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Reference Material 8539
NBS22 Oil
(Carbon and Hydrogen Isotopes in Oil)
REFERENCE MATERIAL INFORMATION SHEET

Purpose: This Reference Material (RM) is a secondary reference material with known stable isotope ratios for hydrogen (H) and carbon (C) [1,2]. It is intended to be a control for hydrogen stable isotope ratios of working standards that have been calibrated to the VSMOW (Vienna Standard Mean Ocean Water) δ-scale or carbon isotope ratios of working standards that have been calibrated to the VPDB (Vienna Pee Dee Belemnite) δ-scale. The equivalent name for this RM, as used by the International Atomic Energy Agency (IAEA) and the U.S. Geological Survey (USGS), is NBS22.

Description: A unit of RM 8539 consists of one ampoule containing approximately 1 mL of oil.

Non-Certified Values: Although not certified, the assigned isotope-delta values for this RM, provided in Table 1 below, are at present the best estimates of the true values.

Table 1. Non-Certified Values for Hydrogen and Carbon Stable Isotopes of RM 8539 (NBS22 Oil)

NIST RM Number	Name	Non-Certified Value $\delta^{13}C_{VPDB}$	Combined Uncertainty $\delta^{13}C_{VPDB}$ [(a)]	Expanded Uncertainty $\delta^{13}C_{VPDB}$ [(a)]	Non-Certified Value $\delta^{2}H_{VSMOW}$	Combined Uncertainty $\delta^{2}H_{VSMOW}$ [(a)]	Expanded Uncertainty $\delta^{2}H_{VSMOW}$ [(a)]
8539	NBS22	–30.02 ‰	0.04 ‰	0.08 ‰	–117.2 ‰	0.6 ‰	1.2 ‰

[(a)] RM 8539 is given with a combined standard uncertainty in addition to an expanded uncertainty value, $k = 2$, for each assigned value. The 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: RM 8539 is a secondary reference material with known values for hydrogen and carbon stable isotope ratios. The carbon stable isotope values assigned for RM 8539 are traceable to NBS 19 (RM 8544) and LSVEC (RM 8545); the hydrogen stable isotope values are traceable to VSMOW (RM 8535) and SLAP (RM 8537), which define the VSMOW scale.

Isotope values for hydrogen and carbon are not traceable to the International System of Units (SI) or other higher-order reference system [3,4]. 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 2031.** 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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Information Sheet Revision History on Page 2

Handling and Use: RM 8539 is stable at normal room temperatures. To minimize the potential for contamination, it is recommended that this RM be stored in the container in which it is supplied.

Additional Information: The distribution of RM 8539 is limited to one unit per customer per three-year period of time. 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

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[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).

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[5] BIPM Traceability Exception: Delta Value Isotope Ratio Measurements (2015); available at https://www.bipm.org/utils/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; available at https://www.bipm.org/utils/en/pdf/CIPM/CIPM2015-I-EN.pdf (accessed Jul 2022).

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[7] 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-Martin, S.; Meijer, H.A.J.; Sauer, P.E.; Sessions, A.L.; Werner, R.A.; *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*; Anal. Chem., Vol 88, pp. 4294–4302 (2016).

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[9] 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).

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Information Sheet Revision History: 25 July 2022 (Non-certified values updated, combined standard uncertainties for δ^2H and $\delta^{13}C$ added; expanded uncertainties for δ^2H and $\delta^{13}C$ revised; units updated in Table 1; updated format; change of period of validity; terminology updated; editorial changes); 06 February 2013 (Reference values revised and uncertainties changed to expanded uncertainties for $\delta^{13}C_{VPDB\text{-}LSVEC}$ and $\delta^2H_{VSMOW\text{-}SLAP}$; expiration date assigned; editorial changes); 22 June 1992 (Original report issue 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.

Sample Preparation: RM 8539 was prepared by S. Silverman, University of California, San Diego, California [6].

Analytical Methods: The $\delta^{13}C$ value and expanded uncertainty reported in Table 1 are taken from results of an inter-laboratory study involving 14 expert laboratories using two-point calibration and a variety of online and offline methods, and instrument manufacturers [7]. Data were combined using a multivariate Bayesian approach for data reduction [7].

The $\delta^{2}H$ values are taken from the same interlaboratory study and involved nine expert laboratories using two-point calibration, a variety of online and offline methods, and instrument manufacturers [7]. Data were combined using a multivariate Bayesian approach for data reduction [7].

These values are within uncertainty of previously documented values [8] but represent an improvement in interlaboratory study design and uncertainty analysis.

Homogeneity: Data from the inter-laboratory comparisons of NBS22 suggest that there is no evidence of carbon or hydrogen isotopic heterogeneity.

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 [9].

Isotope-delta Values: The hydrogen 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 in a sample relative to the isotope-number ratio of hydrogen in VSMOW:

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

The carbon stable isotope-delta values of a measured sample reported on the VPDB scale are defined as the difference in measured isotope-number ratio of carbon in a sample relative to the isotope-number ratio of carbon in VPDB:

$$\delta^{13}C = \frac{\left[\frac{N_{sample}(^{13}C)}{N_{sample}(^{12}C)}\right] - \left[\frac{N_{VPDB}(^{13}C)}{N_{VPDB}(^{12}C)}\right]}{\left[\frac{N_{VPDB}(^{13}C)}{N_{VPDB}(^{12}C)}\right]}$$

Normalization: By convention VSMOW is the zero point of the hydrogen stable isotope δ-scale; δ-value for SLAP is also defined by convention and has a δ^2H value of –428.0 ‰. A formula for normalizing hydrogen isotope measurement results using two laboratory standards LS1 (VSMOW2) and LS2 (SLAP2) can be expressed as:

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

where the normalization factor f is:

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

where *WS* denotes measurements made versus a transfer gas (working standard),
cal denotes calibrated measurements made versus the VSMOW scale, and
δ^2H $_{LS1,cal}$ and δ^2H$_{LS2,cal}$ are the conventionally fixed δ^2H values for VSMOW2 and SLAP2 or those of calibrated laboratory working standards.

The δ-definition above assumes $f = 1$, and does not account for scale compression.

Please note that the reporting scale for δ^2H is still referred to as the VSMOW-SLAP scale despite the exhaustion of the original supply of VSMOW and SLAP [10]. In the normalization equations above, LS1 and LS2 refer to the new international measurement standards VSMOW2 and SLAP2.

A formula for normalizing carbon isotope measurement results using two laboratory standards LS1 (IAEA-603) and LS2 (USGS44) can be expressed as:

$$\delta^{13} C_{sample,cal} = \delta^{13} C_{LS1,cal} + \left(\delta^{13} C_{sample,WS} - \delta^{13} C_{LS1,WS}\right) \times f$$

where the normalization factor f is:

$$f = \frac{\left(\delta^{13} C_{LS2,cal} - \delta^{13} C_{LS1,cal}\right)}{\left(\delta^{13} C_{LS2,WS} - \delta^{13} C_{LS1,WS}\right)}$$

where *WS* denotes measurements made versus a transfer gas (working standard),
cal denotes calibrated measurements made versus the VPDB scale, and
δ^{13}C $_{LS1,cal}$ and δ^{13}C$_{LS2,cal}$ are the conventionally fixed δ^{13}C values for IAEA-603 and USGS44 or those of calibrated laboratory working standards.

The δ-definition above assumes $f = 1$, and does not account for scale compression.

Please note that the reporting scales for δ^{13}C is still referred to as the VPDB scale despite the exhaustion of the original supply of RM 8544 (NBS19).

The following recommendations are provided for reporting the relative difference of hydrogen stable isotope-number ratios using the δ-notation modified from Coplen [9]. It is recommended that:

- δ^2H values of all hydrogen-bearing substances be expressed relative to VSMOW-SLAP,
- reporting of the relative difference of stable isotope-number ratios relative to SMOW and PDB (Pee Dee Belemnite) be discontinued [10],

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