National Institute of Standards & Technology

Report of Investigation

Reference Material 8556

NBS123
(Sulfur Isotopes in Sphalerite)

This Reference Material (RM) is intended for use in developing and validating methods for measuring relative differences in sulfur (S) isotope-number ratios, $R(^{34}S/^{32}S)$ [1]. Even though the value for this RM is a reference value 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 NBS123. A unit of RM 8556 consists of one bottle containing approximately 1.5 g of sphalerite (ZnS).

Table 1. Reference Value[(a)] and Expanded Uncertainty
for the Relative S Isotope-Number Ratio Difference of RM 8556.

RM Number	Name	Reference Value $10^3\ \delta^{34}S_{VCDT}$[(b)]	Expanded Uncertainty $10^3\ \delta^{34}S_{VCDT}$[(b)]
8556	NBS123	+17.09	±0.19

[(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/JCGM 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, $k = 2.179$ (n=13), 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.

Expiration of Value Assignment: RM 8556 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: 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 or register online) will facilitate notification.

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

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

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Gaithersburg, MD 20899
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Report Revision History on Last Page

Steven J. Choquette, Director
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 [5]. The relative differences in isotope-number ratios for sulfur are referenced to VCDT where:

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

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

Metrological Traceability: Delta value isotope ratio measurements for sulfur cannot presently be made traceable to the SI. The BIPM has recognized this via a *Traceability Exception* approved by the CIPM during the Proceedings of Session 1 of the 104th meeting in March 2015 [6]. As noted in the *Traceability Exception*, non-SI traceable delta value isotope ratio measurements "should be made traceable to materials recognized as International Standards" [6]. VCDT is an International Standard and is the accepted "stated reference" [5,6] for the $^{34}S/^{32}S$ VCDT isotope ratio measurement scale and provides the traceability link. VCDT is realized explicitly through the silver sulfide RM 8554, where:

RM 8554 *IAEA-S-1 Sulfur Isotopes in Silver Sulfide*: $\delta^{34}S_{VCDT} \equiv$ -0.3 ‰ exact

Thus, for sulfur generated from RM 8554 as SF_6 or SO_2:

RM 8544 (SF_6 or SO_2): $\delta^{34}S_{VCDT}$ = -0.3 ‰ exact

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Handling and Storage: RM 8556 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 8556 (NBS123) is limited to one unit per customer per three-year period of time.

PREPARATION AND ANALYSIS

Preparation: RM 8556 (NBS123) was prepared by S. Halas, Marie Curie-Skłodowskie University, Lublin, Poland.

Analytical Methods: The $\delta^{34}S$ value and expanded uncertainty reported in Table 1 are taken from an inter-laboratory comparison involving 13 labs from around the world and reported in reference 4.

They 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) and the IAEA as of the date of this report [7].

Isotopic Homogeneity: Data from the inter-laboratory comparison of NBS123 suggest that there is no evidence of sulfur isotopic heterogeneity [4].

Normalization: The $\delta^{34}S$ 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:

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

where the normalization factor f is:

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

Note: In the formulas above, 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 IAEA-S-1 (RM 8554) and IAEA-S-2 (RM 8555). 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.

Reporting of Sulfur Stable Isotope δ-Values: The following recommendations from IUPAC are provided for reporting δ^{34}S values [5, 7]. 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).

In addition, researchers are encouraged to report the isotopic composition of RM 8556 (NBS123) and other internationally distributed sulfur isotopic reference materials [5,7] 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 [8].

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 https://onlinelibrary.wiley.com/doi/pdf/10.1002/rcm.5129 (accessed May 2019).

[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 Spec. Pub. 260-136; U.S. Government Printing Office: Washington, DC, (2000), available at https://www.nist.gov/sites/default/files/documents/srm/SP260-136.PDF (accessed May 2019).

[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 (JCGM) (2008); available at https://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed May 2019); 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 https://www.nist.gov/pml/pubs/tn1297/index.cfm (accessed May 2019).

[4] 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); available at https://inis.iaea.org/collection/NCLCollectionStore/_Public/18/075/18075746.pdf (accessed May 2019).

[5] Krouse, H.R.; Coplen, T.B.; *Reporting of Relative Sulfur Isotope-Ratio Data.* Pure & Applied Chemistry, Vol. 69, No. 2; pp. 293–295 (1997); available at http://www.ciaaw.org/pubs/S%20Isotopic%20Reporting%20Guidelines.pdf (accessed Feb 2019).

[6] 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 May 2019). 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 May 2019).

[7] 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 and Applied Chemistry, Vol. 86(3), pp 425–467 (2014); available at https://pubs.usgs.gov/wri/wri014222/pdf/wri01-4222.pdf (accessed May 2019).

[8] *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 May 2019).

Report Revision History: 10 May 2019 (Changed unit size from 0.5 g to 1.5 g; added metrological traceability statement and references; 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).

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