United States Geological Survey

Reston Stable Isotope Laboratory

Report of Stable Isotopic Composition

Reference Material UC03-0.25 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 UC03 reference water and sealed in a silver tube [1]. This RM is issued in quantities of 50 sealed silver tubes per bottle. There is no limit on distribution. UC03 was prepared by G. Olack and A. Colman of the Department of Geophysical Sciences of The University of Chicago, Chicago, Illinois by laboratory evaporative enrichment of heavy isotopes in water.

Recommended Values: Stable hydrogen and oxygen isotopic compositions are expressed herein as delta values [2] 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 [3,4]. This isotopic reference water was calibrated using VSMOW and SLAP reference water with dual-inlet isotope-ratio mass spectrometry [5,6]. Each stable isotopic composition is given as a reference isotope-delta value with an estimated expanded uncertainty ($U = 2u_c$) about the reference value that provides an interval that has about a 95-percent probability of encompassing the true value.

Stable hydrogen isotopic composition:	$\delta^2H_{VSMOW\text{-}SLAP} = +68.5 \pm 0.7$ ‰
Stable oxygen isotopic composition:	$\delta^{18}O_{VSMOW\text{-}SLAP} = +29.79 \pm 0.04$ ‰
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 of 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.

Reston, Virginia 20192
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Expiration of Reference Value: The reference value for the isotopic composition of UC03-0.25 µL is valid for a period of 5 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. The RSIL will notify the purchaser if substantive technical changes occur that affect the certification before the expiration of this report.

Distribution and Stability: UC03-0.25 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^{2}H 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 GISP can be combined in a single port of a TC/EA carousel to increase the size of the sample.

Preparation of RM: The evaporative enrichment of ^{2}H and ^{18}O was preformed using house reverse osmosis (RO) water (Chicago municipal water supply; the source is Lake Michigan with $\delta^{18}O_{VSMOW}$ ~ –6 ‰). The RO water was allowed to evaporate from either an auto-feed water bath (New Brunswick Innova 3200, ca. 25 L) or a recirculating water bath (Lauda, MS series, ca. 10 L) with a home built auto-feed. Evaporative reduction, ca. three bath volumes, took place over the course of a few days with temperatures ranging from 65 °C (speed evaporation) to ambient temperature (maximium isotopic fractionation). Further evaporation was performed with the auto-feed turned off, and waters enriched in ^{2}H and ^{18}O were combined and evaporated down again in the recirculating bath as needed. Contaminants, for example faint precipitate and slight coloration, were noted in the water highly enriched in ^{2}H and ^{18}O. Contaminants were removed by treatment with activated charcoal (Norite 3-mm pellets, Spectrum Chemical) and vacuum filtration through a 0.22-micron-membrane filter (Waters Durapore or Corning filter bottles/bottle top filters, with some samples gravity filtered through Whatman #1 filter paper prior to the 0.2-micron filtration). Samples of the waters enriched in heavy isotopes were dried down at 60 °C for determination of dissolved solids content, and conductive readings were obtained (0.5 cm spacing, Radio Shack multimeter), and are summarized in the table below.

Sample	Charcoal	Filter	$\delta^{18}O_{VSMOW}$ estimated	Resistance at 0.5 cm	Dissolved solids, mg/mL
UC03	Yes	Yes	+30 ‰	2.0 MΩ	0.59

Reporting of Stable-isotope-delta Values: The following recommendations are provided for reporting stable hydrogen and oxygen isotope-delta values [2]. It is recommended that:

- The δ^2H values of all hydrogen-bearing substances be expressed relative to VSMOW-SLAP on a scale where $\delta^2H_{SLAP2} = -427.5$ ‰ or $\delta^2H_{SLAP} = -428$ ‰ exactly [4,7].
- The $\delta^{18}O$ 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 the $\delta^{18}O$ of SLAP = –55.5 ‰ relative to VSMOW, and for carbonates, that $\delta^{18}O$ of NBS 19 = –2.2 ‰.
- 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

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