National Institute of Standards & Technology

Report of Investigation

Reference Material 8553

IAEA-S-4 (Soufre de Lacq)
(Sulfur Isotopes in Elemental Sulfur)

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], it is on the ^{34}S-enriched end of normal terrestrial sulfur isotope-number ratios, and its use will aid in evaluating the comparability of data from different laboratories. The equivalent name for this RM as currently used by the International Atomic Energy Agency (IAEA) and the U.S. Geological Survey (USGS) is IAEA-S-4. It was formerly known as Soufre de Lacq. A unit of RM 8553 consists of one bottle containing approximately 0.5 g of elemental sulfur.

Table 1. Reference Value[(a)] and Expanded Uncertainty
for the Relative S Isotope-Number Ratio Difference of RM 8553.

RM Number	Name	Reference Value $10^3\ \delta^{34}S_{VCDT}$[(b)]	Expanded Uncertainty $10^3\ \delta^{34}S_{VCDT}$[(b)]
8553	IAEA-S-4	+16.86	±0.03

[(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 $\delta^{34}S_{VCDT}$ value is an adjusted value from the value reported in reference 3. See the *Analytical Methods* section under *Preparation and Analysis* for details of the adjustment. The $\delta^{34}S$ values are 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 [4] 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 (n=66), provides an expanded uncertainty interval that has about a 95 % probability of encompassing the mean.

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 RM 8554 [5], where the symbol ‰ is part per thousand and is equal to 0.001.

Expiration of Value Assignment: RM 8553 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) 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.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Gaithersburg, MD 20899
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See Report Revision History on Last Page

Robert L. Watters, Jr., Director
Office of Reference Materials

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

INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Handling and 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.

Distribution: The distribution of RM 8553 (IAEA-S-4) is limited to one unit per customer per three-year period of time.

PREPARATION AND ANALYSIS

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 δ^{34}S value reported in Table 1 for RM 8553 (IAEA-S-4) is an adjusted value. The original δ^{34}S value (+16.90) reported in reference 3 was normalized using a δ^{34}S value for RM 8555 (IAEA-S-2) of +22.67. The δ^{34}S value for RM 8555 (IAEA-S-2) has been revised to +22.62 [6,7] and the value for RM 8553 has been adjusted to reflect this change.

The δ^{34}S value and expanded uncertainty reported in Table 1 for RM 8553 (IAEA-S-4) 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.

Normalization: The δ^{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:

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

where the normalization factor f is:

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

Note: In the formulas above, cal denotes calibrated measurements made versus the VCDT scale, and $\delta^{34}\mathrm{S}_{\mathrm{LS1,cal}}$ and $\delta^{34}\mathrm{S}_{\mathrm{LS2,cal}}$ are the conventionally fixed δ^{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 $\delta^{34}\mathrm{S}_{\mathrm{LS1,WS}}$ and $\delta^{34}\mathrm{S}_{\mathrm{LS2,WS}}$ are the δ^{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]. 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 8553 (IAEA-S-4) 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 Dec 2012).

[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 http://www.nist.gov/srm/publications.cfm (accessed Dec 2012).

[3] 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).

[4] *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9; 1st ed.; ISO: Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at http://physics.nist.gov/Pubs/ (accessed Dec 2012).

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

[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 Dec 2012).

[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 Dec 2012).

Report Revision History: 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 Group: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.