**REFERENCE MATERIALS**
for $\delta^{34}\text{S}$-isotope values
IAEA-S-1 (NIST – RM8554),
IAEA-S-2 (NIST – RM8555),
IAEA-S-3 (NIST – RM 8529).

**Assigned values for the stable isotope composition of IAEA-S-1, IAEA-S-2, IAEA-S-3**

<table>
<thead>
<tr>
<th>Reference Material</th>
<th>Assigned value $\delta^{34}\text{S}$, ‰ VCDT</th>
<th>Combined uncertainty with $k=1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAEA-S-1</td>
<td>-0.30</td>
<td>$\pm 0.03$ (1)</td>
</tr>
<tr>
<td></td>
<td>(primary material for scale-realization)</td>
<td></td>
</tr>
<tr>
<td>IAEA-S-2</td>
<td>+22.62</td>
<td>$\pm 0.08$ (2)</td>
</tr>
<tr>
<td>IAEA-S-3</td>
<td>-32.49</td>
<td>$\pm 0.08$ (2)</td>
</tr>
</tbody>
</table>

(1) The uncertainty of value assigned to the primary material in its role of the scale-definition is zero per definition. In order to address a potential inhomogeneity of IAEA-S-1, 1stDev stated in the inter-laboratory comparison [1] is applied to the assigned value.

(2) The uncertainty has been provided in the value revision in [2].
Preparation:
Silver sulphides IAEA-S-1, IAEA-S-2 and IAEA-S-3 (initially named as NZ1, NZ2 and NZ3) were prepared in late 1980s - early 1990s by B.W. Robinson (Institute of Geological and Nuclear Sciences, Lower Hutt, New Zealand) and C. A.M. Brenninkmeijer (the same institute) [1, 3].

Preparation of IAEA-S-1 and IAEA-S-3 was based on natural sphalerite (provided by S.Halas, Univ. Maria Curie-Skłodowska, Lublin, Poland) and IAEA-S-2 was based on natural gypsum. Materials were chemically dissolved (gypsum chemically reduced into S\textsuperscript{2} solution) and then precipitated as Ag\textsubscript{2}S by using a solution of AgNO\textsubscript{3} (more details in [1, 2]). Precipitation of each material (IAEA-S-1, IAEA-S-2 and IAEA-S-3) was done in batches; the batches obtained were tested for homogeneity. As batches of the same material were shown to be identical within analytical uncertainty of the method available [1], these were mixed in the final products.

Homogeneity of the material:
According to the initial study [1] and later study [2], the three materials were found to be homogeneous within the uncertainty of analytical methods in use. No further details were provided. Later, IAEA-S-1 and IAEA-S-2 were found to be homogeneous at the 0.4 mg level within the method uncertainty [4], the study was done on a limited number of units.

No homogeneity study has been reported with the purpose to cover a statistically representative selection of units ready for distribution (0.5 g in vials with plastic cups) and decouple the material inhomogeneity from the uncertainty related to the analytical method(s) in use and the minimal sample size which is a method-related parameter.

No storage alteration affects are supposed to effect sulfur stable isotope values.

Characterization of RMs:
History of VCDT scale for δ\textsuperscript{34}S:
The Canon Diablo troilite (CDT) of meteorite origin was historically used for defining the CDT scale for δ\textsuperscript{34}S. When CDT material was found to be not homogenous, with δ\textsuperscript{34}S variability of 0.4 ‰ [5], the use of CDT for calibration and also for reporting measurement results relative to CDT was discontinued [6].

As a replacement for CDT, silver sulphide material IAEA-S-1 with δ\textsuperscript{34}S = −0.30 ‰ was introduced for the purpose of scale definition (δ\textsuperscript{34}S assigned exactly relative to CTD) and also as the primary material for the scale realization [1, 3, 6-8]. Thereafter, the Vienna-CDT (VCDT) scale is defined by IAEA-S-1 with δ\textsuperscript{34}S=−0.30 ‰ (no uncertainty assigned for the definition). IAEA-S-1 is also used to realise the scale close to zero-point. In the characterisation study of IAEA-S-1 done by inter-laboratory comparison of 17 laboratories, 1StDev=±0.03 ‰ was reported (Table 1 in [1], no aliquot size was specified). In the first instance, this value of 0.03 ‰ may reflect the uncertainty due to material inhomogeneity. This uncertainty specified in Table on the front page is suggested to be taken for a(ny) singe aliquot used for measurements performed on IAEA-S-1.

Realisation of the VCDT δ\textsuperscript{34}S scale:
The 8th IAEA Advisory Group Meeting on Future Trends in Stable Isotope Reference Materials which took place in 2000 [7] recommended IAEA-S-1, IAEA-S-2 and IAEA-S-3 to be used for the VCDT scale realisation; this recommendation stays valid [6-8].
Determination of $\delta^{34}\text{S}$ values of IAEA-S-2 and IAEA-S-3 (Table 1) were performed by several laboratories, by using both $\text{SO}_2$ and $\text{SF}_6$ as an analyte gas. While $\delta^{34}\text{S}$ determinations on $\text{SO}_2$ requires correction due to isobaric contribution of $^{18}\text{O}$, analyses on $\text{SF}_6$ (on $\text{SF}_5^+$ ion-fragment) allow to determine all sulfur isotope ratios ($^{33}\text{S}, ^{34}\text{S}, ^{36}\text{S}$) without isobaric corrections.

### Table 1. $\delta^{34}\text{S}$ values reported for IAEA-S-2 and IAEA-S-3 on VCDT scale (uncertainty is given with $k=1$) Note, $\delta^{33}\text{S}$ values are given for information purpose only.

<table>
<thead>
<tr>
<th>Publication</th>
<th>$\delta^{34}\text{S}$, IAEA-S-2</th>
<th>$\delta^{33}\text{S}$, IAEA-S-2</th>
<th>$\delta^{34}\text{S}$, IAEA-S-3</th>
<th>$\delta^{33}\text{S}$, IAEA-S-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teccdoc-825 [1, 3]</td>
<td>+21.7</td>
<td>n/a</td>
<td>-32.30 ± 0.12</td>
<td>n/a</td>
</tr>
<tr>
<td>8th IAEA Advisory Working Group [7], values selected based on several determinations</td>
<td>+22.66 ± 0.13</td>
<td>n/a</td>
<td>-32.06 ± 0.11</td>
<td>-16.56 ± 0.31</td>
</tr>
<tr>
<td>Ding et al., 2001 [9]</td>
<td>+22.64 ± 0.11</td>
<td>+11.65 ± 0.11</td>
<td>-32.55 ± 0.12</td>
<td>-16.65 ± 0.31</td>
</tr>
<tr>
<td>Ding et al. 1999 [10], cited based on Table 8 in [9]</td>
<td>+22.67 ± 0.15</td>
<td>+11.48 ± 0.33</td>
<td>-32.49 ± 0.08</td>
<td>n/a</td>
</tr>
<tr>
<td>Mann et al. [2], values based on previous determinations and their own work</td>
<td>+22.62 ± 0.08</td>
<td>n/a</td>
<td>-32.49 ± 0.08</td>
<td>n/a</td>
</tr>
<tr>
<td>IUPAC review [8] of available values, uncertainty based on [2]</td>
<td>+22.62 ± 0.08</td>
<td>n/a</td>
<td>-32.49 ± 0.08</td>
<td>n/a</td>
</tr>
</tbody>
</table>

$\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values on the VCDT scale:
The same three materials have often been used for $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ calibrations and realisation of corresponding scales. However, currently there is no agreement values for three materials, partly due to some inconsistencies in preparation and analytical methods on $\text{SF}_6$ gas (related to purification from isobaric interferences at the masses used to measure the small signals of interest) and partly due to potential inconsistencies in the way of data reporting.

As no inter-laboratory characterization studies for $\Delta^{33}\text{S}$ and $\Delta^{33}\text{S}$ values have been organised, the $\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ values in Table 1 are given for the information purpose only.

$\delta^{33}\text{S}$ and $\delta^{36}\text{S}$ are often reported as $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ deviation from expected mass-dependent values as following (slightly different values of the exponent and linear approximations can also be found):

$$\Delta^{33}\text{S} = \delta^{33}\text{S} - 1,000 \times [(1 + \delta^{34}\text{S}/1,000)^{0.515} - 1]$$

$$\Delta^{36}\text{S} = \delta^{36}\text{S} - 1,000 \times [(1 + \delta^{34}\text{S}/1,000)^{1.91} - 1].$$

**Absolute isotope amount ratios:**

Determination of absolute isotope amount ratios in these materials (Table 2) is based on conversion to $\text{SF}_6$ by fluorination [9]; determinations are done on $\text{SF}_5^+$ fragment-ion which does not require an isobaric correction (fluorine is monoisotopic). Calibration of mass-spectrometer in terms of the absolute isotope amount ratios was performed by gravimetric mixing of sulfur isotope-enriched Ag$_2$S compounds.

Note: slight disagreement between values for IAEA-S-3 given in [9] and [10] (see Table 1) may indicate for small scale-shrinking in $\delta^{34}\text{S}$ for the IAEA-S-3 values reported in [9].
Table 2. $^{32}$S/$^{33}$S and $^{32}$S/$^{34}$S isotope amount ratios of IAEA-S-1, IAEA-S-2, IAEA-S-3 reported in [9]. (The uncertainties are given with k=1, as estimated in the report [9]).

<table>
<thead>
<tr>
<th>Materials</th>
<th>$^{32}$S/$^{33}$S</th>
<th>$^{32}$S/$^{34}$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAEA-S-1</td>
<td>126.942 ± 0.047</td>
<td>22.6504 ± 0.0020</td>
</tr>
<tr>
<td>IAEA-S-2</td>
<td>125.473 ± 0.055</td>
<td>22.1424 ± 0.0020</td>
</tr>
<tr>
<td>IAEA-S-3</td>
<td>129.072 ± 0.032</td>
<td>23.3933 ± 0.0017</td>
</tr>
</tbody>
</table>

Statement on the metrological traceability of assigned values and uncertainties:

For the scale definition, IAEA-S-1 serves as the primary RM on the relative VCDT scale for sulfur isotopes, without uncertainty. Values for IAEA-S-2 and IAEA-S-3 are traceable to IAEA-S-1. Together with IAEA-S-1, these reference materials serve for realisation of the artefact-based relative VCDT scale. For the scale realization at user-laboratory, values of all three materials shall be taken, including the uncertainty stated on the front page of this reference sheet. Besides, analytical uncertainty of their actual measurements shall be included.

Absolute isotope amount ratios (Table 2) are reported as SI-traceable, as based on gravimetric mixtures of isotopic entities. For further details, see the original publication [9].

Intended use:

The reference materials IAEA-S-1, IAEA-S-2 and IAEA-S-3 are intended to be used for realisation of the relative VCDT scale for $\delta^{34}$S. The use of specific preparation technique (combustion, fluorination or other) and aliquot size depends on the methods in use at end-user laboratory. Regardless of the method, it is recommended for all calibrations at end-user laboratory to include two reference materials, thus realising the two-point data normalisation. Note, there is no agreement on $\delta^{33}$S and $\delta^{36}$S values; users are suggested to refer to the latest publications by the sulfur isotope community.

Instructions for use:

The reference materials IAEA-S-1, IAEA-S-2 and IAEA-S-3 are supplied as 0.5 g units in glass vials with a plastic cup. Storage in closed desiccators in dark is recommended.

Expiry date:

Based on experience with similar materials, the expiry date is set to 2030-05-01.

Limit of distribution:

The material is available for limited distribution by allowing the purchase of up to 1 unit of each material within a year per laboratory. This limit is set to keep these reference materials available to as many laboratories as possible for an extended time period, and therefore a to maximize the reference material usability.

Legal disclaimer:

The IAEA makes no warranties, expressed or implied, with respect to the data contained in this reference sheet and shall not be liable for any damage that may result from the use of such data.
Since the year of the latest re-determination in 2009 [2], the accepted $\delta^{34}\text{S}$ values have not been re-confirmed.
The $\delta^{33}\text{S}$ values are given for information purpose only.

**Compliance with ISO Guide 31:2015:**

**Citation of this reference sheet:**
It is suggested to cite this reference sheet according to the following example, as appropriate to the citation format used: INTERNATIONAL ATOMIC ENERGY AGENCY, Reference Sheet for IAEA-S-1, IAEA-S-2, IAEA-S-3. IAEA, Vienna, 2020-04-16, 6pp, available for download at https://nucleus.iaea.org/sites/ReferenceMaterials/Pages/Stable-isotopes.aspx (The latest version published applies, see “Note” below).

**Notes:**
Assigned values and associated uncertainties as stated in this reference sheet may be updated if more information and/or improvements of analytical techniques become available. Users should ensure that the reference sheet in their possession is current. The current version may be found in the IAEA’s Reference Materials online catalogue.
When reporting sulfur isotope data for samples, the authors should provide detailed information regarding (i) their preparation method for the sulfur compounds of interest and the reproducibility, (ii) the measuring gas and mass spectrometer technique used, and (iii) the values for reference materials used in their study.

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Rev 0: original version

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