National Institute of Standards & Technology

Report of Investigation

Reference Material 8555

IAEA-S-2
(Sulfur Isotopes in Silver Sulfide)

This Reference Material (RM) provides sulfur samples with known isotopic composition for measuring relative isotope ratios of sulfur (S), $R(^{34}S/^{32}S)$ [1]. It can also be used for anchoring normalizations on the ^{34}S-enriched end of the Vienna Cañon-Diablo Troilite (VCDT) isotope-delta (δ) scale ($\delta^{34}S_{VCDT}$) [2,3]. The reference value for this RM is not certified [4]; however, its use provides comparability of data among 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-2. This material was formerly called NZ-2 (New Zealand) [5]. A unit of RM 8555 (IAEA-S-2) consists of one bottle containing approximately 0.5 g of silver sulfide (Ag_2S).

Table 1. Isotope-Delta Reference Value[a] and Uncertainties[b] for RM 8555 (IAEA-S-2)

NIST RM Number	IAEA Name	Reference Value[b,e] $\delta^{34}S_{VCDT}$	Combined Uncertainty[b,c,e] $\delta^{34}S_{VCDT}$	Expanded Uncertainty[b,d,e] $\delta^{34}S_{VCDT}$
8555	IAEA-S-2	+22.62 ‰	± 0.08 ‰	0.16 ‰

[a] A reference value is a non-certified value that is the present best estimate of the true value; however, the value may reflect only the measurement precision and may not include all sources of uncertainty [4].

[b] The sulfur isotope-delta ($\delta^{34}S_{VCDT}$) reference value, reported relative to Vienna Cañon-Diablo Troilite (VCDT), is expressed as a mean and the uncertainties are given both as a combined standard uncertainty (u_c) as well as an expanded uncertainty (U). The isotope-delta value and uncertainties are the values reported in references 6 and 7.

[c] The combined standard uncertainty (u_c) 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).

[d] The expanded uncertainty (U) is equal to $U = ku_c$, where u_c is the combined standard uncertainty as defined by the ISO/JCGM Guide [8] and k is the coverage factor. The coverage factor, $k = 2$ ($n = 23$), provides an expanded uncertainty interval that has about a 95 % probability of encompassing the mean.

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

Metrological Traceability: Isotope-delta values for sulfur (S) cannot presently be made traceable to the International System of Units (SI). 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 [9]. As noted in the *Traceability Exception*, non-SI traceable isotope delta-values "should be made traceable to materials recognized as International Standards" [9]. The International Standard VCDT is the accepted "stated reference" point for the sulfur isotope ratio measurement scale [2,3]. 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)

Expiration of Value Assignment: RM 8555 (IAEA-S-2) is valid, within the measurement uncertainty specified, until **01 May 2030**, provided the RM is handled and stored in accordance with instructions given in this Report of Investigation (see "Instructions for Handling and Storage). This report is nullified if the RM is damaged, contaminated, or otherwise modified.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Gaithersburg, MD 20899
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Report Revision History on Last Page

Steven J. Choquette, Director
Office of Reference Materials

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 J.L. Mann.

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

INSTRUCTIONS FOR HANDLING AND STORAGE

Handling and Storage: RM 8555 (IAEA-S-2) 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 8555 (IAEA-S-2) is limited to one unit per three-year period.

PREPARATION AND ANALYSIS OF RM 8555

Preparation: RM 8555 (IAEA-S-2) was prepared and purified by B.W. Robinson, Lower Hutt, New Zealand from gypsum produced through natural evaporation from ponds owned by Dominion Salt, Ltd., New Zealand [5].

Analytical Methods: The $\delta^{34}S_{VCDT}$ value and uncertainties reported in Table 1 are derived by 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 $\delta^{34}S_{VCDT}$ value and uncertainties reported in Table 1 for RM 8555 (IAEA-S-2) 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) [2] and the IAEA as of the date of this report (https://nucleus.iaea.org/sites/ReferenceMaterials/Pages/IAEA-S-2.aspx).

Isotopic Homogeneity: Homogeneity assessment of 10 mg samples (n = 8) of RM 8555 (IAEA-S-2) [5] and many years of use by the isotope ratio community affirm 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 [1].

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 [2,3]:

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

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 (LS), LS1 (e.g., RM 8554 (IAEA-S-1)) and LS2 (e.g., RM 8555 (IAEA-S-2)), can be expressed as:

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

where the normalization factor f is:

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

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.

Reporting of Sulfur Stable Isotope-delta (δ) values: The following recommendations from IUPAC are provided for reporting $\delta^{34}S$ isotope-delta values [2,3,10]. 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 be realized through the use of RM 8554 (IAEA-S-1), silver sulfide.

In addition, researchers are encouraged to report the isotopic composition of RM 8555 (IAEA-S-2) and other internationally distributed sulfur isotopic reference materials [3,10] 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 [11].

REFERENCES

[1] 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).

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

[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.; Phinney, K.W.; Polakoski, M.; Possolo, A.; Sharpless, K.E.; Sieber, J.R.; 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, 2020 Edition; U.S. Government Printing Office: Washington, DC (2020); available at https://nvlpubs.nist.gov/nistpubs/SpecialPublications/NIST.SP.260-136-2020.pdf (accessed Sep 2021).

[5] Robinson, B.W.; *Sulfur Isotope Standards,* In Reference and Intercomparison Materials for Stable Isotopes of Light Elements*,* Proceedings of a Consultants Meeting Held in Vienna, 1–3 December 1993; IAEA-TECDOC-825: Vienna, Austria, pp. 39–45 (1995).

[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 Commun. Mass Spectrom., 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 Commun. Mass Spectrom., Vol. 23, p. 1746 (2009).

[8] 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 Sep 2021); 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/nist-technical-note-1297 (accessed Sep 2021).

[9] BIPM Traceability Exception: *Delta Value Isotope Ratio Measurements, Executive Summary of Decision CIPM/104-26*; In *International Committee for Weights and Measures (CIPM)*, Proceedings of Session I of the 104th meeting (9-10 March 2015), p. 34 (2015).

[10] 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).

[11] *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 Sep 2021).

Report Revision History: 17 September 2021 (Change of expiration date; addition of combined standard uncertainty; coverage factor of expanded uncertainty updated from $k = 2.201$ to $k = 2$ to provide consistency with other NIST stable light isotopes and international organizations; addition of metrological traceability statement and terminology section; 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; e-mail srminfo@nist.gov; or via the Internet at https://www.nist.gov/srm.