National Institute of Standards & Technology

Report of Investigation

Reference Material 8557

NBS127
(Sulfur and Oxygen Isotopes in Barium Sulfate)

This Reference Material (RM) is intended for use in developing and validating methods for measuring relative differences in sulfur (S) isotope-number ratios, $R(^{34}S/^{32}S)$, and oxygen (O) isotope-number ratios, $R(^{18}O/^{16}O)$ [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 NBS127. A unit of RM 8557 consists of one bottle containing approximately 0.5 g of barium sulfate ($BaSO_4$).

Table 1. Reference Values[(a)] and Expanded Uncertainties
for the Relative S and O Isotope-Number Ratio Differences of RM 8557

RM Number	Name	Reference Value $10^3\ \delta^{34}S_{VCDT}$ [(b)]	Expanded Uncertainty $10^3\ \delta^{34}S_{VCDT}$ [(b)]	Reference Value $10^3\ \delta^{18}O_{VSMOW\text{-}SLAP}$ [(c)]	Expanded Uncertainty $10^3\ \delta^{18}O_{VSMOW\text{-}SLAP}$ [(c)]
8557	NBS127	+21.17	±0.09	+8.59	±0.23

(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 $\delta^{34}S$ 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 combined standard uncertainty is intended to represent, at the level of one standard deviation, the effects of random errors on the reference value that were evaluated by statistical means (Type A). The coverage factor for the $\delta^{34}S$ value, k = 2.262 (n=10), provides an expanded uncertainty interval that has about a 95 % probability of encompassing the mean. The $\delta^{34}S_{VCDT}$ value and expanded uncertainty are taken from data in reference 4.

(c) The $\delta^{18}O$ 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 $\delta^{18}O$ value, k = 2.0 (n=210), provides an expanded uncertainty interval that has about a 95 % probability of encompassing the mean. The $\delta^{18}O_{VSMOW\text{-}SLAP}$ value is from [5] and the expanded uncertainty has been recalculated from the reported "estimated combined uncertainty" in reference 5 in accordance with the ISO Guide [3].

Expiration of Reference Value: RM 8557 is valid, within the measurement uncertainty specified, until **31 December 2020**, provided the RM is handled in accordance with instructions given in this Report of Investigation (see "Instructions for Handling, Storage, and Use"). This report is nullified if the RM is damaged, contaminated, or otherwise modified.

Maintenance of RM Certification: NIST 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, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

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

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Report Issue Date: 30 January 2013
See Report Revision History on Last Page

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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 sulfur isotopes in substance P, $R(^{34}S/^{32}S)_P = [N(^{34}S)_P / N(^{32}S)_P]$, are reported as $\delta^{34}S$ values [6]. The differences in measured isotope-number ratios of stable oxygen isotopes in substance P, $R(^{18}O/^{16}O)_P = [N(^{18}O)_P / N(^{16}O)_P]$, are reported as $\delta^{18}O$ values [7]. The relative differences in isotope-number ratios for sulfur are referenced to VCDT while those for oxygen are referenced to VSMOW, where:

$$\delta^{34}S = [R(^{34}S/^{32}S)_{sample} / R(^{34}S/^{32}S)_{VCDT}] - 1$$

$$\delta^{18}O = [R(^{18}O/^{16}O)_{sample} / R(^{18}O/^{16}O)_{VSMOW\text{-}SLAP}] - 1$$

VCDT refers to the Vienna Cañon-Diablo Troilite scale which is defined by assigning a consensus $\delta^{34}S$ value of –0.3 ‰ to IAEA-S-1 (RM 8554) [6]. 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 $\delta^{18}O$ value of 0 to VSMOW2 (RM 8535a) and a value of –55.5 ‰ exactly to measurements of SLAP (RM 8537) or SLAP2 (RM 8537a) for the purpose of normalizing stable oxygen isotope measurements (see *Normalization* [8–10]). The symbol ‰ is part per thousand and is equal to 0.001.

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Handling and Storage: RM 8557 (NBS127) is stable at room temperature. 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 8557 (NBS127) is limited to one unit per three-year period of time.

PREPARATION AND ANALYSIS

Preparation: RM 8557 (NBS127) was prepared by J.R. O’Neil, USGS Menlo Park, California and bottled by I. Friedman, USGS Denver, Colorado. It was produced from sulfate in seawater from Monterey Bay, California by ion exchange [9].

Analytical Methods: The $\delta^{34}S$ value and expanded uncertainty reported in Table 1 are taken from results reported in [4], using thermal decomposition to convert the sulfate to SO_2 followed by mass spectrometric measurements and corrections for instrumental and oxygen isobaric interferences.

The $\delta^{18}O$ value and expanded uncertainty reported in Table 1 are taken from [5] which was a comprehensive inter-laboratory calibration of 11 oxygen isotopic RMs using a variety of on-line high-temperature conversion techniques. All measurements were normalized to the VSMOW-SLAP scale. The uncertainties had originally been reported as “estimated combined uncertainties” and these values have been converted into Expanded Uncertainties in accordance with GUM [3].

The $\delta^{34}S$ and $\delta^{18}O$ values and expanded uncertainties reported in Table 1 for RM 8557 (NBS127) 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/Sulfur.htm; http://ciaaw.org/Oxygen.htm) and the IAEA as of the date of this report.

Isotopic Homogeneity: Data from the inter-laboratory comparisons of NBS127 suggest that there is no evidence of sulfur or oxygen isotopic heterogeneity [4,9].

Normalization: The δ^{34}S values in samples should be normalized to the VCDT δ-scale by calibrating the measurement with respect to the δ-value for IAEA-S-1 (RM 8554) and the δ-value from the appropriate ^{34}S-enriched or ^{34}S-depleted anchor RMs. IAEA-S-2 (RM 8555) should be used as the anchor for the ^{34}S-enriched end while IAEA-S-3 (RM 8529) is appropriate for the ^{34}S-depleted end of the scale. A general formula for normalizing measured sulfur isotope number ratios using two laboratory standards LS1 (e.g. IAEA-S-1, RM 8554) and LS2 (e.g. IAEA-S-2, RM 8555) can be expressed as:

$$\delta^{34}\mathrm{S}_{\mathrm{sample,\ cal}} = \delta^{34}\mathrm{S}_{\mathrm{LS1,\ cal}} + \left(\delta^{34}\mathrm{S}_{\mathrm{sample,\ WS}} - \delta^{34}\mathrm{S}_{\mathrm{LS1,\ WS}}\right) \times f \qquad (1)$$

where the normalization factor f is:

$$f = \left(\delta^{34}\mathrm{S}_{\mathrm{LS2,cal}} - \delta^{34}\mathrm{S}_{\mathrm{LS1,cal}}\right) \Big/ \left(\delta^{34}\mathrm{S}_{\mathrm{LS2,WS}} - \delta^{34}\mathrm{S}_{\mathrm{LS1,WS}}\right) \qquad (2)$$

Note: In the above formulas, cal denotes calibrated measurements made versus the VCDT scale, and $\delta^{34}\mathrm{S}_{\mathrm{LS1,cal}}$ and $\delta^{34}\mathrm{S}_{LS2,cal}$ are the conventionally fixed δ^{34}S values for IAEA-S-1 (RM 8554) and IAEA-S-2 (RM 8555). WS denotes measurements made versus a transfer gas (working standard), and $\delta^{34}\mathrm{S}_{\mathrm{LS1,WS}}$ and $\delta^{34}\mathrm{S}_{\mathrm{LS2,WS}}$ are the δ^{34}S values for calibrated laboratory working standards.

Similar formulae are used for normalizing δ^{18}O values in samples to the VSMOW-SLAP scale where LS1 would be VSMOW2 (RM 8535a) and LS2 would be SLAP (RM 8537) or SLAP2 (RM 8537a) [10].

Please note that the reporting scale for δ^{18}O 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 δ^{34}S values [6]. It is recommended that:

- the use of meteoritic troilite and the reporting of δ^{34}S data relative to Cañon-Diablo Troilite (CDT) be discontinued;
- all relative sulfur isotopic compositions be reported relative to VCDT;
- the VCDT scale be realized through the use of IAEA-S-1, silver sulfide (RM 8554).

The following recommendations from IUPAC are provided for reporting δ^{18}O values [7,10-12]. It is recommended that:

- δ^{18}O values of all oxygen-bearing substances be expressed relative to VSMOW-SLAP or relative to Vienna Peedee belemite (VPDB; for carbonates) on a scale such that $\delta^{18}\mathrm{O}_{\mathrm{SLAP2}} = -55.5$ ‰ or $\delta^{18}\mathrm{O}_{\mathrm{NBS19}} = -2.2$ ‰, respectively;
- the reporting of the relative difference of stable isotope-number ratios relative to SMOW and PDB (Peedee belemnite) be discontinued.

In addition, researchers are encouraged to report the isotopic compositions of RM 8557 (NBS127) 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 Reference Materials mentioned in this report are available on the NIST Standard Reference Materials web site [14].

REFERENCES

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Report Revision History: 30 January 2013 (Reference values updated and expanded uncertainties added for $\delta^{34}S$ and for $\delta^{18}O$; expiration date assigned; editorial changes); 22 June 1992 (Original report issue date).

Users of this RM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Group at: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.