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Reference Material 8553

IAEA-S-4 (Soufre de Lacq)

(Sulfur Isotopes in Elemental Sulfur)

REFERENCE MATERIAL INFORMATION SHEET

Purpose: This Reference Material (RM) is a material with known isotope-number ratios for sulfur (S), $R(^{34}S/^{32}S)$ [1-3]. It is intended for use in method development, method harmonization and as a control for sulfur isotope-number ratios of working standards that have been calibrated to the VCDT (Vienna Canyon Diablo Troilite) δ-scale. 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-4. This material has historically been known as Soufre de Lacq.

Description: A unit of RM 8553 consists of one bottle containing approximately 0.5 g of elemental sulfur.

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

Table 1. Isotope-delta Non-Certified Value and Uncertainty for RM 8553 (IAEA-S-4)

NIST RM Number	IAEA Name	Non-Certified Value[a,b] $\delta^{34}S_{VCDT}$	Uncertainty[a,b,c,] $\delta^{34}S_{VCDT}$
8553	IAEA-S-4	+16.86 ‰	±0.12 ‰

[a] The sulfur isotope-delta ($\delta^{34}S_{VCDT}$) value, reported relative to Vienna Cañon-Diablo Troilite (VCDT), is expressed as a mean and standard deviation (1sd). The isotope-delta value is an adjusted value from that reported in reference 5. See the *Analytical Methods* section under *Preparation and Analysis of RM 8553* in Appendix A for details of the adjustment. The uncertainty is the reported value in reference 5.

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

[c] The uncertainty reported is based on $n = 63$ measurements and includes variation in the measurement precision and material homogeneity.

Isotope-delta values for sulfur (S) are presently not traceable to the International System of Units (SI) or other higher-order reference system [4,6]. 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 [7]. As noted in the *Traceability Exception*, non-SI traceable isotope delta-values "should be made traceable to materials recognized as International Standards" [4,7]. The International Standard VCDT is the accepted "stated reference" point for the sulfur isotope ratio measurement scale [2,8]. 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)

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

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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 value 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 8553 (IAEA-S-4) 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 8553 (IAEA-S-4) 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] ISO/IEC; *International Vocabulary of Metrology (VIM) - Basic and General Concepts and Associated Terms;* Guide 99-12:2007; Joint Committee for Guides in Metrology (JCGM), International Organization for Standardization, Geneva, pp. 1-127 (2008); 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] Qi, H.P.; Coplen, T.B.; *Evaluation of the $^{34}S/^{32}S$ Ratio of Soufre de Lacq Elemental Sulfur Isotopic Reference Material by Continuous Flow Isotope-Ratio Mass Spectrometry;* Chemical Geology, Vol. 199, pp. 183–187 (2003).

[6] 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).

[7] 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); https://www.bipm.org/utils/en/pdf/CIPM/CIPM2015-I-EN.pdf (accessed Mar 2022).

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

[9] 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).

[10] Mann, J.L.; Vocke, R.D. Jr.; 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).

[11] 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).

[12] *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: 01 March 2022 (Uncertainty value updated with standard deviation that replaced expanded uncertainty to be in-line with that reported by other international organizations including the IAEA and IUPAC; added traceability statement; change of expiration date; updated and added references; 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 8553

Preparation: RM 8553 (IAEA-S-4) was derived from natural gas and was prepared by E. Roth, Centre d'Etudes Nucléaires de Saclay, France.

Analytical methods: The $\delta^{34}S_{VCDT}$ value is derived from reference [5] where SO_2 gas was measured by continuous flow isotope-ratio mass spectrometry to obtain the sulfur isotope measurements. This value for RM 8553 (IAEA-S-4) is an adjusted value. The original $\delta^{34}S_{VCDT}$ value (+16.90 ‰) reported in reference [5] was normalized using a $\delta^{34}S_{VCDT}$ value for RM 8555 (IAEA-S-2) of +22.67 ‰. The $\delta^{34}S_{VCDT}$ value for RM 8555 (IAEA-S-2) has been revised to +22.62 ‰ [2,9,10] and the value for RM 8553 has been adjusted to reflect this change. The $\delta^{34}S_{VCDT}$ value and uncertainty reported in Table 1 for RM 8553 (IAEA-S-4) is the value accepted by the IAEA as of the date of this information sheet.

Isotopic Homogeneity: Homogeneity assessment of 47 µg to 56 µg samples of RM 8553 (IAEA-S-4) indicates the material's homogeneity is suitable for present measurement applications [5]. Many years of use by the isotope community suggest isotopic heterogeneity does not significantly contribute to the uncertainty of the non-certified value at these sample sizes and larger.

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 [2,8]:

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

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 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:

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

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 *δ*-values: The following recommendations from IUPAC are provided for reporting $\delta^{34}S$ isotope-delta values [2,8,11]. 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.

In addition, researchers are encouraged to report the isotopic composition of RM 8553 (IAEA-S-4) and other internationally distributed sulfur isotopic reference materials [8,11] 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 [12].

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APPENDIX B

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.

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