference Instruments of the NIST Material Measurement Laboratory*; NIST Special Publication (NIST SP) 260-136, 2021 edition; U.S. Government Printing Office: Washington, DC (2021); available at <https://nvlpubs.nist.gov/nistpubs/SpecialPublications/NIST.SP.260-136-2021.pdf> (accessed Jul 2022).
- [5] BIPM Traceability Exception: Delta Value Isotope Ratio Measurements (2015); available at <https://www.bipm.org/utis/common/documents/CIPM-MRA/Traceability-Exception-QM1.pdf> (accessed Jul 2022). Note that this document is a summary of Decision CIPM/104-26 from the International Committee for Weights and Measures (CIPM); *Proceedings of Session 1 of the 104th meeting: Executive Summary*; 9-10 March 2015, page 34; <https://www.bipm.org/utis/en/pdf/CIPM/CIPM2015-I-EN.pdf> (accessed Jul 2022).

- [6] Hagemann, R.; Nief, G.; Roth, E.; *Absolute Isotopic Scale for Deuterium Analysis of Natural Waters. Absolute D/H ratio for SMOW*; Tellus, Vol. 22, pp. 712–715 (1970).
- [7] 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, Vol. 4, pp. 33–36 (1980).
- [8] Tse, R.S.; Wong, S.C.; Yuen, C.P.; *Determination of Deuterium/Hydrogen Ratios in Natural Waters by Fourier Transform Nuclear Magnetic Resonance Spectrometry*; Anal. Chem., Vol. 52, pp. 2445–2448 (1980).
- [9] Jabeen, I.; Kusakabe, M.; *Determination of $\delta^{17}\text{O}$ values of Reference Water Samples VSMOW and SLAP*; Chemical Geology, Vol. 143, pp. 115–119 (1997).
- [10] International Atomic Energy Agency (IAEA); *Reference Sheet for VSMOW and SLAP International Measurement Standards*; IAEA, Vienna, pp. 1–5 (01 December 2006).
- [11] Gonfiantini, R.; *Standards for Stable Isotope Measurements in Natural Compounds*; Nature, Vol. 271, pp. 534–536 (1978).
- [12] Gonfiantini, R.; *Consultants' Meeting on Stable Isotope Standards and Intercalibration in Hydrology and in Geochemistry*; IAEA, Vienna, pp. 1–10 (8–10 September 1976).
- [13] Coplen, T.B.; Hopple, J.; *Audit of VSMOW Distributed by the United States National Institute of Standards and Technology*; IAEA-TECDOC-825; *Reference and Intercomparison Materials for Stable Isotopes of Light Elements; Proceedings of a Consultants Meeting Held in Vienna*; IAEA, Vienna, pp. 35–38 (1–3 December 1993).
- [14] Coplen, T.B.; *Guidelines and Recommended Terms for Expression of Stable-Isotope-Ratio and Gas-Ratio Measurement Results*; Rapid Communications in Mass Spectrometry, Vol. 25, pp. 2538–2560 (2011).
- [15] Coplen, T.B.; *Discontinuance of SMOW and PDB*; Nature, Vol. 375, p. 285 (1995).
- [16] Coplen, T.B.; *Reporting of Stable Hydrogen, Carbon, and Oxygen Isotopic Abundances*; Pure and Appl. Chem., Vol. 66, pp. 273–276 (1994).

Information Sheet Revision History: 20 July 2022 (Editorial changes); 08 June 2022 (Correction to references; editorial changes); 01 June 2022 (Correctly assigned isotopic abundance values for 8537 that were previously assigned to 8536; expanded uncertainty values added; terminology updated, change of period of validity; updated format and separated from RMs 8536 and 8535; editorial changes); 03 March 2005 (Change of expiration date); 09 May 2001 (Reference values updated; expiration date added); 15 October 1992 (Original report date).

Certain commercial equipment, instruments, or materials may be identified in this Reference Material Information Sheet to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Users of this RM should ensure that the Reference Material Information Sheet in their possession is current. This can be accomplished by contacting the Office of Reference Materials 100 Bureau Drive, Stop 2300, Gaithersburg, MD 20899-2300; telephone (301) 975-2200; e-mail srminfo@nist.gov; or the Internet at <https://www.nist.gov/srm>.

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APPENDIX A

PREPARATION AND ANALYSIS

Technical aspects involved in the issuance of this RM were coordinated through the NIST Chemical Sciences Division by R.A. Kraft.

Support aspects involved in the issuance of this RM were coordinated through the NIST Office of Reference Materials.

Preparation: SLAP was obtained from a South Pole snow sample collected by E. Picciotto, Université Libre de Bruxelles, at Plateau Station, Antarctica, in 1967 [11].

Analytical methods: Samples of VSMOW, NBS-1, NBS-1A, and SLAP were sent out to 114 laboratories around the world for an interlaboratory comparison; 45 laboratories returned results. Values deviating from the average by more than 2 standard deviations were removed. Based on the remaining results, the IAEA Consultant's Group recommended the values for SLAP be fixed at $\delta^2\text{H}$ of -428.0‰ and $\delta^{18}\text{O}$ of -55.50‰ [11,12]. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for SLAP are assigned by international consensus as the depleted end of the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ scales and therefore have no associated uncertainty [11,12].

Homogeneity: Isotopic homogeneity testing prior to distribution showed values are within the analytical uncertainty. In 1993 bright orange matter, possibly algae, was observed in some ampoules and in one 10 mL primary storage flask from the NIST VSMOW supply. An audit of the NIST VSMOW supply was conducted by Coplen and Hopple at the USGS and presented at the IAEA Consultants Group Meeting in 1993. Although none of the SLAP storage containers and ampoules appeared to contain orange matter, samples of SLAP were also included in the audit. The audit revealed the composition of ampoules with and without the bright orange matter were identical in $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotopic composition within the experimental uncertainty [13].

REPORTING

Terminology: The terminology used here is based on the guidance given by IUPAC for isotope terminology, where stable isotope-number ratio refers to the number of atoms of one isotope relative to the number of atoms of a second isotope in the same system [2]. This is often abbreviated to stable isotope ratio. Isotope-delta value refers to the stable isotope-number ratio of a measured sample relative to the stable isotope-number ratio of a reference material (see example below). Isotope-amount ratio is numerically the same as isotope-number ratio but refers specifically to the amount (moles) of an isotope relative to the amount (moles) of another isotope in the same system [14].

Isotope-delta Values: The hydrogen and oxygen stable isotope-delta values of a measured sample reported on the VSMOW scale are defined as the difference in measured isotope-number ratio of hydrogen or oxygen in a sample relative to the isotope-number ratio of hydrogen or oxygen in VSMOW:

$$\delta^2\text{H} = \frac{\left[\frac{N_{\text{sample}}(^2\text{H})}{N_{\text{sample}}(^1\text{H})} \right] - \left[\frac{N_{\text{VSMOW}}(^2\text{H})}{N_{\text{VSMOW}}(^1\text{H})} \right]}{\left[\frac{N_{\text{VSMOW}}(^2\text{H})}{N_{\text{VSMOW}}(^1\text{H})} \right]}$$

and

$$\delta^{18}\text{O} = \frac{\left[\frac{N_{\text{sample}}(^{18}\text{O})}{N_{\text{sample}}(^{16}\text{O})} \right] - \left[\frac{N_{\text{VSMOW}}(^{18}\text{O})}{N_{\text{VSMOW}}(^{16}\text{O})} \right]}{\left[\frac{N_{\text{VSMOW}}(^{18}\text{O})}{N_{\text{VSMOW}}(^{16}\text{O})} \right]}$$

Normalization: By convention VSMOW is the zero point of the hydrogen and oxygen stable isotope δ -scales; δ -value for SLAP is also defined by convention and has a $\delta^2\text{H}$ value of -428.0 ‰ and a $\delta^{18}\text{O}$ value of -55.50 ‰. A formula for normalizing hydrogen isotope measurement results using two laboratory standards LS1 (VSMOW or VSMOW2) and LS2 (SLAP or SLAP2) can be expressed as:

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

where the normalization factor f is:

$$f = \frac{(\delta^2 H_{\text{LS2},\text{cal}} - \delta^2 H_{\text{LS1},\text{cal}})}{(\delta^2 H_{\text{LS2},\text{WS}} - \delta^2 H_{\text{LS1},\text{WS}})}$$

where *WS* denotes measurements made versus a transfer gas (working standard), *cal* denotes calibrated measurements made versus the VSMOW–SLAP scale, and $\delta^2 H_{\text{LS1},\text{cal}}$ and $\delta^2 H_{\text{LS2},\text{cal}}$ are the conventionally fixed $\delta^2\text{H}$ values for VSMOW and SLAP, or those of calibrated laboratory working standards.

The same formula can be used for $\delta^{18}\text{O}$. The δ -definition above assumes $f=1$, and does not account for scale compression.

Please note that the reporting scales for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are still referred to as the VSMOW-SLAP scales despite the exhaustion of the original supply of VSMOW and SLAP [15].

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

- $\delta^2\text{H}$ values of all hydrogen-bearing substances be expressed relative to VSMOW-SLAP,
- $\delta^{18}\text{O}$ values of all oxygen-bearing substances be expressed relative to VSMOW-SLAP or relative to Vienna Pee Dee Belemnite (VPDB; for carbonates),
- reporting of the relative difference of stable isotope-number ratios relative to SMOW and PDB (Pee Dee Belemnite) be discontinued [15].

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