

United States Geological Survey

Reston Stable Isotope Laboratory

Report of Stable Isotopic Composition

Reference Material USGS78-0.15 μL

(Hydrogen and Carbon Isotopes in Oil Sealed in a Silver Tube)

This reference material (RM) is intended for normalization of stable hydrogen ($\delta^2\text{H}$) and carbon ($\delta^{13}\text{C}$) measurements of unknown oils and similarly-behaving hydrogen- and carbon-bearing. This RM consists of 0.15 μL of USGS78 oil [1] sealed in a silver tube [2]. This RM is issued in quantities of 50 sealed silver tubes per bottle. This RM is available from the Reston Stable Isotope Laboratory in units of 1 mL in a sealed glass ampule.

Recommended Values: Stable hydrogen isotopic compositions are expressed herein as delta values [3] relative to VSMOW (Standard Mean Ocean Water) on a scale normalized such that the $\delta^2\text{H}$ value of SLAP (Standard Light Antarctic Precipitation) is -428‰ , respectively [4,5]. Stable carbon isotopic compositions are expressed relative to VPDB (Vienna Pee Dee belemnite) on a scale normalized such that the $\delta^{13}\text{C}$ values of NBS 19 calcium carbonate and LSVEC lithium carbonate are $+1.95\text{‰}$ and -46.6‰ , respectively [6]. The isotopic compositions of USGS78-0.15 μL are identical to the stable hydrogen isotopic composition [1] and the stable carbon isotopic composition [6] of USGS78, except that each combined standard uncertainty value (μ_C) has been increased to account for anticipated hydrogen and carbon blanks, both of which were below detection [1].

Stable hydrogen isotopic composition: $\delta^2\text{H}_{\text{VSMOW-SLAP}} = +397.0 \pm 2.6\text{‰}$

Stable carbon isotopic composition: $\delta^{13}\text{C}_{\text{VPDB-LSVEC}} = -29.72 \pm 0.06\text{‰}$

Nominal volume of oil: 0.15 μL (Although the RSIL attempts to ensure that each silver tube has the same volume of oil, 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 percent, but this cannot be guaranteed.)

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

Expiration of Reference Value: The reference values for the isotopic compositions of USGS78-0.15 μL are valid until December 31, 2029, provided the RM is handled in accordance with the instructions given in this Report of Stable Isotopic Composition (see “Instructions for Use”). A reference value is nullified if the RM is damaged by freezing or other means, contaminated, or otherwise modified.

Maintenance of RM Report of Isotopic Composition: The U.S. Geological Survey RSIL will monitor these RMs and will notify the purchaser if substantive technical changes occur that affect their isotopic compositions.

Distribution and Stability: USGS78-0.15 μL is stable at normal room temperatures. The reference value is nullified if the RM is damaged by freezing or other means, contaminated, or otherwise modified. The RSIL has monitored this RM for a period of two years since the RM 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.

Instructions for use: USGS78 can be used at the beginning, the middle, and the end of the analysis sequence to enable satisfactory correction of drift with time. The amount of hydrogen or carbon in references and unknowns should be the same or similar to minimize bias in measurement results. Two or three silver tubes containing USGS78 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 carbon isotope-delta values. It is recommended that:

- The $\delta^2\text{H}$ values of all hydrogen-bearing substances be expressed relative to VSMOW-SLAP on a scale where $\delta^2\text{H}_{\text{SLAP}2} = -427.5 \text{ ‰}$ or $\delta^2\text{H}_{\text{SLAP}} = -428 \text{ ‰}$ exactly [5,7].
- The $\delta^{13}\text{C}$ values of all carbon-bearing substances be expressed relative to VPDB on a scale such that the $\delta^{13}\text{C}$ values of NBS 19 calcium carbonate and LSVEC lithium carbonate are $+1.95 \text{ ‰}$ and -46.6 ‰ , respectively [6].
- 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] Schimmelmann, A., Qi, H., Coplen, T. B., Brand, W. A., Fong, J., Meier-Augenstein, W., Kemp, H. F., Toman, B., Ackermann, A., Assonov, S., Aerts-Bijma, A. T., Brejcha, R., Chikaraishi, Y., Darwish, T., Elsner, M., Gehre, M., Geilmann, H., Gröning, M., Hélie, J-F., Herrero-Martín, S., Meijer, H. A. J., Sauer, P. E., Sessions, A. L., and Werner, R. A., 2016, New organic reference

materials for hydrogen, carbon, and nitrogen stable isotope-ratio measurements: caffeines, *n*-alkanes, fatty acid methyl esters, glycines, L-valines, polyethylenes, and oils, *Analytical Chemistry*, v. 88, p. 4294–4302. <http://dx.doi.org/10.1021/acs.analchem.5b04392> .

- [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] 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.
- [4] Gonfiantini, R., 1978, Standards for stable isotope measurements in natural compounds: *Nature*, v. 271, p. 534–536.
- [5] Coplen, T. B., 1994, Reporting of stable hydrogen, carbon, and oxygen isotopic abundances: *Pure and Applied Chemistry*, v. 66, p. 273–276.
- [6] Coplen, T. B., Brand, W. A., Gehre, M., Gröning, M., Meijer, H. A. J., Toman, B., and Verkouteren, R. M., 2006, New guidelines for $\delta^{13}\text{C}$ measurements: *Analytical Chemistry*, v. 78, 2439–2441.
- [7] International Atomic Energy Agency (IAEA), Reference Sheet for International Measurement Standards, http://nucleus.iaea.org/rpst/Documents/VSMOW2_SLAP2.pdf
- [8] Coplen, T. B., 1995, Discontinuance of SMOW and PDB: *Nature*, v. 375, 285.