CERTIFIED REFERENCE MATERIAL

IAEA-456

MASS FRACTIONS OF TRACE ELEMENTS AND METHYL MERCURY
IN MARINE SEDIMENT SAMPLE

Certified mass fraction values  
*(based on dry mass)*

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Unit</th>
<th>Certified value(a)</th>
<th>Expanded uncertainty(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>mg kg(^{-1})</td>
<td>$55.4 \times 10^3$</td>
<td>$4.0 \times 10^3$</td>
</tr>
<tr>
<td>As</td>
<td>mg kg(^{-1})</td>
<td>6.14</td>
<td>0.52</td>
</tr>
<tr>
<td>Cd</td>
<td>mg kg(^{-1})</td>
<td>0.198</td>
<td>0.020</td>
</tr>
<tr>
<td>Co</td>
<td>mg kg(^{-1})</td>
<td>47.2</td>
<td>2.5</td>
</tr>
<tr>
<td>Cr</td>
<td>mg kg(^{-1})</td>
<td>589</td>
<td>42</td>
</tr>
<tr>
<td>Cu</td>
<td>mg kg(^{-1})</td>
<td>44.6</td>
<td>2.4</td>
</tr>
<tr>
<td>Fe</td>
<td>mg kg(^{-1})</td>
<td>$49.5 \times 10^3$</td>
<td>$3.2 \times 10^3$</td>
</tr>
</tbody>
</table>

(a) Information on calculation of certified values
Certified values are calculated from the accepted data sets, each set being obtained by a different laboratory and/or a different method of determination following ISO Guide 35 ‘Reference materials – General and statistical principles for certification’ [1].

(b) Information on method used for uncertainty estimation
The uncertainty is expressed as a combined uncertainty with a coverage factor $k = 2$, corresponding to a level of probability 95%, estimated in accordance with the JCGM 100:2008 ‘Evaluation of measurement data – Guide to the expression of uncertainty in measurement’ [2] and ISO Guide 35 [1].
Certified mass fraction values (Contd.)

*(based on dry mass)*

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Unit</th>
<th>Certified value(^{(a)})</th>
<th>Expanded uncertainty(^{(b)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>mg kg(^{-1})</td>
<td>0.077</td>
<td>0.005</td>
</tr>
<tr>
<td>CH(_3)Hg</td>
<td>mg kg(^{-1}) as Hg</td>
<td>0.125 × 10(^{-3})</td>
<td>0.019 × 10(^{-3})</td>
</tr>
<tr>
<td>Mn</td>
<td>mg kg(^{-1})</td>
<td>825</td>
<td>52</td>
</tr>
<tr>
<td>Ni</td>
<td>mg kg(^{-1})</td>
<td>760</td>
<td>56</td>
</tr>
<tr>
<td>Pb</td>
<td>mg kg(^{-1})</td>
<td>33.4</td>
<td>2.1</td>
</tr>
<tr>
<td>V</td>
<td>mg kg(^{-1})</td>
<td>223</td>
<td>16</td>
</tr>
<tr>
<td>Zn</td>
<td>mg kg(^{-1})</td>
<td>203</td>
<td>9</td>
</tr>
</tbody>
</table>

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Origin and preparation of the material

The sediment material was collected in New Caledonia, immediately frozen and then freeze dried. The sediment was first sieved at 500 µm, ground, and then sieved at 125 µm followed by mechanical homogenization of the collected fraction. The sieving cut-off value (125 µm) was selected to ensure that the physical properties of the material are sufficiently uniform, whilst retaining sufficient material to make an adequate number of units. Aliquots of about 15 g were packed into amber glass bottles with polyethylene caps and sealed in plastic bags.

Homogeneity of the material

The between-bottle homogeneity was tested by the determination of the mass fractions of selected certified analytes (Cr, Cd, Cu, Hg, Mn, Ni, Pb, Zn and CH\(_3\)Hg). In total 10 bottles were selected using random stratified sampling. Three subsamples from each bottle were analysed for their total element mass fractions. For all elements except Hg and CH\(_3\)Hg, subsamples of 0.2 g were mineralized with 5 ml HNO\(_3\) in a microwave oven. The final measurements were performed by flame and graphite furnace atomic absorption spectrometry. The determination of total Hg was done in solid subsamples (50mg) with solid mercury analyser, and methyl mercury was determined by gas chromatography coupled with atomic fluorescence spectrometer (GC-AFS) after alkaline digestion and room temperature derivatization.

The analysis of homogeneity study was performed under repeatability conditions and in a randomized way in order to separate a potential analytical drift from a trend in the filling sequence and minimize variations. The homogeneity test results provided experimental evidence that satisfactory levels of between and within-bottles homogeneity have been attained and the uncertainty due to the between and within-bottles heterogeneity were within acceptable limits.
**Characterization study**

The values above were established on the basis of results reported to the IAEA-MESL by 18 laboratories (19 data sets). Laboratories were requested to analyse Al, As, Cd, Co, Cr, Cu, Fe, Hg, CH$_3$Hg, Mn, Ni, Pb, V and Zn using a validated analytical method. They were asked to report the measurement results (three replicates) along with the expanded uncertainty in addition to the information about the applied quality control procedure. The moisture determination method was preliminary validated in MESL (Marine environmental Study Laboratory) and detailed description of the method sent to participants in this characterization study.

The agreement between results obtained with different analytical methods selected for the IAEA-456 characterization study confirms the absence of any significant method bias and demonstrates commutability of the material for all certified trace elements and for the analytical methods applied for characterization of the IAEA-456 sediment sample. In addition, the agreement between the results confirms the identity of the analytes.

**Assignment of values – Certification procedure**

The assigned property values were established on the basis of results reported by participating laboratories to the IAEA-MESL. The robust mean concentrations for the sets of individual data were chosen as the best estimate of the property values [3]. A certified value was assigned when at least 7 independent results obtained by at least 2 independent analytical methods were available and the relative expanded uncertainty was less than 15%.

The details concerning all reported results as well as the criteria for certification can be found in [3]. The report may be downloaded free of charge from:


Based on the evidence on calibrators used, quality control procedures applied by the participating laboratories and their generally high quality performance in previous IAEA interlaboratory comparisons, the Certification Committee has decided to accept the certified values presented in the Table above.

**Statement on metrological traceability, commutability and uncertainty of assigned values**

The property values assigned to the IAEA-456 certified reference material are calculated as mass fractions of specified trace elements, expressed in the derived SI unit mg kg$^{-1}$. Certified values are SI traceable and evidence on their metrological traceability to the SI units may be found in reference [3].

Expanded uncertainties with a coverage factor of $k = 2$, corresponding to a level of confidence of about 95 %, were calculated according to the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [2]. The measurement uncertainty associated with the certified value is expressed as mg kg$^{-1}$.

The agreement between results obtained with different analytical methods selected for the IAEA-456 characterization study confirms the absence of any significant method bias and demonstrates commutability of the material for all certified trace elements. More information on commutability of certified values may be found in reference [3].
**Intended use**

This Certified Reference Material is intended to be used for quality assurance and quality control purposes. The IAEA-456 Certified Reference Material is also suitable for method development and validation of analytical procedures, including potential bias evaluation, and for training purposes.

**Instructions for use**

The IAEA-456 Certified Reference Material is supplied in 15 g units. The material homogeneity is guaranteed if a minimum test portion of 0.2 g is used for Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V, Zn and CH₃Hg and 0.05 g for total Hg.

To overcome segregation effects due to storage or transportation, the material should be mixed before opening the bottle. All necessary precautions should be taken when opening the bottle to prevent any spread of the fine powder in the laboratory.

**Dry mass determination**

The average moisture content of the material was determined by drying several test portions of 1 g in an oven at 105°C until constant mass and was found to be (2.1 ± 0.5)% \((k = 2)\). Since the moisture content may vary with ambient humidity and temperature, it is recommended to check it prior to analysis and to report all results on a dry mass basis.

**Handling and storage**

The original unopened bottle should be stored securely at ambient temperature in a dark and dry place. It is recommended to avoid direct exposure to sunlight or to a source of heat.

**Issue and validity date**

The issue date of this Certified Reference Material is 20 May 2017. Based on experience with similar materials, the validity date is 20 May 2020. The IAEA is monitoring the long term stability of the material and customers will be informed in case of any observed change.

**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.

**Compliance with ISO Guide 31:2015**

The content of this IAEA Reference Sheet is in compliance with the ISO Guide 31:2015: Reference materials – Contents of certificates and labels [4].

**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 CRM IAEA-456, Mass fractions of Trace Elements And Methyl Mercury In Marine Sediment Sample, IAEA, Vienna, 6 pp. (The latest version published applies, see “Note” below).
Note

Certified values as stated in this reference sheet may be updated if more information becomes available. Users of this material 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: http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Trace_Elements_Methylmercury/index.htm

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