National Institute of Standards & Technology

Report of Investigation

Reference Material 8529
IAEA-S-3
(Sulfur Isotopes in Silver Sulfide)

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]. It can also be used for anchoring normalizations on the ^{34}S-depleted end of the Vienna Cañon Diablo Troilite (VCDT) δ-scale for $\delta^{34}S$ values [2]. Even though the value for this RM is a reference value and not certified [3], 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 IAEA-S-3. This material was formerly called NZ-3 (New Zealand) [4]. A unit of RM 8529 consists of one bottle containing approximately 0.5 g of silver sulfide (Ag_2S).

Table 1. Reference Value[(a)] and Expanded Uncertainty for the Relative S Isotope-Number Ratio Difference of RM 8529

RM Number	Name	Reference Value $10^3 \times \delta^{34}S_{VCDT}$[(b)]	Expanded Uncertainty $10^3 \times \delta^{34}S_{VCDT}$[(b)]
8529	IAEA-S-3	–32.49	±0.17

[(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 [3].

[(b)] The $\delta^{34}S_{VCDT}$ 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 [5] 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, $k = 2.201$ (n = 12), provides an expanded uncertainty interval that has about a 95 % probability of encompassing the mean. The $\delta^{34}S_{VCDT}$ value and combined standard uncertainty are the revised values reported in references 6 and 7 after adjusting the coverage factor from k = 2 to k = 2.201.

Expiration of Value Assignment: RM 8529 is valid, within the specified 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 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 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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Robert L. Watters, Jr., Director
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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 [2]. 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 RM 8554 [2], where the symbol ‰ is part per thousand and is equal to 0.001.

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Handling and Storage: RM 8529 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 8529 (IAEA-S-3) is limited to one unit per three-year period of time.

PREPARATION AND ANALYSIS OF THE REFERENCE MATERIAL

Preparation: RM 8529 was prepared and purified by B.W. Robinson, Lower Hutt, New Zealand from a sphalerite provided by S. Halas, Maria Curie-Skłodowskie University, Lublin Poland [4].

Analytical Methods: The $\delta^{34}S$ value and expanded uncertainty reported in Table 1 are the values resulting from combining data from gas isotope ratio mass spectrometry (after converting IAEA-S-2 to SF_6) and double-spike thermal ionization mass spectrometry (with Carius-Tube dissolution after spiking) [6,7].

The $\delta^{34}S$ value and expanded uncertainty reported in Table 1 for RM 8529 (IAEA-S-3) 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.

Isotopic Homogeneity: Data from an inter-laboratory comparison of IAEA-S-3 suggest that there is no evidence of isotopic heterogeneity in this reference material [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-3, RM 8529) 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-3 (RM 8529). 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 $\delta^{34}S$ values [2]. It is recommended that:

- the use of meteoritic troilite and the reporting of $\delta^{34}S$ data relative to 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 8529 (IAEA-S-3) and other internationally distributed sulfur isotopic reference materials [8] 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 [9].

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 Feb 2013).

[2] Krouse, H.R.; Coplen, T.B.; *Reporting of Relative Sulfur Isotope-Ratio Data;* Pure Appl. Chem., Vol. 69, pp. 293–295 (1997) 8; available at http://www.iupac.org/publications/pac/1997/pdf/6902x0293.pdf (accessed Feb 2013).

[3] 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 http://www.nist.gov/srm/publications.cfm (accessed Feb 2013).

[4] Robinson, B.W.; *Sulfur Isotope Standards, IAEA-TECDOC-825*, IAEA Vienna pp. 39–45 (1995); available at http://www-pub.iaea.org/MTCD/publications/PDF/te_825_prn.pdf (accessed Feb 2013).

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[6] Mann. J.L.; Vocke, R.D. Jr.; Kelly, W.R.; *Revised $\delta^{34}S$ Reference Values for IAEA Sulfur Isotope Reference Materials S-2 and S-3;* Rapid Communications in Mass Spectrometry, Vol. 23, pp. 1116–1124 (2009).

[7] Mann. J.L.; Vocke, R.D. ; Kelly, W.R.; *Erratum: Revised $\delta^{34}S$ Reference Values for IAEA Sulfur Isotope Reference Materials S-2 and S-3;* Rapid Communications in Mass Spectrometry, Vol. 23, p. 1746 (2009).

[8] 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 Feb 2013).

[9] *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 Feb 2013).

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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 http://www.nist.gov/srm.