National Institute of Standards & Technology

Report of Investigation

Reference Material 8539

NBS 22 Oil

(Carbon and Hydrogen Isotopes in Oil)

This Reference Material (RM) is intended for use in developing and validating methods for measuring relative differences in carbon (C) isotope-number ratios, $R(^{13}C/^{12}C)$, and hydrogen (H) isotope-number ratios, $R(^{2}H/^{1}H)$ [1]. Even though the values for this RM are reference values and not certified [2], its use will improve the comparability of data from different laboratories. The equivalent name for this RM as used by the International Atomic Energy Agency (IAEA) and the U.S. Geological Survey (USGS) is NBS 22. A unit of RM 8539 consists of one ampoule containing approximately 1 mL of oil.

Table 1. Reference Values[(a)] and Expanded Uncertainties for the Relative C and H Isotope-Number Ratio Differences of RM 8539

RM Number	Name	Reference Value $10^3\,\delta^{13}C_{VPDB\text{-}LSVEC}$[(b)]	Expanded Uncertainty $10^3\,\delta^{13}C_{VPDB\text{-}LSVEC}$[(b)]	Reference Value $10^3\,\delta^{2}H_{VSMOW\text{-}SLAP}$[(c)]	Expanded Uncertainty $10^3\,\delta^{2}H_{VSMOW\text{-}SLAP}$[(c)]
8539	NBS 22	–30.03	±0.09	–116.9	±0.3

[(a)] A reference value is a non-certified value that is the best estimate of the true value; however, the value may reflect only the measurement precision and may not include all sources of uncertainty [2].

[(b)] The $\delta^{13}C$ value is expressed as a mean and an expanded uncertainty. An expanded uncertainty is equal to $U = ku_c$, where u_c is the combined standard uncertainty as defined by the ISO Guide [3] and k is the coverage factor. The value of the consensus mean and the associated combined standard uncertainty were calculated using a multivariate Bayesian approach [4]. The combined standard uncertainty is intended to represent, at the level of one standard deviation, the combined effects of uncertainty sources evaluated by both Type A and B methods. Uncertainty in the bias of the methods is not included. The coverage factor, $k = 2$, provides an expanded uncertainty interval that has about a 95 % probability of encompassing the consensus mean. The $\delta^{13}C$ value and expanded uncertainty are taken from Table S-4 (Supporting Info) [4]. (VPDB - Vienna Peedee belemnite; LSVEC – Li Svec [named for H. Svec, formerly of Ames Laboratory, Iowa]).

[(c)] The $\delta^{2}H$ value is expressed as a mean and an expanded uncertainty. The expanded uncertainty is equal to $U = ku_c$, where u_c is the combined standard uncertainty as defined by the ISO Guide [3] and k is the coverage factor. The combined standard uncertainty is intended to represent, at the level of one standard deviation, the effect of random errors on the reference value that were evaluated by statistical means (Type A). Any uncertainty due to biases in the methods is not included in the expanded uncertainty. The coverage factor for the $\delta^{2}H$ value, k = 2.042 (n = 31), provides an expanded uncertainty interval that has about a 95 % probability of encompassing the mean. The $\delta^{2}H$ value and expanded uncertainty are taken from data in [5]. (VSMOW – Vienna Standard Mean Ocean Water; SLAP-Standard Light Antarctic Precipitation).

Expiration of Value Assignment: RM 8539 is valid, within the measurement uncertainty specified, until **31 December 2020**, provided the RM is handled and stored in accordance with instructions given in this Report of Investigation (see "Instructions for Handling and Storage"). The reference values are nullified if the RM is damaged, contaminated, or otherwise modified.

Maintenance of RM: NIST will monitor this RM over the period of its validity. If substantive technical changes occur that affect the value assignment before the expiration of this report, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The technical aspects involved in the issuance of this RM were coordinated by R.D. Vocke, Jr of the NIST Chemical Sciences Division.

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

Reference Difference in Isotope-Number Ratio Values: The differences in measured isotope-number ratios of stable carbon isotopes in substance P, $R(^{13}C/^{12}C)_P = [N(^{13}C)_P / N(^{12}C)_P]$, are reported as $\delta^{13}C$ values [6]. The differences in measured isotope-number ratios of stable hydrogen isotopes in substance P, $R(^{2}H/^{1}H)_P = [N(^{2}H)_P / N(^{1}H)_P]$, are reported as $\delta^{2}H$ values [6]. The relative differences in isotope-number ratios for carbon are referenced to VPDB while those for hydrogen are referenced to VSMOW, where:

$$\delta^{13}C = [R(^{13}C/^{12}C)_{sample} / R(^{13}C/^{12}C)_{VPDB\text{-}LSVEC}] - 1$$

$$\delta^{2}H = [R(^{2}H/^{1}H)_{sample} / R(^{2}H/^{1}H)_{VSMOW\text{-}SLAP}] - 1$$

VPDB-LSVEC refers to the Vienna PDB-LSVEC scale which is defined by assigning a $\delta^{13}C$ value of +1.95 ‰ to NBS 19 (RM 8544) and a consensus value of –46.6 ‰ to LSVEC (RM 8545) [7] for the purpose of normalizing stable carbon isotopic measurements (see "Normalization" [6,7]). The symbol ‰ is part per thousand and is equal to 0.001.

VSMOW-SLAP refers to the Vienna SMOW-SLAP scale which is defined by assigning a $\delta^{2}H$ value of 0 to VSMOW2 (RM 8535a) and a value of –428 ‰ to measurements of SLAP (RM 8537) or –427.5 ‰ to measurements of SLAP2 (RM 8537a) [9] for the purpose of normalizing stable hydrogen isotope measurements (see "Normalization" [8,9]). The symbol ‰ is part per thousand and is equal to 0.001.

INSTRUCTIONS FOR HANDLING AND STORAGE

Handling and Storage: 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.

Distribution: The distribution of RM 8539 (NBS 22) is limited to one unit per customer per three-year period of time.

PREPARATION AND ANALYSIS

Sample Preparation: RM 8539 was prepared by S. Silverman, University of California, San Diego, California [10].

Analytical Methods: The $\delta^{13}C$ value and expanded uncertainty reported in Table 1 are taken from results of an inter-laboratory study involving a two point calibration [4]. Results from four expert laboratories (Centrum voor Isotopen Onderzoek, Rijksuniversiteit Groningen, Groningen, Netherlands; Max-Planck-Institute for Biogeochemistry, Jena, Germany; UFZ [Umweltforschungszentrum] Leipzig-Halle GmbH, Leipzig, Germany; USGS, Reston, Virginia, USA) using continuous flow elemental-analyzer isotope-ratio mass spectrometry and following the general method of Qi *et al.* [11] were combined using a multivariate Bayesian approach for data reduction [4].

The $\delta^{2}H$ values were measured by continuous flow elemental-analyzer isotope-ratio mass spectrometry incorporating a high-temperature conversion technique at the USGS, Reston, VA, USA. The measured values were normalized to yield a value of –428 ‰ for RM 8537 (SLAP). The conversion technique uses a new silver tube sample introduction method that eliminates evaporation of reference water interspersed among aliquots of RM 8539 (NBS 22) [5].

The $\delta^{13}C$ and $\delta^{2}H$ values and expanded uncertainties reported in Table 1 for RM 8559 (NBS 22) are the values accepted by the Commission on Isotopic Abundances and Atomic Weights of the International Union of Pure and Applied Chemistry (IUPAC) (http://ciaaw.org/Carbon.htm and http://ciaaw.org/Hydrogen.htm, respectively) for this RM as of the date of this report.

Isotopic Homogeneity: Data from the inter-laboratory comparisons of NBS 22 suggest that there is no evidence of carbon or hydrogen isotopic heterogeneity.

Normalization: The $\delta^{13}C$ values in samples should be normalized to the VPDB-LSVEC δ-scale by calibrating the measurement with respect to the δ-value for NBS 19 and the δ-value for LSVEC (RM 8545), the ^{13}C-depleted anchor RM [6,7]. A general formula for normalizing measured carbon isotope-number ratios using two laboratory standards LS1 (NBS 19) and LS2 (LSVEC) can be expressed as:

$$\delta^{13}C_{\text{sample, cal}} = \delta^{13}C_{\text{LS1, cal}} + \left(\delta^{13}C_{\text{sample, WS}} - \delta^{13}C_{\text{LS1, WS}}\right) \times f \quad (1)$$

where the normalization factor f is:

$$f = \left(\delta^{13}C_{\text{LS2, cal}} - \delta^{13}C_{\text{LS1, cal}}\right) \Big/ \left(\delta^{13}C_{\text{LS2, WS}} - \delta^{13}C_{\text{LS1, WS}}\right) \quad (2)$$

Note: In the formulae above, cal denotes calibrated measurements made versus the VPDB scale, and $\delta^{13}C_{\text{LS1,cal}}$ and $\delta^{13}C_{\text{LS2,cal}}$ are the conventionally fixed $\delta^{13}C$ values for NBS 19 and LSVEC. WS denotes measurements made versus a transfer gas (working standard), and $\delta^{13}C_{\text{LS1,WS}}$ and $\delta^{13}C_{\text{LS2,WS}}$ are the $\delta^{13}C$ values for calibrated laboratory working standards.

Similar formulae are used for normalizing $\delta^{2}H$ values in samples to the VSMOW-SLAP scale where LS1 is VSMOW2 and LS2 is SLAP or SLAP2 [8,9].

Please note that the reporting scale for $\delta^{2}H$ is still denoted and referred to as the VSMOW-SLAP scale in spite of the exhaustion of the original supply of VSMOW and SLAP [12]. Of course, the combined standard uncertainties of VSMOW2 and SLAP2 isotopic values have to be included in any uncertainty budget.

Reporting of Stable Isotope δ values: The following recommendations from IUPAC are provided for reporting $\delta^{13}C$ and $\delta^{2}H$ values [6–9]. It is recommended that:

- $\delta^{13}C$ values of all carbon-bearing substances be measured and expressed relative to VPDB on a normalized scale where LSVEC has a consensus value of –46.6 ‰ and NBS 19 has a value of +1.95 ‰;
- $\delta^{2}H$ values of all hydrogen-bearing substances be expressed relative to VSMOW-SLAP on a scale where SLAP or SLAP2 has a consensus value of –428 ‰ or –427.5 ‰, respectively and VSMOW2 has a value of 0;
- Authors should clearly state that their data have been normalized.

In addition, researchers are encouraged to report the isotopic compositions of RM 8539 and other internationally distributed carbon or hydrogen isotopic reference materials [13] in their publications, as appropriate to the method, as though they have been interspersed among unknowns.

Current Reports of Investigation (ROI) for all light stable isotopic RMs mentioned in this report are available on the SRM web site [14].

REFERENCES

[1] 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); available at http://onlinelibrary.wiley.com/doi/10.1002/rcm.5129/pdf (accessed Jan 2013).

[2] May, W.E.; Parris, R.M.; Beck II, C.M.; Fassett, J.D.; Greenberg, R.R.; Guenther, F.R.; Kramer, G.W.; Wise, S.A.; Gills, T.E.; Colbert, J.C.; Gettings, R.J.; MacDonald, B.S.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136; U.S. Government Printing Office: Washington, DC, (2000), available at http://www.nist.gov/srm/publications.cfm (accessed Jan 2013).

[3] JCGM 100:2008; *Evaluation of Measurement Data - Guide to the Expression of Uncertainty in Measurement*; (ISO GUM 1995 with Minor Corrections), Joint Committee for Guides in Metrology (JCGM) (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Dec 2012); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at http://www.nist.gov/pml/pubs/index.cfm (accessed Jan 2013).

[4] Coplen, T.B.; Brand, W.A.; Gehre, M.; Groening, M.; Meijer, H.A.J.; Toman, B.; Verkouteren, R.M.; *New Guidelines for $\delta^{13}C$ Measurements*; Analytical Chemistry, Vol. 78, pp. 2439–2441 (2006).

[5] Coplen, T.B.; Qi, H.; *Applying the Silver-Tube Introduction Method for Thermal Conversion Elemental Analyses and a New $\delta^{2}H$ Value for NBS 22 Oil*; Rapid Communications in Mass Spectrometry, Vol. 24, pp. 2269-2276 (2010).

[6] Coplen, T.B.; *Reporting of Stable Hydrogen, Carbon and Oxygen Isotopic Abundances*; Pure & Applied Chemistry, Vol. 66, No. (2), pp. 273-276 (1994).

[7] Coplen, T.B.; Brand, W.B.; Gehre, M.; Groening, M.; Meijer, H.A.; Toman, B.; Verkouteren, M.R.; *After Two Decades a Second Anchor for the VPDB $\delta^{13}C$ Scale*; Rapid Communications in Mass Spectrometry, Vol. 20, pp. 3165–3166 (2006).

[8] Coplen, T.B.; *Normalization of Oxygen and Hydrogen Data*; Chemical Geology, Vol. 72, pp. 293–297 (1988).

[9] Gröning, M.; *International Stable Isotope Reference Materials*; Stable Isotope Analytical Techniques; Vol. 1, De Groot, P.A., Eds.; Elsevier, Amsterdam, pp. 874–906 (2004).

[10] Hut, G.; *Stable Isotope Reference Samples for Geochemical and Hydrological Investigations* (Rep. Consultants Group Meeting, Vienna, 1985). International Atomic Energy Agency, Vienna, pp. 1–42 (1987).

[11] Qi, H.P.; Coplen, T.B.; Geilmann, H.; Brand, W.A.; Böhlke, J.K.; *Two New Organic Reference Materials for $\delta^{13}C$ and $\delta^{15}N$ Measurements and a New Value for the $\delta^{13}C$ of NBS 22 Oil*; Rapid Communications in Mass Spectrometry, Vol. 17, pp. 2483–2487 (2003).

[12] Coplen, T.; *Discontinuance of SMOW and PDB*; Nature 375; Nature Publishing Group, pp. 285 (1995).

[13] Coplen, T.B.; Hopple, J.A.; Böhlke, J.K.; Peiser, H.S.; Rieder, S.E.; Krouse, H.R.; Rosman, K.J.R.; Ding, T.; Vocke, Jr., R.D.; Révész, K.M.; Lamberty, A.; Taylor, P.; De Bièvre, P; *Compilation of Minimum and Maximum Isotope Ratios of Selected Elements in Naturally Occurring Terrestrial Materials and Reagents*; U.S. Geological Survey Water-Resources Investigations Report 01-4222, p. 98 (2001); available at http://pubs.usgs.gov/wri/wri014222/pdf/wri01-4222.pdf (accessed Jan 2013).

[14] Light Stable Isotopic Materials (gas, liquid and solid forms) *Report of Investigation*; National Institute of Standards and Technology; U.S. Department of Commerce: Gaithersburg, MD 20899; available at https://www-s.nist.gov/srmors/viewTableV.cfm?tableid=42 (accessed Jan 2013).

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