## REFERENCE SHEET

### CERTIFIED REFERENCE MATERIAL

**IAEA-475**

**MASS FRACTIONS OF TRACE ELEMENTS IN MARINE SEDIMENT SAMPLE**

**Certified mass fraction values**

*(based on dry mass)*

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Unit</th>
<th>Certified value&lt;sup&gt;(a)&lt;/sup&gt;</th>
<th>Expanded uncertainty&lt;sup&gt;(b)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>12.6</td>
<td>0.7</td>
</tr>
<tr>
<td>Co</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>12.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Cr</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>65.8</td>
<td>2.9</td>
</tr>
<tr>
<td>Cu</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>27.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Fe</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>34.2 × 10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>1.9 × 10&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Hg</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>29.9 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>1.5 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>MeHg</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt; as Hg</td>
<td>0.199 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>0.034 × 10&lt;sup&gt;-3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ni</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>28.5</td>
<td>1.1</td>
</tr>
<tr>
<td>Pb</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>29.9</td>
<td>1.5</td>
</tr>
<tr>
<td>Zn</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>100</td>
<td>6</td>
</tr>
</tbody>
</table>

<sup>(a)</sup> 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].

<sup>(b)</sup> 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].
### Information mass fraction values
*(based on dry mass)*

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Unit</th>
<th>Information value&lt;sup&gt;(a)&lt;/sup&gt;</th>
<th>Expanded uncertainty&lt;sup&gt;(b)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>0.121</td>
<td>0.036</td>
</tr>
<tr>
<td>Al</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>$73.1 \times 10^3$</td>
<td>$7.2 \times 10^3$</td>
</tr>
<tr>
<td>Cd</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>0.066</td>
<td>0.014</td>
</tr>
<tr>
<td>Li</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>41.2</td>
<td>2.4</td>
</tr>
<tr>
<td>Mn</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>573</td>
<td>37</td>
</tr>
<tr>
<td>Sr</td>
<td>mg kg&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>251</td>
<td>16</td>
</tr>
</tbody>
</table>

<sup>(a)</sup> Information on calculation of information values

Information 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].

<sup>(b)</sup> 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].

### Origin and preparation of the material

The raw material for IAEA-475 coastal sediment was collected around Townsville, Australia during the sampling campaign organised by the Marine Environment Study Laboratory (MESL), James Cook University and ANSTO, Australia. Approximately 50 kg sediment sample were collected at 2.2–2.5 m depth into polyester buckets and transferred at 4ºC to MESL, Monaco. After freeze drying, the sample was grinded by micronisation. Obtained sample showed 100% of particulates below 20 µm. The bulk material was then sterilised by gamma irradiation (30 kGy). The homogenization of the sediment sample was performed by dividing the total mass of material to 7 lots with the weight of 800 g. The material of each lot was transferred into a clean plastic bottle and mixed with a shaker (Turbula, Switzerland) for 2 hours. Immediately after finalizing the mixing operation, aliquots of about 20 g were packed into pre-cleaned polyethylene bottles with secured screw caps. The process was repeated seven times and bottles were labelled with the respective bottle numbers.

### Homogeneity of the material

The between-unit homogeneity was evaluated to ensure that the certified values of the CRM are valid for all produced units, within the stated uncertainty. In total, 14 bottles from the whole batch were selected, using random stratified sampling. Duplicate subsamples from each bottle were analyzed for their total element mass fractions. Quantification of within-unit (in this case: within-bottles) inhomogeneity is necessary to determine the minimum sample intake. In total 6 subsamples from the same unit were prepared and each subsample was analyzed in triplicates.

The between and within-unit homogeneities were tested by the determination of the mass fractions of Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, MeHg, Li, Mn, Ni, Pb, Sr, and Zn in the subsamples that were selected for the respective study. For all analytes except for Hg, subsamples of 0.2 g were mineralized with 5 ml of nitric acid (HNO₃) and 2ml of hydrofluoric acid (HF) in a microwave oven. Digested solutions were then treated with boric acid to remove excess of HF and fluoride precipitates. The final measurements were performed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) or Flame Atomic Absorption Spectrometry (AAS) under repeatability conditions, and in a randomized way. The determination of the total Hg was done in solid subsamples (50 mg) with advanced mercury analyzer.
Methylmercury determination are performed by gas chromatography coupled to atomic fluorescence spectroscopy (GC-AFS) after solvent extraction.

The analysis for the 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 provide experimental evidence that satisfactory levels of between and within-bottles homogeneity have been attained (1.2% to 7.8%) and the uncertainty due to the between and within-bottles heterogeneity were within acceptable limits for certified analytes [3].

**Characterization study**

The certified mass fraction values were established on the basis of results reported to the IAEA-MESL by 8 laboratories (14 data sets). Laboratories were requested to analyse Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, MeHg, Li, Mn, Ni, Pb, Sr, and Zn using validated analytical method. They were asked to report measurement results (three replicates and average value), expanded uncertainty, information on the applied quality control procedures as well as the information on the standard calibration solutions used in the measurement step. In addition, each participant also received 1 bottle of IAEA-458 (CRM with similar matrix composition) as a blinded quality control sample. The reported results for the quality control sample were evaluated against the certified values and associated uncertainties of the CRM IAEA-458 [4]. As the result for moisture in the sediment sample is operationally dependent, the method for moisture determination was prescribed to all participating laboratories.

**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 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 5 independent results obtained with at least 2 independent analytical methods were available and the relative expanded uncertainty (k=2) was less than 15%. For Ag, Al, Cd, Li, Mn and Sr above stated criteria were not fulfilled. Therefore, for those elements the mean and uncertainty are given for information only.

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 performances in the previous IAEA interlaboratory comparisons, the Certification Committee decided to accept presented certified and information values shown in the Table above.

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

The property values, assigned to the IAEA-475 Certified Reference Material, were calculated as mass fractions of specified analytes, expressed in the derived SI unit mg kg⁻¹. Certified values are SI traceable and evidence on their metrological traceability to the SI system of units may be found in the 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 also in mg kg⁻¹.

The agreement between results obtained with different analytical methods selected for the IAEA-475 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 the reference [3].

**Intended use**

This Certified Reference Material is intended to be used for quality assurance and quality control purposes. The IAEA-475 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-475 Certified Reference Material is supplied in 20 g units. The material homogeneity is guaranteed if a minimum test portion of 0.2 g is used for As, Co, Cr, Cu, Fe, Hg Ni, Pb and Zn 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 ± 3) °C until constant mass and was found to be (2.3 ± 0.4) % (k = 2).

Since the moisture content may vary with ambient humidity and temperature, it is recommended to determine the correction for moisture on a separate sub-sample (different from that used for analysis) by heating at (105 ± 3) °C until constant mass is achieved 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 **November 2019**. Based on experience with similar materials, the validity date is **November 2022**. 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 following the requirements of the ISO Guide 31:2015: Reference materials – Contents of certificates and labels [5].

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-475, Mass fractions of Trace Elements 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: https://nucleus.iaea.org/sites/ReferenceMaterials/Pages/IAEA-475.aspx

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REFERENCES


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Chair, RM Certification Committee                          Project Officer, Marine Environmental Studies Laboratory

Revision Information:
- Rev.00.01 (2020-04-27): update of web link to the online catalogue in section ‘Note’

- Rev.00.02 (2020-07-30): update of web link in section “Assignment of values – Certification procedure” and of reference [3]