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Reference Material 8557
NBS127

(Sulfur and Oxygen Isotopes in Barium Sulfate)

REFERENCE MATERIAL INFORMATION SHEET

Purpose: This Reference Material (RM) is a material with known isotope-number ratios for sulfur (S), $R(^{34}S/^{32}S)$, and oxygen (O), $R(^{18}O/^{16}O)$ [1–3]. It is intended for use in method development, method harmonization and as a control for sulfur isotope-number ratios and oxygen isotope-number ratios of working standards that have been calibrated to the VCDT (Vienna Cañon Diablo Troilite) and VSMOW-SLAP (Vienna Standard Mean Ocean Water – Standard Light Antarctic Precipitation) δ-scales. The equivalent name for this RM, as used by the International Atomic Energy Agency (IAEA) and the U.S. Geological Survey (USGS), is NBS127.

Description: A unit of RM 8557 (NBS127) consists of one bottle containing approximately 0.5 g of barium sulfate ($BaSO_4$).

Non-Certified Values: The assigned non-certified values for this RM are not certified but are at present the best estimates of the true values; however, the values may not include all sources of uncertainty [4]. The assigned isotope-delta values for this RM are provided in Table 1 below.

Table 1. Isotope-delta Non-Certified Values and Uncertainties for RM 8557 (NBS127)

NIST RM Number	IAEA Name	Non-Certified Value[a,b] $\delta^{34}S_{VCDT}$	Uncertainty[a,b] $\delta^{34}S_{VCDT}$	Non-Certified Value[b,c] $\delta^{18}O_{VSMOW}$	Uncertainty[b,c] $\delta^{18}O_{VSMOW}$
8557	NBS127	+21.12 ‰	±0.22 ‰	+8.59 ‰	±0.26 ‰

[a] The sulfur isotope-delta ($\delta^{34}S_{VCDT}$) value, reported relative to Vienna Cañon Diablo Troilite (VCDT), is expressed as a mean and the uncertainty as a standard deviation (1 sd). The isotope-delta value and uncertainty are taken from reference 5 and are based on $n = 14$ measurements. The isotope-delta value and uncertainty reported include only variation in the measurement precision.

[b] The symbol ‰ is part per thousand and is equal to 0.001.

[c] The oxygen isotope-delta ($\delta^{18}O_{VSMOW}$) value is reported relative to Vienna Standard Mean Ocean Water (VSMOW) and Standard Light Antarctic Precipitation (SLAP), which are the anchors of the oxygen isotope scale. The value is expressed as a weighted mean and the uncertainty as a combined uncertainty. The isotope-delta value and the uncertainty are taken from Brand et al., 2009 [6] and are based on $n = 210$ measurements. The reported combined uncertainty is derived from three times the standard error of the mean plus 0.1 ‰ evaporation correction [6].

Isotope-delta values for sulfur (S) and oxygen (O) are presently not traceable to the International System of Units (SI) or other higher-order reference system [4,7]. The Bureau International des Poids et Mesures (BIPM) has recognized this via a *Traceability Exception* approved by the International Committee for Weights and Measures (CIPM) during the Proceedings of Session 1 of the 104th meeting in March 2015 [8]. As noted in the *Traceability Exception*, non-SI traceable isotope-delta values "should be made traceable to materials recognized as International Standards" [4,8]. The International Standard VCDT is the accepted "stated reference" point for the sulfur isotope ratio measurement scale [2,9]. VCDT is realized primarily and explicitly through the silver sulfide RM 8554 (IAEA-S-1), where:

RM 8554 (IAEA-S-1) *Silver Sulfide*: $\delta^{34}S_{VCDT} \equiv -0.30$ ‰ (exact)

The International Standard VSMOW is the accepted "stated reference" point for the oxygen isotope ratio measurement scale [2,10]. VSMOW is realized primarily and explicitly through the water RM 8535a (VSMOW2), where:

RM 8535a (VSMOW2): $\delta^{18}O_{VSMOW} \equiv 0.0$ ‰ ± 0.02 ‰ (combined standard uncertainty)

Period of Validity: The non-certified values are valid within the measurement uncertainty specified until **01 May 2030**. The value assignments are nullified if the material is stored or used improperly, damaged, contaminated, or otherwise modified.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Steven J. Choquette, Director
Office of Reference Materials

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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. Before making use of any of the values delivered by this material, users should obtain the most recent version of this documentation, available free of charge through the https://www.nist.gov/srm website.

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.

Additional Information: Additional information is provided in Appendix A. The distribution of RM 8557 (NBS127) is limited to one unit per three-year period. Users are encouraged to prepare their own standards for daily use and calibrate those standards against international reference materials.

REFERENCES

[1] JCGM 200:2012; *International Vocabulary of Metrology - Basic and General Concepts and Associated Terms (VIM)*, 3rd ed.; Joint Committee for Guides in Metrology (JCGM) (2012); available at https://www.bipm.org/en/publications/guides (accessed Mar 2022).

[2] Brand, W.A.; Coplen, T.B.; Vogl, J.; Rosner, M.; Prohaska, T.; *Assessment of International Reference Materials for Isotope-Ratio Analysis (IUPAC Technical Report)*; Pure Appl. Chem., Vol. 86, pp. 425–467 (2014).

[3] Coplen, T.B.; *Guidelines and Recommended Terms for Expression of Stable-Isotope-Ratio and Gas-Ratio Measurement Results*, Rapid Commun. Mass Spectrom., Vol. 25, pp. 2538–2560 (2011).

[4] Beauchamp, C.R.; Camara, J.E.; Carney, J.; Choquette, S.J.; Cole, K.D.; DeRose, P.C.; Duewer, D.L.; Epstein, M.S.; Kline, M.C.; Lippa, K.A.; Lucon, E.; Molloy, J.; Nelson, M.A.; Phinney, K.W.; Polakoski, M.; Possolo, A.; Sander, L.C.; Schiel, J.E.; Sharpless, K.E.; Toman, B.; Winchester, M.R.; Windover, D.; *Metrological Tools for the Reference Materials and Reference Instruments of the NIST Material Measurement Laboratory*; NIST Special Publication (NIST SP) 260-136, 2021 edition; U.S. Government Printing Office: Washington, DC (2021); available at https://nvlpubs.nist.gov/nistpubs/SpecialPublications/NIST.SP.260-136-2021.pdf (accessed Mar 2022).

[5] Guillaume, P.; Sessions, A.L.; Subhas, A.V.; Adkins, J.F.; *MC-ICP-MS Measurement of $\delta^{34}S$ and $\Delta^{33}S$ in Small Amounts of Dissolved Sulfate*; Chemical Geology, Vol. 345, pp. 50–61 (2013).

[6] Brand, W.A.; Coplen, T.B.; Aerts-Bijma, A.T.; Böhlke, J.K.; Gehre, M.; Geilmann, H.; Gröning, M.; Jansen, H.G.; Meijer, H.A.J.; Mroczkowski, S.J.; Qi, H.; Soergel, K.; Stuart-Williams, H.; Weise, S.M.; Werner, R.A.; *Comprehensive Inter-Laboratory Calibration of Reference Materials for $\delta^{18}O$ versus VSMOW Using Various On-Line High-Temperature Conversion Techniques*; Rapid Commun. Mass Spectrom., Vol. 23(7), pp. 999–1019 (2009).

[7] 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 Mar 2022).

[8] 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 Mar 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, p. 34 (2015); available at https://www.bipm.org/utils/en/pdf/CIPM/CIPM2015-I-EN.pdf (accessed Mar 2022).

[9] Krouse, H.R.; Coplen, T.B.; *Reporting of Relative Sulfur Isotope-Ratio Data*; Pure Appl. Chem., Vol. 69(2), pp. 293–295 (1997).

[10] Coplen, T.B.; *Reporting of Stable Hydrogen, Carbon and Oxygen Isotopic Abundances*; Pure Appl. Chem., Vol. 66(2), pp. 273–276 (1994).

[11] Hut, G.; *Stable Isotope Reference Samples for Geochemical and Hydrological Investigations* (Consultants Group Meeting, Vienna, September 16–18, 1985). International Atomic Energy Agency, Vienna, pp. 1–42 (1987); available at https://inis.iaea.org/collection/NCLCollectionStore/_Public/18/075/18075746.pdf (accessed Mar 2022).

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

[13] Gonfiantini, R.; *Standards for Stable Isotope Measurements in Natural Compounds*; Nature, Vol 271, pp. 534–536, (1978).

[14] Coplen, T.B.; *Discontinuance of SMOW and PDB*; Nature, Vol 375, p. 285 (1995).
[15] 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, R.D., Jr.; 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 (2002).
[16] Gröning, M.; *International Stable Isotope Reference Materials*; *Handbook of Stable Isotope Analytical Techniques*, Vol. 1; De Groot, P.A., Ed.; Elsevier: Amsterdam, pp. 874–906 (2004).
[17] *Light Stable Isotopic Materials (Gas, Liquid and Solid Forms)*; NIST SRM Order Request System; 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 Mar 2022).

Information Sheet Revision History: 07 March 2022 (Updated sulfur isotope-delta value; updated sulfur isotope-delta expanded uncertainty to standard deviation to be in-line with that reported by other international organizations; updated oxygen isotope expanded uncertainty to combined uncertainty to reflect the accepted reported uncertainties adopted by international organizations; addition of traceability statement; change of expiration date; updated format; editorial changes); **30 January 2013** (Reference value updated and expanded uncertainty added for $\delta^{34}S_{VCDT}$; 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 OF RM 8557

Technical aspects involved in the issuance of this RM were coordinated through the NIST Chemical Sciences Division by J.L. Mann.

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

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 [11].

Analytical Methods: The $\delta^{34}S_{VCDT}$ value and uncertainty reported in Table 1 for RM 8557 (NBS127) are taken from results reported in [5], where S measurements were made using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) coupled to a heated spray chamber/membrane desolvator.

The $\delta^{18}O_{VSMOW}$ value and uncertainty reported in Table 1 are taken from [6] 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 ($\delta^{18}O$ of 0.0 ‰) scale (see information on Normalization in Reporting section below) and SLAP ($\delta^{18}O$ of −55.5 ‰ exactly).

The $\delta^{34}S_{VCDT}$ and $\delta^{18}O_{VSMOW}$ values and 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) (https://ciaaw.org/sulfur-references.htm; https://ciaaw.org/oxygen-references.htm) [2], and the IAEA as of the date of this report.

Isotopic Homogeneity: Assessment of 20 µmole/L S samples (n = 14) of RM 8557 (NBS127) [6] and many years of use of this material suggest that at these sample sizes there is no evidence of sulfur isotopic heterogeneity in this reference material. We are currently unaware of any formal homogeneity evaluation for O in this material. However, many years of use by the isotope ratio community seem to indicate that the material's homogeneity is suitable for present measurement applications.

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 [3].

Isotope-delta (δ) Values: The sulfur isotope-delta value of a measured sample ($\delta^{34}S_{sample}$) reported on the VCDT scale is defined as the difference in the measured isotope-number ratio of sulfur [$N(^{34}S)/N(^{32}S)$] in the sample relative to the stable isotope-number ratio of sulfur in VCDT [2,9]:

$$\delta^{34}S_{sample} = \frac{\left[\frac{N_{sample}(^{34}S)}{N_{sample}(^{32}S)}\right] - \left[\frac{N_{VCDT}(^{34}S)}{N_{VCDT}(^{32}S)}\right]}{\left[\frac{N_{VCDT}(^{34}S)}{N_{VCDT}(^{32}S)}\right]}$$

The oxygen isotope-delta value of a measured sample ($\delta^{18}O_{sample}$) reported on the VSMOW scale is defined as the difference in the measured isotope-number ratio of oxygen [$N(^{18}O/N(^{16}O)$] in the sample relative to the stable isotope-number ratio of oxygen in VSMOW [2,10]:

$$\delta^{18}O_{sample} = \frac{\left[\frac{N_{sample}(^{18}O)}{N_{sample}(^{16}O)}\right] - \left[\frac{N_{VSMOW}(^{18}O)}{N_{VSMOW}(^{16}O)}\right]}{\left[\frac{N_{VSMOW}(^{18}O)}{N_{VSMOW}(^{16}O)}\right]}$$

Normalization: The $\delta^{34}S$ value in a sample should be normalized to the VCDT δ-scale by calibrating the measurement with respect to the δ value for RM 8554 (IAEA-S-1) and the δ value from the appropriate ^{34}S-enriched or ^{34}S-depleted anchor RM. RM 8555 (IAEA-S-2) should be used as the anchor for the ^{34}S-enriched end while RM 8529 (IAEA-S-3) is appropriate for the ^{34}S-depleted end of the scale. A general formula for normalizing a measured sulfur isotope number ratio [$N(^{34}S)/N(^{32}S)$] using two laboratory standards LS1 (e.g., RM 8554 (IAEA-S-1)) and LS2 (e.g., RM 8555 (IAEA-S-2)) can be expressed as:

$$\delta^{34}S_{sample,cal} = \delta^{34}S_{LS1,cal} + \left(\delta^{34}S_{sample,WS} - \delta^{34}S_{LS1,WS}\right) \times f \quad (1)$$

where the normalization factor f is:

$$f = \left(\delta^{34}S_{LS2,cal} - \delta^{34}S_{LS1,cal}\right) \Big/ \left(\delta^{34}S_{LS2,WS} - \delta^{34}S_{LS1,WS}\right) \quad (2)$$

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

Similar formulae are used for normalizing $\delta^{18}O$ values in samples to the VSMOW scale where LS1 would be RM 8535a (VSMOW2) and LS2 would be RM 8537 (SLAP) or RM 8537a (SLAP2) [12].

The VSMOW scale is defined by assigning a $\delta^{18}O$ value of 0 ‰ to RM 8535a (VSMOW2) and a value of –55.5 ‰ exactly to measurements of RM 8537 (SLAP) or RM 8537a (SLAP2) for the purpose of normalizing stable oxygen isotope measurements [11–13].

Please note that the reporting scale for $\delta^{18}O$ is still denoted and referred to as the VSMOW scale despite the exhaustion of the original supply of VSMOW [14].

Reporting of Sulfur and Oxygen Stable Isotope-delta (δ) values: The following recommendations from IUPAC are provided for reporting $\delta^{34}S$ values [2,9,15]. It is recommended that:

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

The following recommendations from IUPAC are provided for reporting $\delta^{18}O$ values [10,12,14,16]. It is recommended that:

- $\delta^{18}O$ values of all oxygen-bearing substances be expressed relative to VSMOW or relative to Vienna Peedee belemnite (VPDB; for carbonates) on a scale such that $\delta^{18}O$ of SLAP2 = –55.5 ‰ or $\delta^{18}O$ of NBS 19 = –2.2 ‰, respectively.
- the reporting of stable isotope-delta values 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 sulfur or oxygen isotopic reference materials in their publications, as appropriate to the method, as though they have been interspersed among unknowns.

Current Reports of Investigation (ROI) and Reference Material Information Sheets (RMIS) for all light stable isotopic Reference Materials mentioned in this report are available on the NIST Standard Reference Materials website [17].

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