United States Geological Survey

Reston Stable Isotope Laboratory

Report of Stable Isotopic Composition

Reference Material VSMOW2-0.25 µL

(Hydrogen and Oxygen Isotopes in Water Sealed in a Silver Tube)

This reference material (RM) is intended for calibration of stable hydrogen (δ^2H) and oxygen (δ^{18}O) measurements of unknown water or hydrogen- or oxygen-bearing substances with a TC/EA (thermal conversion/elemental analyzer) and an isotope-ratio mass spectrometer by quantifying drift with time and isotope-ratio-scale contraction. This RM consists of 0.25 µL of VSMOW2 (Vienna Standard Mean Ocean Water 2) reference water [1] sealed in a silver tube [2]. This RM is issued in quantities of 50 sealed silver tubes per bottle. There is no limit on distribution. VSMOW2 was prepared by the International Atomic Energy Agency (IAEA) under the direction of M. Gröning by the mixing of three selected fresh water samples and subsequent equilibration with gaseous hydrogen to shift the hydrogen isotopic composition slightly [1]. Glass ampoules containing 20 mL of VSMOW2 water are available from the U.S. National Institute of Standards and Technology (NIST) [3] as RM 8535a and from the IAEA [4].

Recommended Values: Stable hydrogen and oxygen isotopic compositions are expressed herein as delta values [5] relative to VSMOW (Standard Mean Ocean Water) on scales normalized such that the δ^2H and δ^{18}O values of SLAP (Standard Light Antarctic Precipitation) are –428 ‰ and –55.5 ‰, respectively [6,7]. The isotopic compositions of VSMOW2-0.25 µL are identical to that of VSMOW2 [1], except that each combined standard uncertainty value (μ_C) has been increased to account for hydrogen and oxygen blank, both of which were below detection.

Stable hydrogen isotopic composition:	$\delta^2H_{VSMOW\text{-}SLAP}$ = 0.0 ± 0.4 ‰
Stable oxygen isotopic composition:	$\delta^{18}O_{VSMOW\text{-}SLAP}$ = 0.00 ± 0.04 ‰
Nominal volume of water:	0.25 µL (Although the RSIL attempts to ensure that each silver tube has the same volume of water, slight differences are observed owing to variations in the inside diameter of the silver tubing provided by the manufacturer. The typical relative variation in volume among 50 tubes is ±3 %, but this cannot be guaranteed.)

Technical coordination for this RM was provided by Haiping Qi of the RSIL.

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Expiration of Reference Value: The reference value for the isotopic composition of VSMOW2-0.25 µL is valid for a period of 10 years, provided the RM is handled in accordance with the instructions given in this Report of Stable Isotopic Composition (see "Instructions for Use"). The reference value is nullified if the RM is damaged by freezing or other means, contaminated, or otherwise modified.

Maintenance of RM Certification: The Reston Stable Isotope Laboratory (RSIL) will monitor this RM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this report, the RSIL will notify the purchaser.

Distribution and Stability: VSMOW2-0.25 µL is stable at normal room temperatures. The RSIL has monitored this RM for a period of two years since the reference water was sealed in the silver tubes, and no change in isotopic composition has been observed. To minimize the potential for contamination, it is recommended that this RM be stored in the container in which it is supplied. The RM container should be sealed well after use to minimize tarnishing of the silver tubes. The RM should not be frozen because it can burst. If shipped, the user should take precautions to ensure that the RM does not freeze.

Instructions for use: The typical sequence of unknown samples and water references for δ^2H and δ^{18}O analysis is 5 reference waters and 10–15 unknown samples, followed by 5 reference waters and 10–15 unknown samples. The sequence ends with 5 reference waters. Ideally, users may choose to use two reference waters with substantially different isotopic compositions. They could be used at the beginning, the middle, and the end of the analysis sequence to enable satisfactory scale correction and correction of drift with time. The amount of hydrogen or oxygen in references and unknowns should be the same or similar to minimize bias in measurement results. Two or three silver tubes containing VSMOW2 can be combined in a single port of a TC/EA carousel to increase the size of the sample.

Reporting of Stable-isotope-delta Values: The following recommendations are provided for reporting stable hydrogen and oxygen isotope-delta values [5]. It is recommended that:

- The δ^2H values of all hydrogen-bearing substances be expressed relative to VSMOW-SLAP on a scale where δ^2H_{SLAP2} = –427.5 ‰ or δ^2H_{SLAP} = –428 ‰ exactly [1,7].
- The δ^{18}O values of all oxygen-bearing substances be expressed relative to VSMOW-SLAP or relative to Vienna Peedee belemnite (VPDB; for carbonates) on a scale such that $\delta^{18}O_{SLAP2}$ = –55.5 ‰ or $\delta^{18}O_{NBS19}$ = –2.2 ‰, respectively.
- Authors report δ values of international distributed (secondary) isotopic reference materials as though they had been interspersed among and used for normalization of unknowns, as appropriate, for the measurement method. In this manner, measurement results can be adjusted in the future as analytical methods improve and consensus values of internationally distributed isotopic reference materials change.
- Reporting of δ values relative to SMOW and PDB (Peedee belemnite) be discontinued [8].

REFERENCES

[1] International Atomic Energy Agency (IAEA), Reference Sheet for International Measurement Standards, http://nucleus.iaea.org/rpst/Documents/VSMOW2_SLAP2.pdf

[2] Qi, H., Gröning, M., Coplen, T. B., Buck, B., Mroczkowski, S. J., Brand, W. A., Geilmann, H., and Gehre, M., 2010, Novel silver-tubing method for quantitative introduction of water into high-temperature conversion systems for stable hydrogen and oxygen isotopic measurements: Rapid Communications in Mass Spectrometry, v. 24, p. 1821–1827.

[3] National Institute of Standards and Technology (NIST), http://ts.nist.gov/measurementservices/referencematerials/index.cfm

[4] International Atomic Energy Agency (IAEA), http://www.iaea.org/programmes/aqcs/

[5] Coplen, T. B., 2011, Guidelines and recommended terms for expression of stable-isotope-ratio and gas-ratio measurement results: Rapid Communications in Mass Spectrometry, v. 25, 2538–2560.

[6] Gonfiantini, R., 1978, Standards for stable isotope measurements in natural compounds: Nature, v. 271, p. 534–536.

[7] Coplen, T. B., 1994, Reporting of stable hydrogen, carbon, and oxygen isotopic abundances: Pure and Applied Chemistry, v. 66, p. 273–276.

[8] Coplen, T. B., 1995, Discontinuance of SMOW and PDB: Nature, v. 375, 285.